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CATALYTIC VAPOUR PHASE HYDROLYSIS OF CHLOROBENZENE - A KINETIC STUDY

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CHAPTER I

CHAPTER I

INTRODUCTION

Phenol is used in large quantities in the manufacture of phenol formaldehyde resins (bakelite) and as a dye intermediate. Another important use is in the manufacture of Nylon; phenol is catalytically hydrogenated to cyclohexanol, a valuable solvent, which is then oxidized to adipic acid, a raw material for Nylon 66. Other uses of phenol are : in the manufacture of non-ionic detergents; in the production of additives for lube oils and rubber; as a solvent in petroleum refining; and in the manufacture of phenol derivatives such as salicylic acid, pentachlorophenol, picric acid, phenyl phosphates and fungicides (e.g. chloranil).

It is expected that phenol production will be on the increase. The reason for this upsurge is (1) that increasing quantities of phenol are likely to be utilised in the manufacture of caprolactum (intermediate for Nylon 6), adipic acid, bisphenol A and alkyl phenols. At the end of 1959, United States phenol plants had a combined capacity of 0.33 million tons, and projects announced since then were expected to raise the production potential by about 40 per cent by the end of 1962 (2). During the same period, the estimated rise in Canadian phenol plant capacity was 150 per cent. A recent estimate forecasts a rise in U.S. demand to 0.435 million tons in 1965. The factors that would cause major changes in the economics of the fast-growing production of phenol have been summed up as follows.

(1) Improvements in the technology of phenol manufacture.

(2) Changes in the phenol end-use pattern.

(3) Competition by other intermediates for phenol markets.

(4) Broadening of the raw materials base for phenol manufacture.

(5) A shift in the supply-demand ratio for phenol.

Summary of existing processes

At present there are four commercial processes for the production of phenol. A fifth process is ready for commercial exploitation, and two other processes of industrial potential have also been reported. A brief summary of these processes is given below[(2)].

Sulfonation process

This process involves the following sequence of steps :

(a) Sulfonation of benzene :

(b) Processing of benzene sulfonic acid :

(c) Caustic fusion :

(d) Springing of phenol :

Sulfurous acid is made from SO_2 for use in the springing of sodium phenate. The yield of phenol is of the order of 90 per cent. This method is being used by several firms : Monsanto Chemical Company, and Reichhold Chemical Corporation.

The Dow process

This process consists of two steps :

(a) Chlorination :

The halogenation reaction is carried out in the liquid phase using ferric chloride as catalyst. Conversion per pass of benzene is 30-50 per cent, and the yield based on benzene ranges from 80-95 per cent.

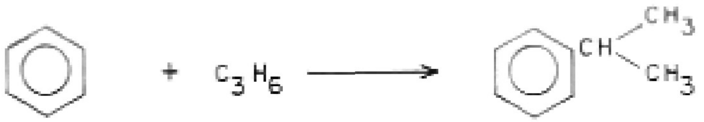
(b) Hydrolysis:

The reaction is carried out at 4000 psig and 370-400°C. A 10-15 per cent aqueous solution of caustic is used in 10 per cent excess over theory. Diphenyl oxide is formed as a by-product, and phenol yield based on benzene is 85-88 per cent.

Cumene Route to phenol

This process consists of three steps :

(a) Synthesis of cumene :

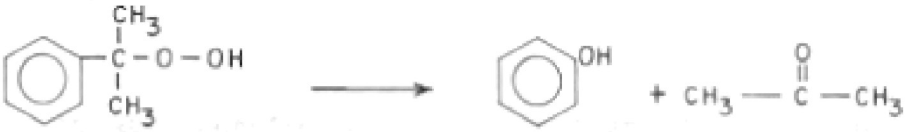


Sulfuric acid or aluminium chloride is used as catalyst in the liquid phase alkylation.

(b) Auto-oxidation of cumene :

The reaction is carried out in an aqueous emulsion containing an emulsifying agent and sodium carbonate to maintain the optimum pH range of 8.5-10. The optimum temperature is 110-130°C. Total conversion per pass is about 25 per cent. The by-products formed in the reaction are acetophenone, dimethylphenyl carbinol, phenol and methylstyrene. The product is purified.

(c) Decomposition :



Dilute sulfuric acid is used as catalyst in this reaction. The reaction temperature is between 45 and 65°C. Acetone and phenol are then recovered in a series of extraction and fractionation steps.

The overall phenol yield in the cumene process is 85-90 per cent based on cumene. The acetone yield is approximately the same. This process is reported to be employed by Hercules Powder Co. and Oronite Chemical Co. in the United States, and by B.A. Shawinigan Ltd. in Canada.

Raschig process

There are two steps in this process :

(a) Oxychlorination :

The reaction is carried out in the vapour phase over a solid catalyst at 250-270°C. Conversions of the order of 10 per cent are obtained.

(b) Steam hydrolysis :

This reaction is also carried out in the vapour phase over a solid catalyst at 450-500°C. Conversion per pass is 8-15 per cent.

The yield of phenol is 85-95 per cent based on benzene. The process is regenerative with respect to hydrochloric acid. Also the exothermic heat of the first reaction can be utilized for the second reaction which is endothermic. This process is employed by Hooker Chemical Co. and by Union Carbide Corpn.

Other processes with industrial potential

(1) Toluene is used as the starting material, and two steps are involved.

(a) Oxidation of toluene :

The oxidation of toluene to benzoic acid is carried out in liquid phase in the presence of oil-soluble cobalt or manganese salts. The overall benzoic acid yield is reported to be 85-90 per cent.

(b) Oxidation of benzoic acid and hydrolysis :

The oxidation is carried out in liquid phase at 230°C. in the presence of a soluble cupric salt which may be promoted by some magnesium salts. Hydrolysis to phenol is effected by steam. The yield of phenol on benzoic acid is reported to be 80-83 per cent. Toluene based phenol synthesis is being tried by Dow Chemical Co.

(2) Benzene is air-oxidized in the presence of radiation from radioactive sources (e.g. cobalt 60). This approach for the preparation of phenol has been announced by Japanese and Russian sources.

(3) Another source has attempted to oxidize benzene by air in the presence of an electric discharge. The route followed is :

Benzene ⟶ Cyclohexane ⟶ Cyclohexanol ⟶ Phenol

This is a case of indirect oxidation of benzene, in the sense that only benzene and air are used as raw materials although intermediate reaction stages are involved. Although a plant constructed for Schenectady Varnish Co. is making an attempt to manufacture phenol by air oxidation of benzene, this route has not so far been commercially exploited.

(4) In this process cyclohexylbenzene is oxidized by molecular oxygen to yield the hydroperoxide which is then decomposed to phenol and cyclohexanone by phosphoric-sulfuric acid mixtures. Cyclohexanone is an intermediate in the production of adipic acid and caprolactam. The maximum yield is reported to be 79 per cent phenol and 75 per cent cyclohexanone. This route is yet to be tried on a commercial scale.

Scope of present work

Each of these processes has its own advantages, and from a basic chemical engineering point of view, offers considerable scope for detailed study and improvement. In the present work, studies on the hydrolysis of chlorobenzene (second step of the Raschig process) are reported as part of an overall programme of investigations on the Raschig process. Using tricalcium phosphate as catalyst, the kinetics of this endothermic reaction has been studied. As the catalyst gets deactivated in 5-7 hours (depending upon the conditions of use), an attempt has also been made to study the deactivation kinetics.

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CHAPTER II

CHAPTER II

LITERATURE SURVEY

In this chapter some salient features of the Raschig process are outlined, and reported results on the catalytic vapour phase hydrolysis of chlorobenzene (which comprises the second step of the process) are summarised.

The Raschig process consists of two stages, in the first of which monochlorobenzene is produced catalytically according to the equation,

$$C_6H_6 + HCl + 1/2\ O_2 \longrightarrow C_6H_5Cl + H_2O,$$

and in the second stage, the monochlorobenzene is catalytically hydrolysed with steam to yield phenol and regenerate the HCl according to the reaction,

$$C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl$$

The first reaction is exothermic whereas the second is endothermic. Conversion per pass in the second step is of the order of 8-15 per cent. With so low a conversion per pass, it is evidently desirable to effect phenol recovery without condensing the entire chlorobenzene and water vapors(1). This consideration of thermal economy is of significant influence on the commercial competitiveness of the process. Operating at certain conditions, practically no by-products are formed; the process converts virtually all of the benzene fed to phenol without producing chlorobenzenes as by-products.

The principal advantage of the process is its amenability to simplification in design (2), and as a result plant investment costs have been substantially reduced. Main improvements : the series of parallel tubes containing the catalyst has been replaced by a single catalyst container; distillation equipment have been combined so that one system can handle product from both stages (in the earlier designs separate systems were used to fractionate the crude and hydrolysis products); the catalyst regeneration system has been simplified through process modifications. Its principal defect, however, is the problem of corrosion and deactivation of the catalyst.

Details of the Raschig process have appeared in two BIOS reports (3,4), and a few other sources (5,6,7,8,9,10).

Vapour phase hydrolysis of chlorobenzene

Catalysts used

Catalysts that have been tried for the vapour phase hydrolysis of chlorobenzene to phenol can be broadly classified under four different groups : metals, metal oxides, salts and acids. These have been tried either independently or by impregnating on supports like silica gel and asbestos. Silica gel itself is known to act as a catalyst, but its activity can be enhanced by promoters like cupric chloride.

Metals such as granular copper and copper-cobalt mixture (11); alkaline earth metals on which cobalt, copper, silver, gold or metals of the platinum group have been deposited (12); oxides such as zinc oxide, titanium dioxide, neutral and acid manganese pyrophosphates on which copper, nickel, cobalt, silver, gold or metals of the platinum group are deposited; and nickel oxide, molybdenum trioxide, zirconium oxide, silica, tungsten trioxide, magnesium oxide, aluminium trioxide (13,14) have been used in several investigations.

Among these catalysts, silica gel has received the maximum attention. Results have been reported on the preparation of different types of silica gels and it is claimed that Okatov's gel is superior to many other varieties of silica gels (15). It is also stated (16,17,18) that the catalytic activity of silica gel in the hydrolysis of chlorobenzene is enhanced by copper, and that the method of preparation of the silica gel-cupric chloride catalyst greatly influences its activity. Another important factor in the activity of this catalyst is the method of addition of the copper component (15,19).

The use of activators like chlorides of silver, aluminium, tin, zinc, magnesium, calcium and sodium has been shown to promote the catalytic action of the silica gel-cupric chloride catalyst (20,21). These activators are also claimed to enhance the durability of the catalyst. It was found that with silver chloride as promoter the catalyst (silica gel-cupric chloride) gave a conversion of 84 per cent after 40 hours of use, whereas without silver chloride the yield of phenol was 73 per cent after 15 hours of use.

The use of inorganic salts in the preparation of silica gel catalysts has been found to generally decrease the yield of phenol, the only exception being copper chloride. Salts such as ammonium molybdate, mercuric chloride, lithium chloride, manganese chloride, barium chloride, calcium chloride and magnesium chloride have all been tried(22). Either there was a diminution of activity, or, as in the case of lithium chloride, the silica gel ceased to function as a catalyst. Iron compounds in general have been found to poison the silica gel catalyst; thus washing the silica gel with nitric acid should increase its catalytic efficiency.

The influence of compression on the properties of silica gel catalysts has been studied(23). Compression of supported catalysts generally improves their mechanical strength, activity, useful life and bulk density. The reaction showed the highest yield of phenol when macroporous silica gel was compressed to 5000 atmospheres, e.g. at 500°C., the yield was 9.2 per cent when uncompressed catalyst was used, 13.4 per cent when compressed to 5000, 9.5 per cent when compressed to 10,000, and 9.2 per cent when compressed to 20,000 atmospheres.

Among the other catalysts which have been extensively studied are tricalcium phosphate or any other salt having magnesium, aluminium, calcium, copper or selenium in the positive radical and phosphorous, chlorine or silica in the negative radical (24). Among this class of catalysts, tricalcium phosphate has received by far the greatest attention.

With tricalcium phosphate as catalyst it was observed (25) that the selectivity of the reaction decreased beyond 575°C., the proportion of side products being higher at higher temperatures. The phosphate catalyst was found to be thermally more stable than silica gel and less sensitive to deactivation by mineral impurities. According to the BIOS report (3), 1000 cc. of tricalcium phosphate gives 100 gm. per hour of phenol in a yield of 90 per cent.

Methods of preparing tricalcium phosphate have been reported in several sources (3,25). The general procedure is briefly as follows : Solutions of phosphoric acid, ammonium chloride and calcium chloride in appropriate concentrations are prepared. The ammonia solution is mixed with dilute phosphoric acid solution, and to this mixture calcium chloride solution is added. The precipitate of tricalcium phosphate is filtered, washed free of impurities, and dried.

Shrivastava et al (26) employed tricalcium phosphate and trimagnesium phosphate as catalysts in their studies and reported that magnesium phosphate is superior to calcium phosphate. These investigators used the phosphate catalysts both directly and supported on a silica base. Supported catalysts were observed to give higher conversions. At 450°C.

silica based tricalcium phosphate gave a conversion of 7.1 per cent, while under the same conditions the unsupported catalyst give less than 1 per cent.

In addition to the catalysts described above, several other catalysts (including salts and acids) have also been used from time to time. Among those are : kieselguhr and colloidal clays (27); aluminium hydrosilicates (28,29,30); materials with strong base exchange properties (30); porous silica prepared from chrysocolla; minerals containing aluminium hydrosilicates such as Fuller's earth in the presence of copper (29); methyl phosphates activated with copper salts (31); acids such as stannic, titanic and aluminic acids (25); salts such as tin vanadate, cadmium phosphate and copper phosphate supported on silica gel (11); and calcium carbonate and calcium phosphate deposited with copper, nickel, cobalt, silver, gold or metals of the platinum group (12).

In an interesting investigation, Russel and James (32,33) passed vapours of chlorobenzene and water over a catalytic metal such as copper capable of forming a volatile salt under the conditions of use. The volatile salt together with the reaction products was then passed over silica gel. They also found that passage of the vapours over copper shavings helps to maintain the catalytic activity of silica gel impregnated with metals.

Reaction mechanism

Free -OH groups present in silica gel are responsible for its catalytic action. The labile hydrogen atom in the -OH group of silica gel reacts with chlorobenzene at the C-Cl bond as shown in stage A of chart (1). The ester group formed intermediately on the surface of the silica gel is subsequently hydrolyzed non-catalytically according to stage B. Phenol is formed in stage B and the -OH groups of silica gel are regenerated and are free to catalyze the reaction repeatedly.

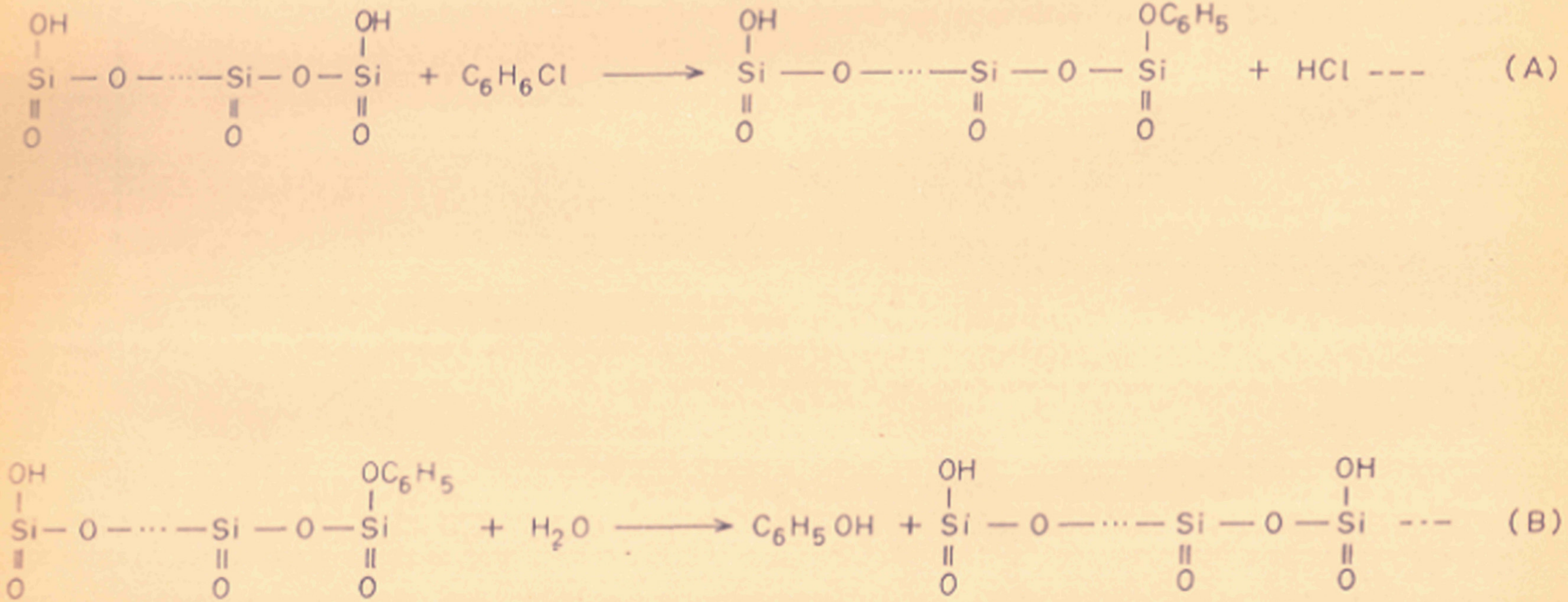
This mechanism is also applicable to calcium phosphate crystal hydrate. The structure of tricalcium phosphate is shown in chart (2). It has been proved (25) that solid crystal hydrates (metallic salts) are compounds with more or less pronounced acidic properties which differ only qualitatively from solid acids and acid salts. At 400-500°C. the lability of hydrogen in crystal hydrates is quite high. This interpretation justifies the assumption that the catalytic activity of tricalcium phosphate is likewise associated with its -OH groups which contain a labile hydrogen atom.

Shrivastava et al (26) state that the role of the catalyst is purely mechanical. It provides the conditions necessary for the most favourable orientation of the reacting molecules. The PO_4 radical is the effective part of the catalyst, the cationic part merely helping to render the catalyst insoluble in water. The PO_4 radical acts as an orienting agent because of the semi-ionic bond between phosphorous and one of the oxygen atoms. The reactants on entering the electrical field provided by the P^+ O^- dipole will arrange themselves in such a manner that the positive and negative poles are towards the negative and positive poles respectively of the nearest PO_4 radicals as shown below.

P^{+} —————— O^{-}
Cl^{-} —————— $C_6H_5^{+}$

H^{+} —————— OH^{-}
O^{-} —————— P^{+}

The hydrolysis will definitely take place even when the chlorobenzene and water molecules are arranged at random without a catalyst, but this will only occur at high temperatures and pressures. It is a reasonable conclusion that, if the cationic portion of the molecule is made smaller, the catalyst will be more effective, so that a larger part of the molecular volume is occupied by the PO_4 radical.



$$\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} - O - \cdots - \underset{\underset{O}{\|}}{Si} - O - \underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} + C_6H_6Cl \longrightarrow \underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} - O - \cdots - \underset{\underset{O}{\|}}{Si} - O - \underset{\underset{O}{\|}}{\overset{\overset{OC_6H_5}{|}}{Si}} + HCl \text{ ---} \qquad (A)$$

$$\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} - O - \cdots - \underset{\underset{O}{\|}}{Si} - O - \underset{\underset{O}{\|}}{\overset{\overset{OC_6H_5}{|}}{Si}} + H_2O \longrightarrow C_6H_5OH + \underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} - O - \cdots - \underset{\underset{O}{\|}}{Si} - O - \underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{Si}} \text{ ---} \qquad (B)$$

CHART - 1.

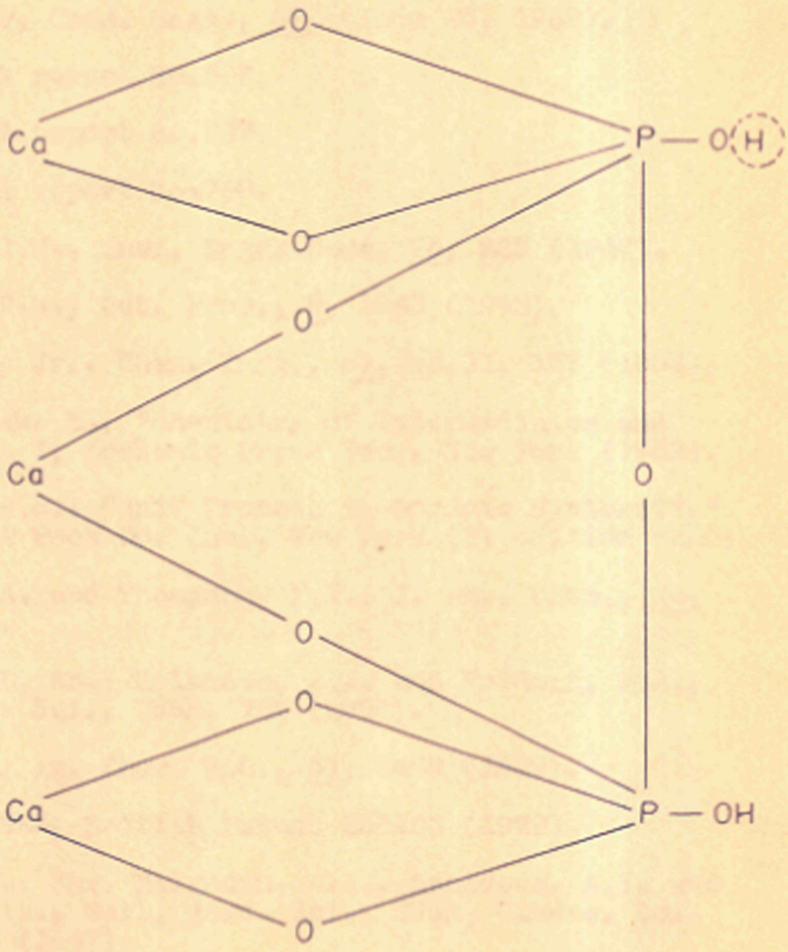


CHART — 2

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CHAPTER III

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THERMODYNAMIC CONSIDERATIONS

The reaction under

is widely used in industrial practice, but no data are reported on the equilibrium conversions obtainable at different temperatures. The thermodynamic properties of phenol, hydrochloric acid and water are reported, and some data on chlorobenzene are also available. In this chapter all the available thermodynamic properties are tabulated, and where necessary they have been estimated for inclusion in the tables. Equations have been developed based on these values for calculating the heat of reaction, free energy of reaction, equilibrium constant, and equilibrium conversion as functions of temperature.

Thermodynamic properties of chlorobenzene

The thermodynamic functions, $\frac{G_T^o - H_o^o}{T}$, $H_T^o - H_o^o$, S^o and C_p^o, of chlorobenzene have been reported (1,2). Using these values, the heat and free energy of formation can be calculated as functions of temperature. For this purpose, ΔH_f^o at one temperature is required, and this may be calculated from the heat of combustion data.

Heat of formation. ΔH_f^o at 298.16°K. was calculated from the heat of combustion value at that temperature.

$\Delta H_c(1)$ at 298.16°K. = -743,3 kcal./g.mol. (3)

$\Delta H_f^o(1)$ at 298.16°K. = -2,53653 kcal./g.mol.

$\Delta H_f^o(g)$ can be calculated from the relation,

$$\Delta H_f(g) = \Delta H_f(1) + \Delta H_v \quad .. \quad (1)$$

The value of ΔH_v at 298.16°K. was estimated from Watson's equation,

$$\frac{\Delta H_{v_1}}{\Delta H_{v_2}} = \left[\frac{1 - Tr_1}{1 - Tr_2}\right]^{0.38} \quad .. \quad (2)$$

where ΔH_{v_1} and ΔH_{v_2} are the heats of vaporization at reduced temperatures Tr_1 and Tr_2, corresponding to 404.9°K. (normal boiling point) and 298.16°K., respectively.

ΔH_{v_1} = 8.735 kcal./g.

$\therefore \Delta H_{v_2}$ = 10.1 kcal./g.mol.

and $\Delta H_f^o(g)$= 12.64 kcal./g.mol.

Heats of formation in the range 298.16°K. to 1000°K. were estimated from the relation,

$$\Delta H^{\circ}_{f_T} = \Delta H^{\circ}_{f_o} + (H^{\circ}_T - H^{\circ}_o)_{comp} - \sum(H^{\circ}_T - H^{\circ}_o)_{ele.} \qquad (3)$$

where $\Delta H^{\circ}_{f_o}$ is the zero point heat of formation, $\Delta H^{\circ}_{f_T}$ is the heat of formation at T°K., and $H^{\circ}_T - H^{\circ}_o$ is the heat content function. Heat content functions for chlorobenzene and for its constituent elements, carbon, hydrogen and chlorine, are available at temperatures up to 1000°K.(1,4,5). By substituting $\Delta H^{\circ}_{f_T}$ for chlorobenzene at 298.16°K. and $(H^{\circ}_T - H^{\circ}_o)$ for chlorobenzene and the elements at the same temperature in Equation (3), the zero point heat of reaction $\Delta H^{\circ}_{f_o}$ was calculated. This value (16.236 kcal./g.mol.) was then used to calculate the heat of formation of chlorobenzene over the temperature range 298.16°-1000°K. These values are summarised in Table 3.1.

Free energy of formation. The following basic equation was used :

$$\Delta G^{\circ}_T = \Delta H^{\circ}_T - T\,\Delta S^{\circ}_T \qquad (4)$$

ΔS°_T of formation was calculated from the entropy values of chlorobenzene listed in Table 3.1 and of the elements(1,4). Then using the values of ΔH°_f from Table 3.1, ΔG°_f was calculated from

Equation (4).

ΔG_f^o was also calculated from Equations (5) and (6) given below :

$$\Delta H_T^o = I_H + (\Delta a)T + 1/2(\Delta b)T^2 + 1/3(\Delta c)T^3 + \ldots \quad .. \qquad (5)$$

$$\Delta G_T^o = I_H - (\Delta a)T \ln T - 1/2(\Delta b)T^2 - (\Delta c)T^3 + I_S \quad .. \qquad (6)$$

The use of Equation (6) requires a knowledge of the constants, a, b, c and d, for chlorobenzene and its constituent elements. The elemental values were taken from the literature (6,7), and those for chlorobenzene were calculated from the reported C_p^o values (5) by the method of least squares. The values of the compounds and elements involved are summarized in Table 3.2. The constants I_H and I_S were estimated from Equations (5) and (6) using the values of ΔH_f^o and ΔG_f^o at 298°K.

The mean values of ΔG_f^o calculated by the two methods are listed in Table 3.1, the average deviation being 0.634 per cent.

Thermodynamic properties of phenol (8,9)

These are listed in Table 3.3.

Thermodynamic properties of hydrochloric acid (5,10)

These are listed in Table 3.4.

Thermodynamic properties of water (11)

These are listed in Table 3.5.

Heat of reaction

The heat of reaction as a function of temperature was calculated over the temperature range 298°-1000°K. from the values of ΔH°_T for the products and reactants. These are listed in Table 3.6.

Equilibrium constant

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

$$\frac{\Delta G^\circ_T}{T} = R \ln K \qquad .. \qquad (7)$$

For the reaction under consideration,

$$\Delta G^\circ_T = \Delta G^\circ_{f(C_6H_5OH)} + \Delta G^\circ_{f(HCl)} - \Delta G^\circ_{f(C_6H_5Cl)} - \Delta G^\circ_{f(H_2O)}$$

Values of ΔG_f^o for chlorobenzene, phenol, hydrochloric acid and water have all been tabulated before. From these, ΔG_T^o was calculated at different temperatures and the resulting values are summarized in Table 3.6.

The equilibrium constants (K) calculated from Equation (7) using the values of ΔG_T^o at several temperatures are also summarized in the same table. A plot of log K vs. T appears in Fig. (3.1).

Equilibrium conversion

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

$$K = \frac{n_R^r \cdot n_S^s}{n_B^b \cdot n_C^c} \left(\frac{\pi}{n_t} \right)^{\overline{r+s} - \overline{b+c}} \cdot K_V \qquad (8)$$

where K_V is the fugacity coefficient term and is given by

$$K_V = \frac{v_R^r \cdot v_S^s}{v_B^b \cdot v_C^c} \qquad (9)$$

The term K_V is a measure of the deviation from ideality of the reaction, and becomes significant at high pressure and low temperature.

At ordinary pressures, K_v may be assumed to be unity over the entire temperature range. Assuming π and K_v each as being equal to unity, and writing x as the moles of phenol formed at equilibrium per mole of chlorobenzene, the following equation can be written.

$$K = \frac{x^2}{(1-x)\ (1-x)} \qquad .. \qquad (10)$$

The values of x calculated from Equation (10) at different values of K corresponding to the temperatures listed in Table 3.6 are also given in the same table.

Table 3.1

Thermodynamic properties of chlorobenzene in the ideal gas state (1)

Temp. (°K.)	$-(G^o_T - H^o_o)/T$	$(H^o_T - H^o_o)/T$	S^o	C^o_p	ΔH^o_f	ΔG^o_f
298.16	61.24	13.62	74.86	23.20	12.6365	23.97703
300	61.32	13.69	75.01	23.34	-	-
400	65.70	16.98	82.68	30.30	11.6217	27.90725
500	69.85	20.26	90.11	36.14	10.8652	32.17669
600	73.84	23.32	97.16	40.80	-	-
700	77.62	26.09	103.71	44.54	10.1494	40.95298
800	81.26	28.58	109.84	47.57	9.7755	45.35753
900	84.80	30.86	115.66	50.12	9.5330	49.820155
1000	88.11	32.86	120.97	52.21	9.1065	54.20793

Table 3.2

Constants of the heat capacity equation, $C_p^o = a + bT + cT^2 + dT^3$

Compound	Formula	Temp. range °K.	a	bx10^3	cx10^6	dx10^9	Ref.
Carbon	C	300-1500	-1.2704	14.0270	-10.3519	2.7582	(6)
Hydrogen	H_2	270-1500	6.7363	0.5972	-4.2370	0.3157	(6)
Chlorine	Cl_2	273-1500	6.8628	5.5271	-4.8843	1.4653	(6)
Chlorobenzene	C_6H_5Cl	298.16-1000	-7.5955	132.2700	-104.3500	32.1600	Calculated by the method of least squares using reported C_p^o data (1)
Water	H_2O	298.16-1000	8.2200	0.0150	1.3400	-	(7)
Hydrochloric acid	HCl	298.16-1000	6.7000	0.8400	-	-	(7)
Phenol	C_6H_5OH	298.16-1000	-8.6269	143.1500	-115.6900	36.6700	Calculated by the method of least squares using reported C_p^o data (8)

Table 3.3

Thermodynamic functions of phenol in the ideal gas state (8,9)

Temp. (°K.)	$-(G^o_T - H^o_o)/T$	$(H^o_T - H^o_o)/T$	S^o	C^o_p	ΔH^o_f	ΔG^o_f
0	0	0	0	0	18.63	-18.63
273.16	60.17	13.18	73.35	22.70	22.72	-9.12
298.16	61.36	14.07	75.43	24.75	23.05	-7.88
300	61.45	14.13	75.58	24.90	23.07	-7.99
400	66.01	17.79	83.80	32.45	24.12	-2.51
500	70.37	21.37	91.74	38.64	24.92	+2.97
600	74.56	24.67	99.23	43.54	25.55	+8.61
700	78.59	27.65	106.24	47.44	26.00	+14.34
800	82.46	30.33	112.79	50.62	26.40	+20.13
900	86.18	32.73	118.91	53.26	26.65	+25.96
1000	89.74	34.90	124.65	55.49	26.82	+31.82

Table 3.4

Thermodynamic functions of HCl in the ideal gas state (5,10)

Temp. (°K.)	$-\frac{(G^o_T - H^o_o)}{T}$	$\frac{(H^o_T - H^o_o)}{T}$	S^o	C^o_p	ΔH^o_f	ΔG^o_f
298.16	37.748	6.925	44.674	6.964	-22.06	-22.77
300	37.791	6.926	44.717	6.964	-12.33	-22.77
400	39.785	6.937	46.722	6.973	-12.41	-23.00
500	41.334	6.946	48.280	7.004	-12.48	-23.21
600	42.602	6.961	49.563	7.068	-12.56	-23.41
700	43.676	6.983	50.569	7.167	-12.63	-23.59
800	44.610	7.013	51.623	7.289	-12.69	-23.76
900	45.439	7.051	52.490	7.423	-12.74	-23.92
1000	46.184	7.095	53.279	7.560	-12.78	-24.07

Table 3.5

Thermodynamic properties of water in the ideal gas state (11)

Temp. (°K.)	$(G_T^o - H_o^o)/T$	$(H_T^o - H_o^o)/T$	S^o	C_p^o	ΔH_f^o	ΔG_f^o
298.16	-37.172	7.934	45.106	8.025	-54.7979	-54.6351
300	-37.221	7.933	45.154	8.026	-57.8022	-54.6152
400	-39.508	7.975	47.483	8.185	-58.0420	-53.5160
500	-41.295	8.039	49.334	8.415	-58.2760	-52.3580
600	-42.768	8.122	50.890	8.677	-58.4990	-51.1540
700	-44.026	8.220	52.248	8.959	-58.7090	-49.9120
800	-45.131	8.330	53.464	9.254	-58.9020	-48.6430
900	-46.120	8.452	54.572	9.559	-59.0800	-47.3490
1000	-47.018	8.590	55.598	9.869	-59.2390	-46.0360

Table 3.6

Equilibrium constants and conversions for the reaction

Temp. (°K.)	ΔH^o_T	ΔG_T kcal./g.mol.	log K	K	Conversion (x)
298.16	-	0.00807	-0.005913	0.9865	0.5184
300	-	-	-	-	-
400	9.8903	-0.09875	0.05393	1.132	0.5189
500	10.0108	-0.05869	0.02564	1.06	0.5063
600	-	-	-	-	-
700	9.9296	-0.29098	0.09078	1.232	0.5259
800	10.0365	-0.34453	0.09408	1.242	0.5269
900	10.1570	-0.431155	0.10470	1.273	0.5302
1000	10.5325	-0.42193	0.09217	1.237	0.5273

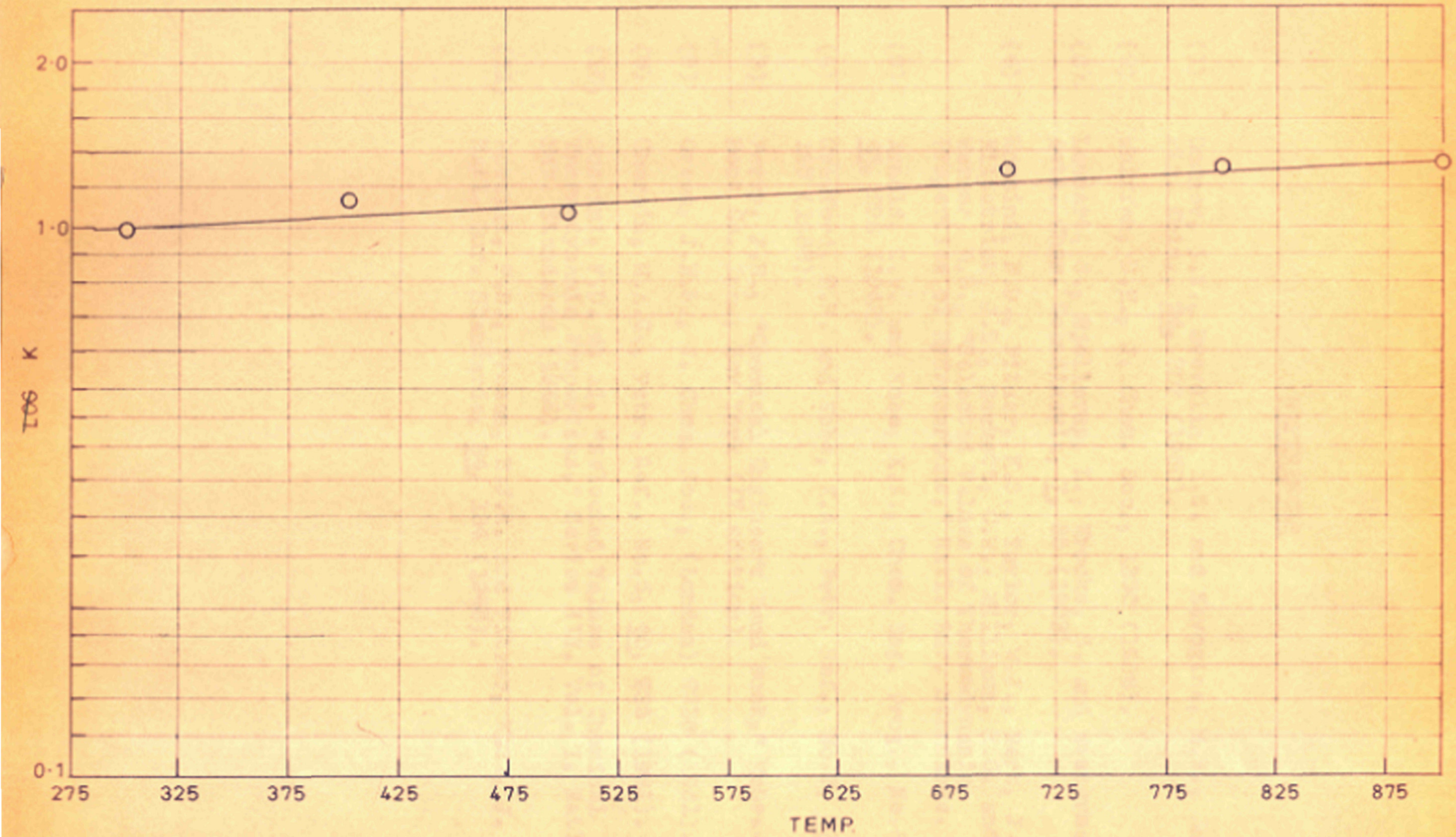

FIG. 3·1. LOG K VS TEMPERATURE

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CHAPTER IV

CHAPTER IV

EXPERIMENTAL

The reactor assembly consisted of : (1) separate feeding arrangements for chlorobenzene and water; (b) separate vaporizers for chlorobenzene and water; (c) super-heater and reactor; and (d) air and water condensers. A diagrammatic sketch of the experimental set-up is shown in Fig. (4.1) and a photograph of the assembly appears in Fig. (4.2).

Reactants feed

The constant flow device used for water [Fig. (4.3)] was similar to that employed by Rihani and Doraiswamy(1). It consisted of a storage vessel, the lower portion of which 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 (2) through a tube cut at an angle as shown in the figure. The cylindrical chamber was in turn connected to a tube ending at the bottom into a drop counting adapter. A glass rod with a Nichrome wire fused to its lower end was fixed in the cylindrical tube. This was necessary since the flows involved were very small and could not be accommodated in the available capillary. Rates of flow were varied by adjusting its length through the capillary.

The vessel was filled with water. Water flowed into the cylindrical zone up to a certain level and this level was maintained in the cylindrical tube. As drops of liquid fell into the adapter from the cylinder, the level of the liquid in the cylindrical chamber 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).

Water from the constant flow device entered a burette. The burette 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 a stop-cock, it was possible to ensure constant flow of water into the reactor.

Chlorobenzene was fed into the chlorobenzene vaporizer from a D.C.L. "M" pump. The capacity of the pump could be varied from 0 to 1710 ml./hr. by manipulating the stroke adjustment micrometer thimble. The thimble was graduated in ten main divisions, covering the entire range from zero to maximum output. A constant check on the constancy of the rate was maintained by passing the liquid through a drop counting connection.

Two separate vaporizers of similar design were provided for chlorobenzene and water. Each vaporizer consisted of a chamber heated by Nichrome wire wound round the surface; a gauge glass indicated the level of the liquid in the chamber. By maintaining a constant level of liquid by appropriate adjustment of the heat input, any desired feed rate within the limits of the design could be achieved. Suitable condensers were provided between the vaporizers and the corresponding adapters to prevent the vapors from entering the adapters and interfering with the flow rates.

Reactor

The reactor system consisted of a super-heater and a reactor. The pyrex glass super-heater ended in a conical bottom (with a stop-cock) and was provided at the top with a B_{29} pyrex joint. Chlorobenzene vapors and steam were admitted separately into the super-heater through tubes provided with B_{10} joints and fused to the main body of the super-heater.

The reactor was made of quartz glass (capable of withstanding high temperatures) of 1 in. diameter and 12 in. length, as shown in Fig. (4.4). The bottom part of the reactor ended in a B_{29} quartz joint which exactly fitted into the B_{29} pyrex joint of the super-heater. The top part of the reactor ended in a B_{29} quartz joint which was provided with an adapter made of quartz. A constriction (for catalyst support) was made 4 in. above the reactor bottom. A quartz thermowell tube with a B_{19} quartz joint fitted into one of the two B_{19} quartz joints of the adapter, and the tip of the thermowell tube just rested over the catalyst support.

The reactor was connected to an air condenser. One end of the condenser was connected to the second B_{19} joint of the quartz adapter through a B_{19} pyrex joint, and the other end to a receiver through a water condenser. The whole assembly was leak-proof.

The reactor was placed in an electrically heated furnace. The furnace and other parts of the assembly were heated by electrical resistance wire. There were in all five heating circuits : two for the vaporizers, one for the super-heater, one for the main reactor, and one for heating the path between the vaporizer and super-heater. Temperatures were controlled by regulating the heat input through variable autotransformers. A voltage stabilizer was introduced in the electrical circuit to ensure a constant voltage.

Experimental procedure

The reactor was filled with the catalyst (-22 + 30 B.S. mesh) to the required height. Heating of all the units was commenced, and when the required temperatures were reached chlorobenzene and water were introduced into the vaporizers at predetermined rates. The reaction being endothermic, there was a slight fall in the temperature of the reactor, and it was brought to the desired level by adjustment of the voltage.

One of the principal difficulties encountered was that, unless the reactants were uniformly distributed in the catalyst bed, there was noticeable chanelling leading also to the further complication of catalyst carryover. Care was taken to avoid this situation in all the runs. The products of reaction collected in the receiver consisted essentially of water, phenol, chlorobenzene and hydrochloric acid. At the temperatures employed, the extent of side reactions was negligible.

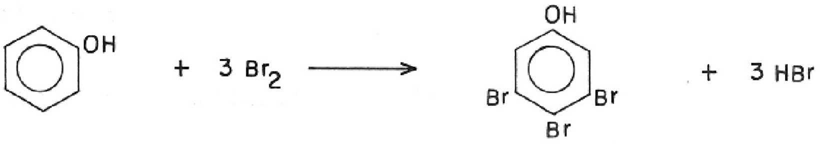
Product analysis

Hydrochloric acid in the products was determined by titration against standard alkali and phenol by bromination. The stock solutions required for the estimation were sodium thiosulfate (0.1 N), KBr-$KBrO_3$ (0.1 N), and potassium hydroxide (0.5 N). Hydrochloric acid was determined by titrating against standard potassium hydroxide using methyl orange as indicator. Phenol was determined as follows :

Estimation of phenol by bromination (2) :

After the estimation of hydrochloric acid present in the catalyzate, the chlorobenzene left unconverted was separated and the solution was made up to a known volume, usually 1 litre. 25 ml. of this solution were pipetted out in a conical flask. 50 ml. of the brominating solution, 50 ml. of distilled water and 5 ml. of concentrated hydrochloric acid were added to it. The flask was stoppered immediately, shaken for 1 minute, and allowed to stand for 30 minutes with occasional swirling of the contents. $KBrO_3$ reacted with KBr in the presence of hydrochloric acid liberating bromine which brominated the phenol present to tribromophenol :

$$KBrO_3 + 5\,KBr + 6HCl \longrightarrow 6KCl + 3H_2O + 3Br_2$$



The flask was cooled and excess bromine was displaced by iodine by the addition of 10 ml. of 20% potassium iodide, and the liberated iodine was titrated against standard thiosulfate.

$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

A blank analysis was carried out without using the solution containing phenol. The difference in the amounts of thiosulfate consumed between the blank and sample titrations gave the quantity of thiosulfate required by the phenol present. The amount of phenol present in the total volume was calculated, keeping in view the fact that 6000 ml. of IN thiosulfate ≡ 94 gm. of phenol. In the absence of side reactions the molar quantities of HCl and phenol should be identical.

Sample estimation :

(1) Estimation of hydrochloric acid :

Alkali required to neutralize HCl present in the catalyzate = 108.7 ml.

Strength of alkali solution = 0.2498 N

∴ Amount of hydrochloric acid present in the catalyzate = 0.02716 mol.

Chlorobenzene fed in 1 hour = 0.2000 mol.

∴ Conversion = 13.58 per cent

(2) Estimation of phenol by $KBr-KBrO_3$ method :

Quantity of sample pipetted = 20 ml.

Quantity of brominating solution = 75 ml.

Strength of sodium thiosulfate solution = 0.09993 N

Standard thiosulfate required for excess iodine = 14.71 ml.

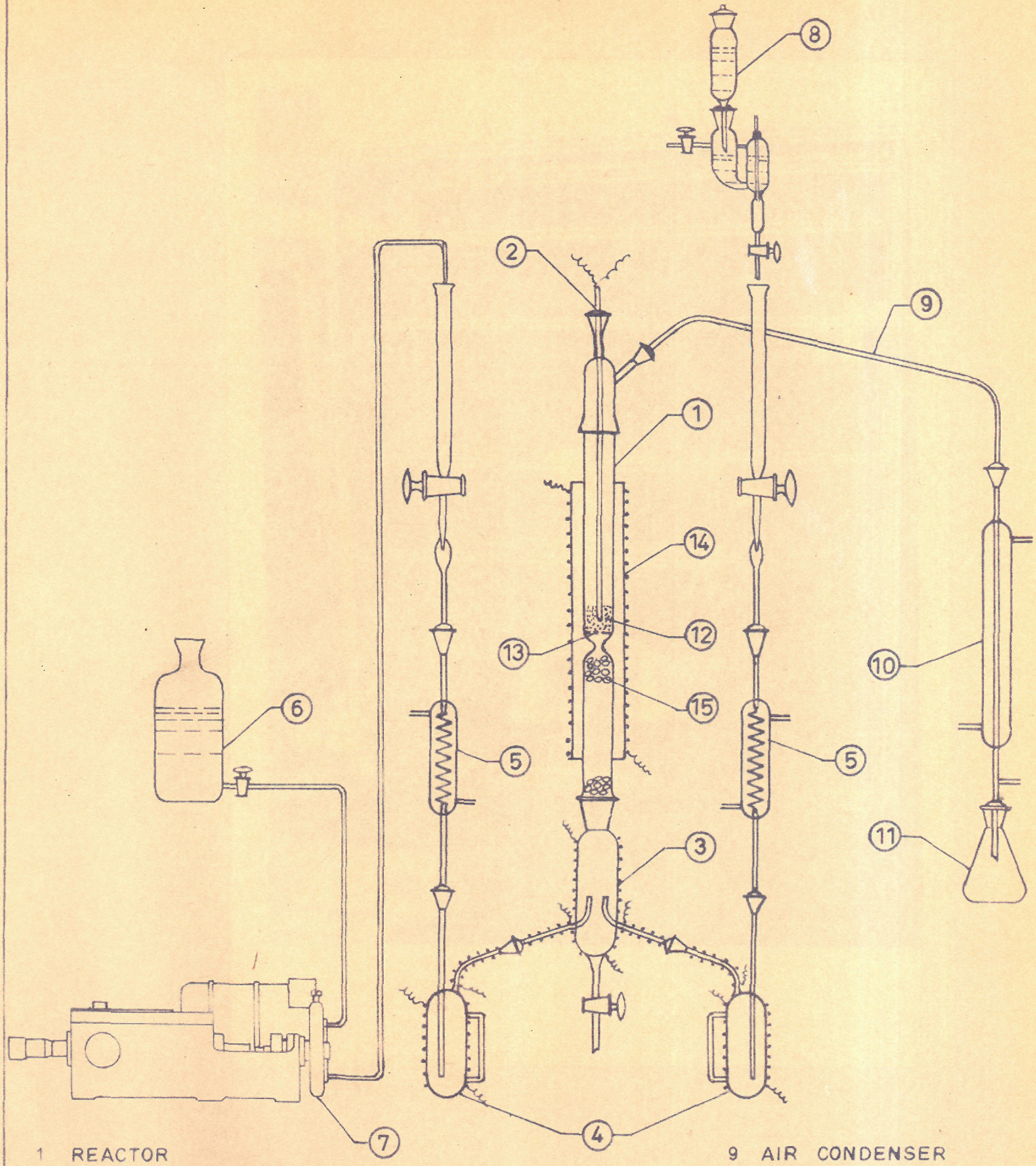
Blank reading = 79.95 ml.

∴ 65.24 ml. of 0.09993 N sodium thiosulfate ≡ 20 ml. of phenol solution (out of 500 ml.)

Since 1000 ml. of 1 N $Na_2S_2O_3$ ≡ $\frac{94}{6}$ gm. of phenol,

amount of phenol in 500 ml. = 0.02716 mol.

∴ Conversion = 13.58 per cent



1 REACTOR
2 THERMOWELL
3 SUPER HEATER
4 VAPORISERS
5 CONDENSERS
6 CHLOROBENZENE FEED BOTTLE
7 CHLOROBENZENE FEED PUMP
8 WATER FEED
9 AIR CONDENSER
10 DOUBLE-WALL WATER CONDENSER
11 RECEIVER
12 CATALYST
13 CATALYST SUPPORTING MESH
14 FURNACE
15 PORCELAIN BEADS

FIG. 4·1. EXPERIMENTLE SET-UP

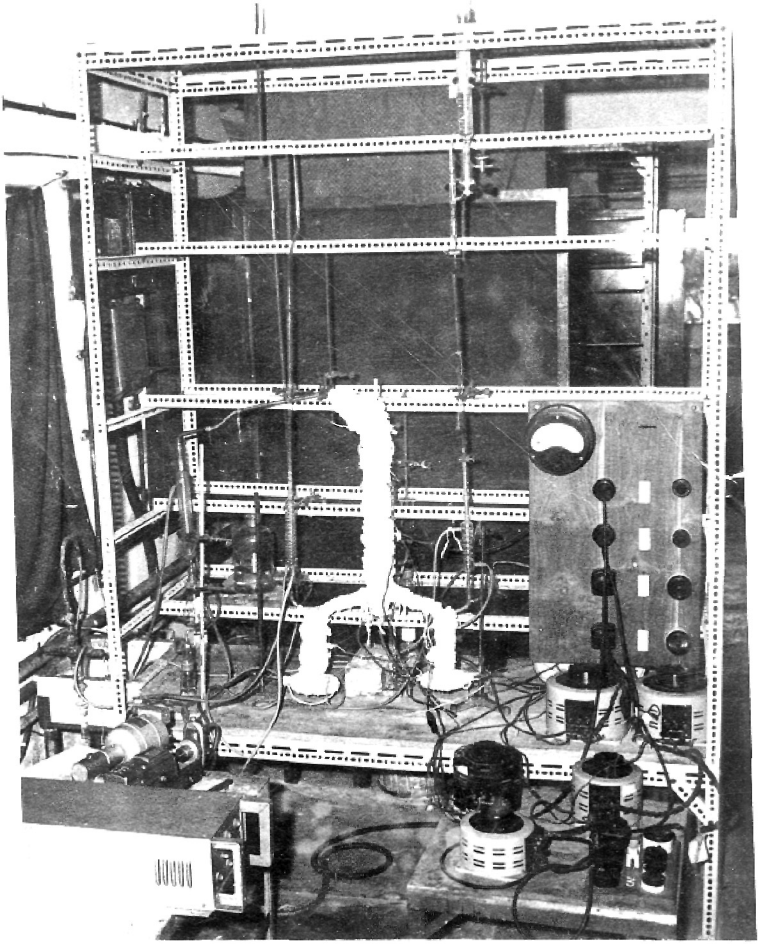
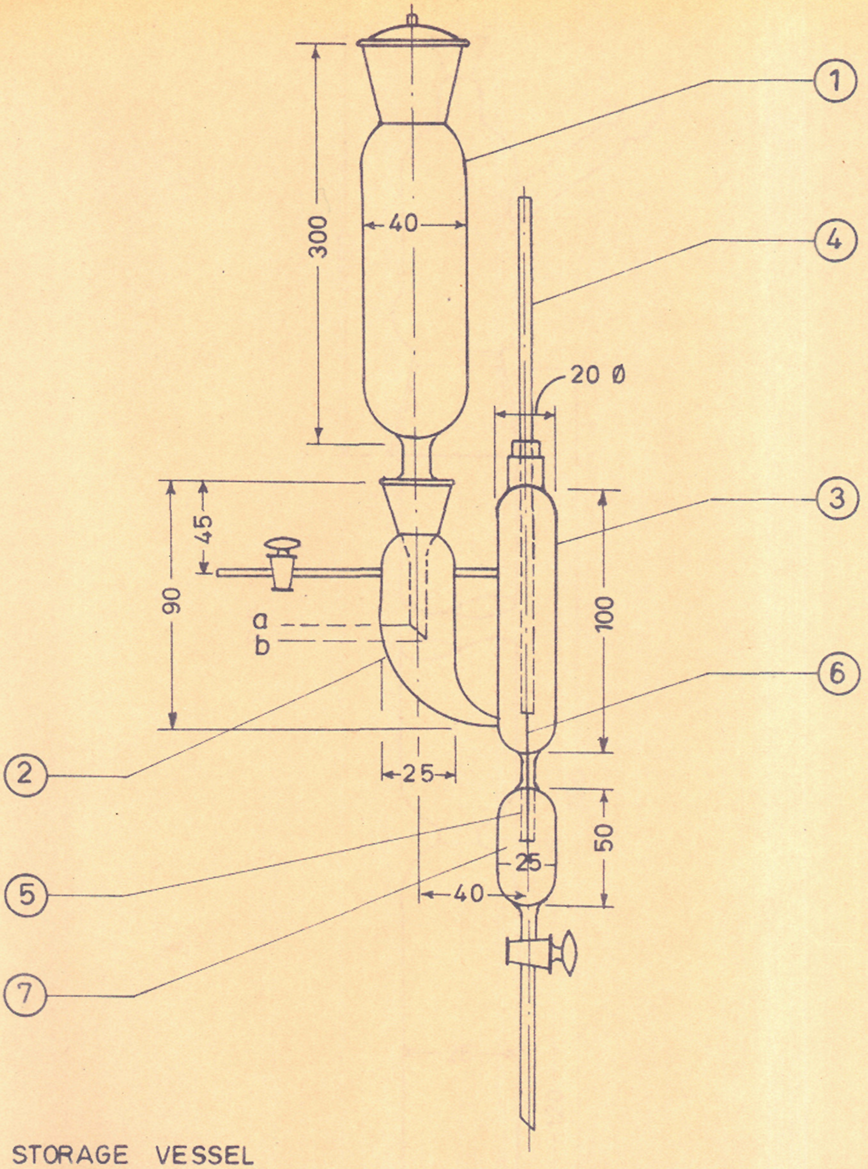
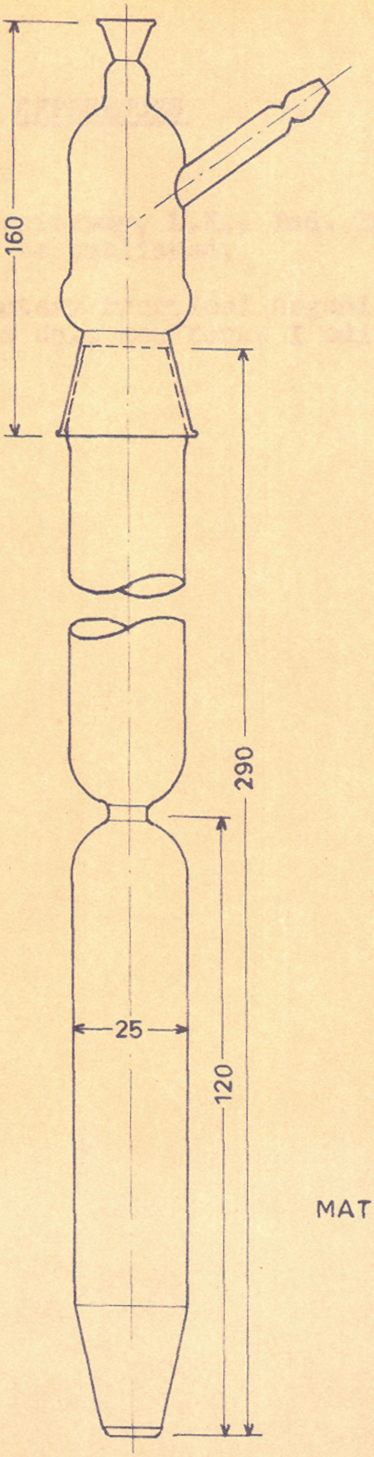


FIG.4·2. PHOTOGRAPH OF THE ASSEMBLY



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

FIG. 4·3. WATER FEED



MATERIAL - TRANSPARENT
SILICA

FIG. 4·4. REACTOR

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CHAPTER V

CHAPTER V

RESULTS AND DISCUSSIONS

Organization of experiments

The experimental work in this study was organized with the principal objective of determining the effect of process variables on the vapor phase hydrolysis of chlorobenzene to phenol using unsupported tricalcium phosphate as catalyst. The preparation of the catalyst and its reactivation were also considered in some detail. The results and discussion are presented under the following broad sections : (1) catalyst preparation; (2) catalyst activation and life; (3) mass transfer studies; (4) rate data : (effect of the variables, reactants ratio, space velocity and temperature); (5) analysis of data and mechanism; and (6) conclusions.

Catalyst preparation

Preliminary experiments established the fact that catalysts such as bauxite and charcoal impregnated with cupric chloride and thorium nitrate exhibit low and short-lived activity. The industrially used catalyst, tricalcium phosphate, was then chosen for detailed studies.

The following solutions were first prepared : (1) 280 ml. phosphoric acid (59.5 Be) was diluted to 70 litres with water; (2) 1.05 litres aqueous ammonia of specific gravity 0.91 was diluted to 5 litres with water; and (3) 1.3 kg. hydrated calcium chloride ($CaCl_2.6H_2O$) was dissolved in 25 litres water.

The ammonia solution was mixed with the diluted phosphoric acid solution, and to the mixture the calcium chloride solution was added slowly over a period of one hour with continuous and energetic stirring. The precipitate of tricalcium phosphate was sucked off, freed from impurities by repeated washings, and dried at 80°C.

Catalyst activation and life

Tricalcium phosphate prepared according to the procedure described above exhibits no catalytic activity as such. It has to be activated by passing air at an elevated temperature for a few hours. From reported data and a few preliminary experiments, a temperature of 550°C. was found to be the most suitable for activation. Using this temperature, the effect of activation time was systematically studied. In all the experiments, air was dried and purified by passing through sulfuric acid, potassium hydroxide, and anhydrous calcium chloride.

Freshly prepared samples of tricalcium phosphate, each weighing 6 gm., were heated in the reactor at 550°C. in a stream of air for 2, 4, 5, 6 and 8 hours respectively. The conversion in each case was determined, and a time vs. conversion curve was plotted. It can be seen from the Table (5.1) and Fig. (5.1) that beyond a period of 5 hours, the conversion is not affected by increase in time. In all the runs reported in this work, the catalyst was activated for 5 hours at 550°C.

Before undertaking kinetic investigations on the catalyst, a life test was carried out to ensure that all the kinetic data were taken when the effect of fouling was absent. It was observed that the catalyst was coated with a deposit of carbon after a few hours of use, leading to a progressive fall in conversion. The carbon deposit on the deactivated catalyst could be burnt off by heating it in a stream of air at 550°C. for a period of 5 hours, the optimum regeneration time determined earlier. The amenability of the catalyst to repeated regenerations was then ascertained by the following procedure.

For each conversion cycle, the degree of conversion of chlorobenzene to phenol was estimated at different process times. The regeneration cycle was then carried out at 550°C. by passing air for 5 hours. At the end of this cycle, conditions were brought back to those of the conversion cycle, and the conversion cycle completed by carrying out the reaction till the catalyst was again deactivated. The results plotted in Fig. (5.2) clearly show that, for each conversion cycle, during the first 3 hours there is a steady rise in conversion, then for a period of about 4 hours uniform conversions are obtained, after which there is a steady fall in conversion.

From these results it appears that the catalyst can be regenerated several times. In industrial practice, a continuous fluidized bed or moving bed reactor can be advantageously used for a catalyst of this type which gets deactivated within a few hours. Alternatively, two reactors can be used such that one is in the production cycle while the other is in the reactivation cycle.

In any kinetic study of this catalyst, therefore, the experiments should be so organized that rate data are obtained under conditions of constant catalyst activity. Thus, for obtaining the conversion at a given set of conditions, it will be necessary to prepare a conversion vs. process time curve under these conditions; then the actual conversion will be given by the flat portion of the curve shown in Fig. (5.2). Obtaining kinetic data for a reaction of this kind, in which the catalyst tends to be deactivated so rapidly, is therefore a time consuming operation involving the determination of a complete process time vs. conversion plot for a single experimental rate point.

Mass transfer studies

In catalysts which are very active, mass transfer may be the limiting step. But for catalysts of low activity, the mass transfer effect may not be significant since the chemical reaction, being comparatively slow, may frequently be the rate determining step.

For the present catalyst, the conversion obtained even at a very high value of W/F (112.5) is less than 20 per cent suggesting that mass transfer may not be a significant step. However, several experiments were carried out to evaluate the mass transfer effect by increasing the velocity of the feed for the same residence time (i.e. the same value of W/F). The mass transfer effect can be minimized by operating at high feed rates, since at these high velocities the equivalent fluid film surrounding the catalyst particle will be destroyed and the partial pressures of the reactants and products in the fluid bulk may be considered to be equal to the partial pressures on the catalyst surface. This is a necessary requirement in any kinetic study since catalytic rate equations are based on concentrations on the catalyst surface, while the experimentally determined concentrations are those in the fluid bulk. Even if the data are obtained under conditions where this identity does not exist, the concentrations on the catalyst surface can be estimated from the bulk concentration values from known correlations (1,2).

Experimentally the effect of velocity can be determined by increasing the feed rate of chlorobenzene (with a corresponding increase in the water rate to keep the same ratio) and also correspondingly increasing the weight of the catalyst so that the residence time (denoted dimensionally by W/F) is maintained constant. It is assumed that the flow is tubular, and that the flow patterns are not affected by increased velocities. However, as it is experimentally difficult to adjust the values of W and F accurately so that W/F remains constant at different velocities, conversion data were determined for different weights of catalyst (6, 10 and 12 gm.) by changing the feed rate several times for a given catalyst weight. Thus three sets of W/F vs. x plots were obtained for the three weights of catalyst used as shown in Table (5.2) and Fig. (5.3).

A cross plot of Fig. (5.3) giving conversion as a function of feed (chlorobenzene) velocity for W/F = 50 is shown in Fig. (5.4). It is evident that for each value of W/F, conversion tends to be independent of velocity beyond a certain value; this value for W/F = 50 is 13 feet per second.

It is necessary to ensure that the velocity is beyond the critical value for any given W/F in all the kinetics experiments. It is interesting to note that although the conversions obtained by this catalyst are quite low, there is a distinct mass transfer effect at low velocities.

Rate data

The three principal variables to be investigated in obtaining rate data for a system involving two reactants are : space velocity with respect to the key component (chlorobenzene), represented by W/F; ratio of the two reactants (chlorobenzene and water); and temperature.

In order to obtain a suitable rate equation, it is always advisable to correlate the data at different ratios and space velocities at the most suitable temperature, and then to introduce the effect of temperature. In the present study a series of preliminary runs showed that 550°C. is the most suitable temperature, and therefore the bulk of the experimental data for determining the reaction mechanism were obtained at this temperature. The following ranges of the variables were studied :

Ratio of chlorobenzene (CB) to water : 1:1 to 1:8

W/F, gm. catalyst/gm. mole CB/hr. : 28 to 112

Temperature, $^{\circ}$C. : 475 to 575

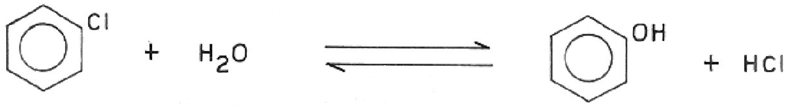
A total of about 30 experiments were carried out to study the effect of these variables. This actually involved 30x10 or 300 conversion determinations since, as stated earlier, each rate point could only be determined after preparing a process time vs. conversion curve for any given set of conditions, and this normally involved ten experimental determinations. Typical time-conversion curves for runs R4, R13, R6 and T6, T10, T12, T14 are shown in Figs. (5.5) and (5.6) respectively. The flat portions of these curves represent the actual conversions for the corresponding runs.

Curves showing conversion as a function of W/F for four different ratios of chlorobenzene to water, 1:1, 1:3, 1:6, 1:8, are shown in Figs. (5.7), (5.8), (5.9) and (5.10) respectively, and the experimental results are tabulated in Table (5.3). Their use in the determination of reaction mechanism is discussed in the next section.

The effect of temperature was studied at a fixed chlorobenzene : water ratio of 1:6. Plots of W/F vs. conversion at three other temperatures 475°, 515° and 575°C. are shown in Figs. (5.11), (5.12) and (5.13) respectively; the experimental results are tabulated in Table (5.4).

Analysis of data

Initial rate studies. For any vapour phase reaction catalysed by a solid surface, the effect of pressure on the initial reaction rate suggests a clue to the probable mechanism. The nature of this curve is different for different mechanisms. For the present reaction,



which can be written in more general form

$$A + B \rightleftharpoons R + S$$

where A stands for chlorobenzene, B for water, R for phenol and S for hydrochloric acid, the effect of the ratio of the reactants can be used in place of pressure as an initial guide to the probable mechanism.

It has been pointed out by Hougen(3) that for most industrial catalysts, surface reaction offers the controlling resistance. Thus it seems no longer necessary, particularly when an industrial catalyst is used, as in the present case, to consider mechanisms other than surface reaction. It is only when this mechanism fails that adsorption and desorption mechanisms should be considered. In such an event the catalyst in question should probably be either improved or replaced.

For the present reaction the following mechanisms were considered.

(1) Dual site surface reaction with adsorption of all the components of the reaction system (A, B, R and S).

$$r = \frac{k\left(P_A P_B - \frac{P_R P_S}{K}\right)}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \quad .. \quad (5.1)$$

(2) Dual site surface reaction between adsorbed chlorobenzene and water in the gas phase

$$r = \frac{k\left(P_A P_B - \frac{P_R P_S}{K}\right)}{(1 + K_A P_A + K_R P_R + K_S P_S)^2} \quad .. \quad (5.2)$$

The initial rate equations for these two cases may be derived as follows. When $r = r_o$, $P_A = P_R = 0$. If we denote the mole fraction of A by y_A, then the mole fraction of B, $y_B = (1-y_A)$. The equation for mechanism (1) then reduces to

$$r_o = \frac{k\,\pi^2 y_A(1-y_A)}{\left[1 + k_A \pi y_A + k_B \pi(1-y_A)\right]^2} \quad .. \qquad (5.3)$$

This equation can be written as

$$r_o = \frac{y_A(1-y_A)}{\frac{1}{\pi^2 k}\left[1 + K_A \pi y_A + K_B \pi(1-y_A)\right]^2} \quad ..$$

$$= \frac{y_A(1-y_A)}{(a'+b'y_A)^2} \quad .. \qquad (5.4)$$

where

$$a' = \frac{1}{\sqrt{k}}\left(\frac{1}{\pi} + K_B\right)$$

$$b' = \frac{1}{\sqrt{k}} (K_A - K_B)$$

The form of Equation (5.4) shows that a plot of r_o against y_A should show a maximum. In the present reaction y_A was changed from 0.11 to 0.5. For every value of y_A (i.e. ratio of A to B), several runs were made, and the conversion determined as a function of W/F as shown in Table 5.3; then the initial rate r_o was determined by plotting the reaction rate r as a function of conversion, r being determined by graphical differentiation of the curves of Figs. (5.7), (5.8), (5.9) and (5.10). The curves of r vs. W/F, shown in Figs. (5.14), (5.15), (5.16) and (5.17), were extrapolated to $x = 0$ in each case to give the corresponding value of r_o. These values are summarized below.

Ratio of CB to water	y_A	r_o
1:8	0.111	0.00203
1:6	0.143	0.00326
1:3	0.250	0.00370
1:1	0.500	0.00143

r_o is plotted as a function of y_A in Fig. (5.18). It can be seen that the nature of the curve corresponds to the mechanism where surface reaction is rate controlling. By simplifying the rate equation for the second case of surface reaction considered, it can be shown that a similar curve will result.

Determination of rate equation. Let m = moles of B used per mole of A. Then,

$$P_R = P_S = \frac{x}{m+1}\pi \quad \cdot\cdot \quad (5.5)$$

$$P_A = \frac{1-x}{m+1}\pi$$

$$= \frac{\pi}{m+1} - P_R \quad \cdot\cdot \quad (5.6)$$

$$P_B = \frac{m-x}{m+1}\pi$$

$$= \frac{m}{m+1}\pi - P_R \quad \cdot\cdot \quad (5.7)$$

Equation (5.1) can be written as

$$R = \frac{\left(P_A P_B - \frac{P_R P_S}{K}\right)}{r}$$

$$= \frac{1}{\sqrt{k}} + \frac{K_A}{\sqrt{k}} P_A + \frac{K_B}{\sqrt{k}} P_B + \frac{K_R}{\sqrt{k}} P_R + \frac{K_S}{\sqrt{k}} P_S \quad .. \quad (5.8)$$

Since $P_R = P_S$, this equation reduces to

$$R = a + bP_A + cP_B + (d+e)P_R \quad .. \quad (5.9)$$

where

$$a = \frac{1}{\sqrt{k}}$$

$$b = \frac{K_A}{\sqrt{k}}$$

$$c = \frac{K_B}{\sqrt{k}}$$

$$d+e = \frac{(K_R+K_S)}{\sqrt{k}}$$

Substituting the values of P_A, P_B and P_S in terms of P_R and m, and separating the variables

$$R = (d + e - b - c)P_R + \left(a + \frac{\pi}{m+1} b + \frac{m\pi}{m+1} c\right) \quad .. \quad (5.10)$$

If the reaction takes place according to the second mechanism, the constant c will vanish and Equation (5.10) reduces to

$$(d + e - b)P_R + \left(a + \frac{\pi}{m+1} b\right) = R \quad .. \quad (5.11)$$

A plot of the function R against P_R should give a straight line whose slope is (d + e - b) and intercept is

$a + \frac{\pi}{m+1} b$. Different values of m will give straight lines of different intercepts but of the same slope.

Fig. (5.19) shows a plot of P_R vs. R for the four ratios considered in this study. It can be seen that straight lines are obtained for each of these ratios up to R=8 and that the slope of these four lines are the same.

The intercept term can be rewritten as

$$am + (a + \pi b) = I(1 + m) \quad .. \quad (5.12)$$

where I represents the intercepts for the different ratios read from Fig. (5.19). According to Equation (5.12), when m is plotted against I(1 + m), a straight line should be obtained whose slope gives a and intercept $(a + \pi b)$. This plot is shown in Fig. (5.20). From the values of the slope (average) and intercepts,

$$a = 5.8$$

$$b = 1.28$$

Substituting these values in the slope (a + c - b) of the straight lines shown of Fig. (5.19) the value of (d + e) is obtained as

$$(d + e) = 96.28$$

From the defining equations of a, b, d and e the following values of the constant of Equation (5.2) may be obtained.

$$k = \frac{1}{a} = 0.03$$

$$K_A = b\sqrt{k} = 0.22$$

$$(K_R + K_S) = (d + e)\sqrt{k} = 16.1$$

$(K_R + K_S)$ can be put together and a constant K_{RS} defined such that $K_{RS} = K_R + K_S$. The separate determination of K_R and K_S is not possible, since the partial pressures of R and S were not independently varied in this investigation. The final equation can therefore be written as

$$r = \frac{0.03\left(P_A P_B - \frac{P_R P_S}{K}\right)}{(1 + 0.22P_A + 16.1P_R)^2} \quad .. \quad (5.13)$$

This equation suggests that surface reaction between adsorbed chlorobenzene and water in the gas phase is rate controlling, and since the values of the constants are positive this mechanism can be considered to be plausible. Mechanism (1) was not found to be satisfactory since negative values were obtained for the constants.

The correctness of the equation was determined by calculating the reaction rate from the estimated values of the constants and comparing these rates with the corresponding values determined by graphical differentiation of the experimental x - W/F curves. Calculated and experimental values are shown in Table (5.5). The average errors for the different ratios were as follows :

Ratio	Error, %
1:8	8.33
1:6	22.12
1:3	6.82
1:1	Mechanism does not hold.

The average error for all the three ratios, 1:8, 1:6 and 1:3, up to a conversion of 12% is 12.5%. The error for the ratio 1:1 was more than 50% indicating that this mechanism probably does not hold at such a high mole fraction of A in the feed.

The rate equation developed holds good only at 550°C. No attempt was made in this study to determine the constants at different temperatures, since the experimental work at these temperatures was restricted to one ratio only.

Conclusion

Although more work is necessary to arrive at a definite conclusion regarding the mechanism of the reaction, it can be tentatively postulated that the controlling mechanism in the hydrolysis of chlorobenzene on tricalcium phosphate is the surface reaction between adsorbed chlorobenzene and water in the gas phase. In this investigation the adsorption equilibrium constants for phenol and water have been put together as a single constant. More experiments are necessary to estimate these constants separately. The experimental work has shown that the mechanism suggested by the behaviour of the initial rate as a function of initial mole fraction is in fact the most plausible mechanism. The variation of the rate constant and the adsorption constants with temperature has not been studied. Also, the kinetics of deactivation has not been fully investigated. Further work in this subject should therefore include (1) a temperature correlation for the rate and adsorption constants, and (2) a study of the behaviour of these constants as a function of process time.

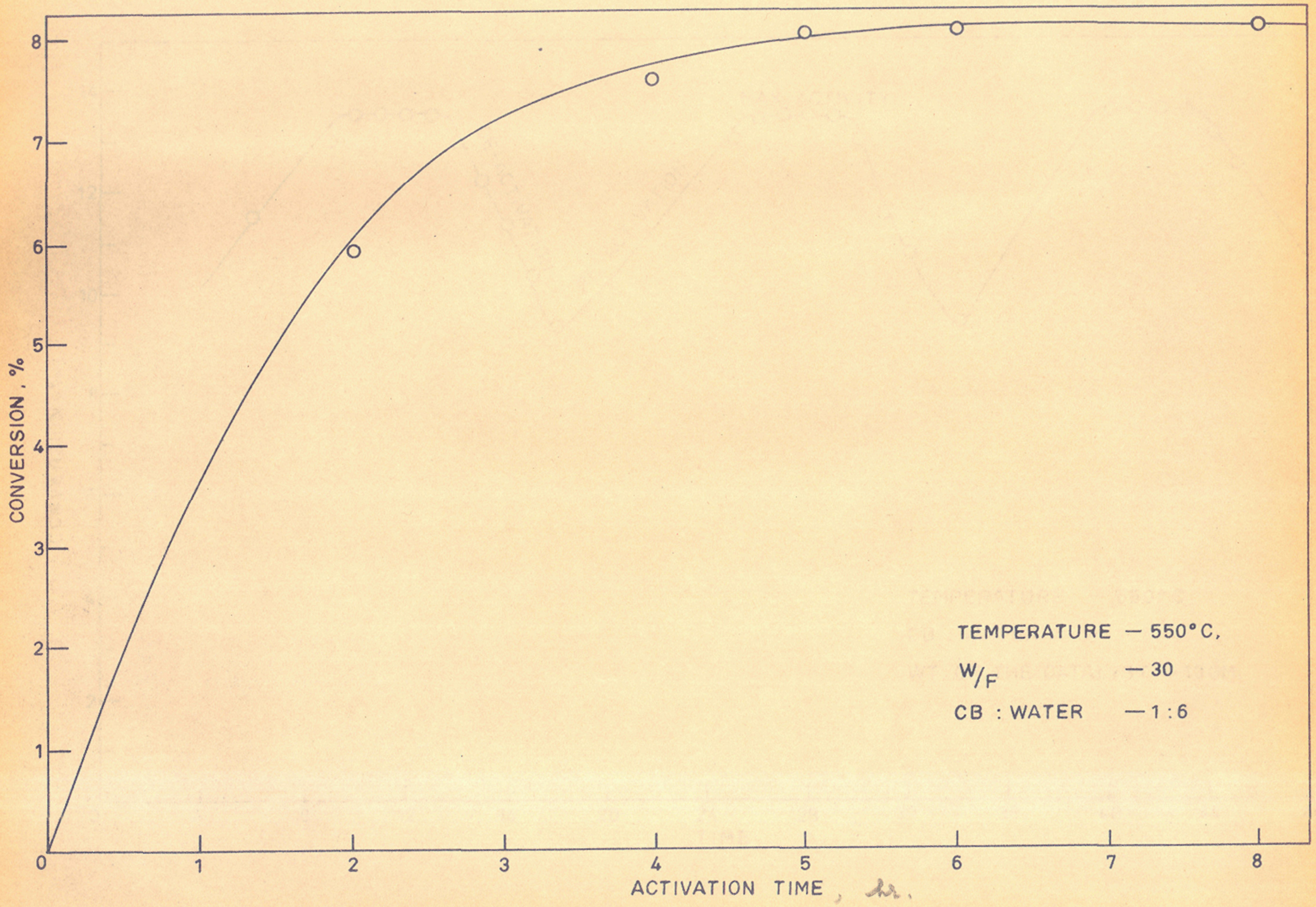


FIG. 5·1. OPTIMUM ACTIVATION TIME OF THE CATALYST

Table 5.1

Effect of catalyst activation time on conversion

Activation temperature = 550°C.
Wt. of catalyst = 6 gm.
CB feed rate = 0.20 moles/hr.
CB : water = 1:6

Run No.	Activation time hr.	Conversion %
A1	2	5.90
A2	4	7.50
A3	5	8.02
A4	6	8.02
A5	7	8.02

Table 5.2

Effect of mass transfer

Temperature = 550°C.

CB : water = 1:6

Run No.	Rate of CB moles/hr.	Rate of water moles/hr.	Wt. of catalyst gm.	W/F	Conversion %
M1	0.2667	1.60	6	30.00	8.020
M2	0.2000	1.20	6	22.50	6.15
M3	0.1334	0.80	6	44.98	11.50
M4	0.2667	1.60	10	37.50	10.74
M5	0.2000	1.20	10	50.00	13.58
M6	0.1334	0.80	10	74.96	16.30
M7	0.0889	0.53	10	112.50	17.15
M8	0.2667	1.60	12	45.00	12.70
M9	0.2000	1.20	12	60.00	15.10
M10	0.1334	0.80	12	94.19	16.90

Table 5.3

Effect of ratio of reactants

Temperature = 550°C.
Wt. of catalyst = 10 gm.

Run No.	Chlorobenzene feed rate moles/hr.	Ratio of CB to water (molar)	W/F	Conversion %
R1	0.3556	1:1	28.13	3.65
R2	0.3112		32.14	4.45
R3	0.2667		37.50	5.20
R4	0.2000		50.00	6.15
R5	0.2667	1:3	37.50	11.40
R6	0.2000		50.00	13.77
R7	0.1334		74.96	15.73
R8	0.2667	1:6	37.50	10.74
R9	0.2000		50.00	13.58
R10	0.1334		74.96	16.30
R11	0.0889		112.50	17.15

Table 5.3 (contd.)

Run No.	Chlorobenzene feed rate moles/hr.	Ratio of CB to water (molar)	W/F	Conversion %
R12	0.2667	1:8	37.50	5.94
R13	0.2000		50.00	9.195
R14	0.1334		74.96	12.16
R15	0.0889		112.50	14.55

Table 5.4

Effect of temperature on conversion

CB : water = 1:6

Wt. of catalyst = 10 gm.

Run No.	Temperature °C.	Rate of CB moles/hr.	W/F	Conversion %
T 1	475	0.2667	37.50	5.10
T2		0.2000	50.00	6.78
T3		0.1334	74.96	7.20
T4		0.0889	112.50	7.99
T5	515	0.2667	37.50	8.45
T6		0.2000	50.00	9.33
T7		0.1334	74.96	10.35
T8		0.0889	112.50	11.55
R8	550	0.2667	37.50	10.74
R9		0.2000	50.00	13.58

Table 5.4 (contd.)

Run No.	Temperature °C.	Rate of CB moles/hr.	W/F	Conversion %
R10	550	0.1334	74.96	16.30
R11		0.0889	112.50	17.15
T9	575	0.2000	50.00	15.38
T10		0.1334	74.96	16.50
T11		0.0889	112.50	17.25

Table 5.5

Comparison of calculated and experimental rates

Temperature = 550°C.

No.	CB to water ratio	$rx10^3$ Experimental	$rx10^3$ Calculated	Deviation %
1	1:3	3.37	3.3771	11.9000
2		3.26	3.505	7.5160
3		3.12	3.264	4.6150
4		2.99	3.038	1.6050
5		2.82	2.835	0.4167
6		2.64	2.651	2.4390
7		2.42	2.479	6.3750
8		2.18	2.319	19.7200
9		3.70	2.328	37.08
10	1:6	2.87	2.22	32.65
11		2.78	2.117	23.85
12		2.66	2.020	24.06

Table 5.5 (contd.)

No.	CB to water ratio	$rx10^3$ Experimental	$rx10^3$ Calculated	Deviation %
13	1:6	2.54	1.932	23.94
14		2.4	1.834	23.58
15		2.22	1.752	21.08
16		1.97	1.676	14.92
17		1.64	1.589	3.111
18		1.20	1.524	27.00
19		1.95	1.998	2.461
20	1:8	1.88	1.914	1.808
21		1.79	1.838	2.1290
22		1.685	1.762	4.569
23		1.555	1.692	8.810
24		1.415	1.626	14.91
25		1.260	1.559	23.73

TABLE OF SYMBOLS

A, B - Chlorobenzene, water.

R, S - Phenol, hydrochloric acid.

C_p^o - Heat capacity, cal./°K./g.mole.

a, b, c, d, e - Constants in equation 3.5 and equation 5.9.

$\triangle G_f^o$ - Free energy of formation, kcal./g.mole.

$\triangle G_T^o$ - Free energy of reaction, kcal./g.mole.

$\frac{G_T^o - H_o^o}{T}$ - Free energy function, cal./°K./g.mole.

$\triangle H_c^o$ - Heat of combustion, kcal./g.mole.

$\triangle H_f^o$ - Heat of formation, kcal./g.mole.

$\triangle H_T^o$ - Heat of reaction, kcal./g.mole.

$(H_T^o - H_o^o)$ - Enthalpy function, kcal./g.mole.

$\triangle H_v^o$ - Heat of vaporisation, kcal./g.mole.

K - Equilibrium constant.

K_A, K_B, K_R, K_S - Adsorption equilibrium constants.

K_v - Fugacity coefficient term.

l, g - Liquid, gas.

I - Intercept of equation 5.12.

m - Moles of B used per mole of A.

n - Number of moles.

p_A, p_B, p_R, p_S - Partial pressures of A, B, R, S.

R - Gas constant, cal./°K./g.mole.

R - Rate factor.

r - Reaction rate, g.moles/g.cat./hr.

r_o - Initial rate, g.moles/g.cat./hr.

S^o - Entropy, cal./°K./mole.

T - Temperature, °K.

x - Moles of phenol formed per mole of chlorobenzene.

W/F - gm./g.mole/hr.

\- Total pressure, atm.

\- Fugacity coefficient.

y_A - Mole fraction of A.

y_B - Mole fraction of B.

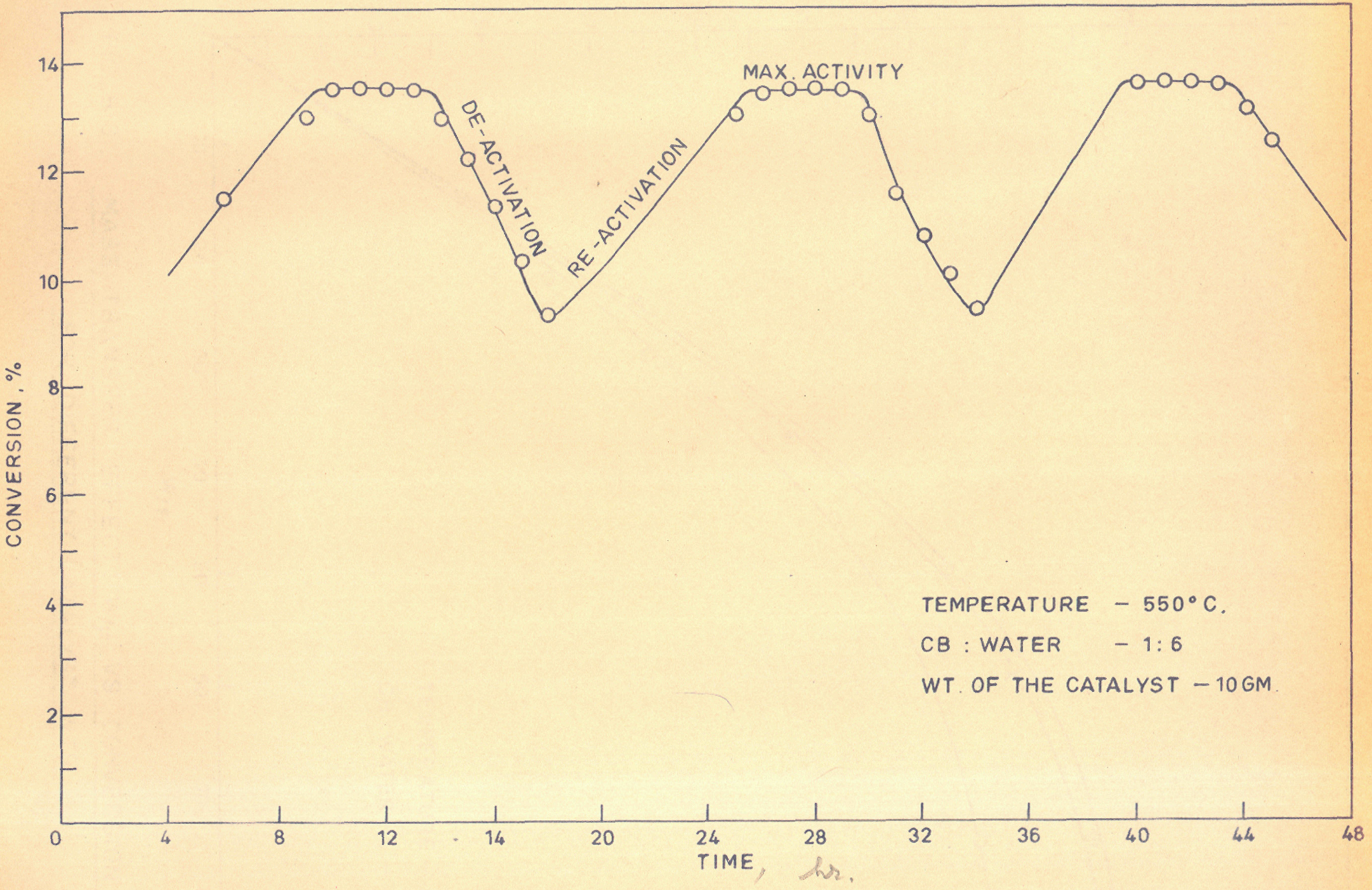


FIG. 5·2. CATALYST ACTIVITY AS A FUNCTION OF PROCESS TIME

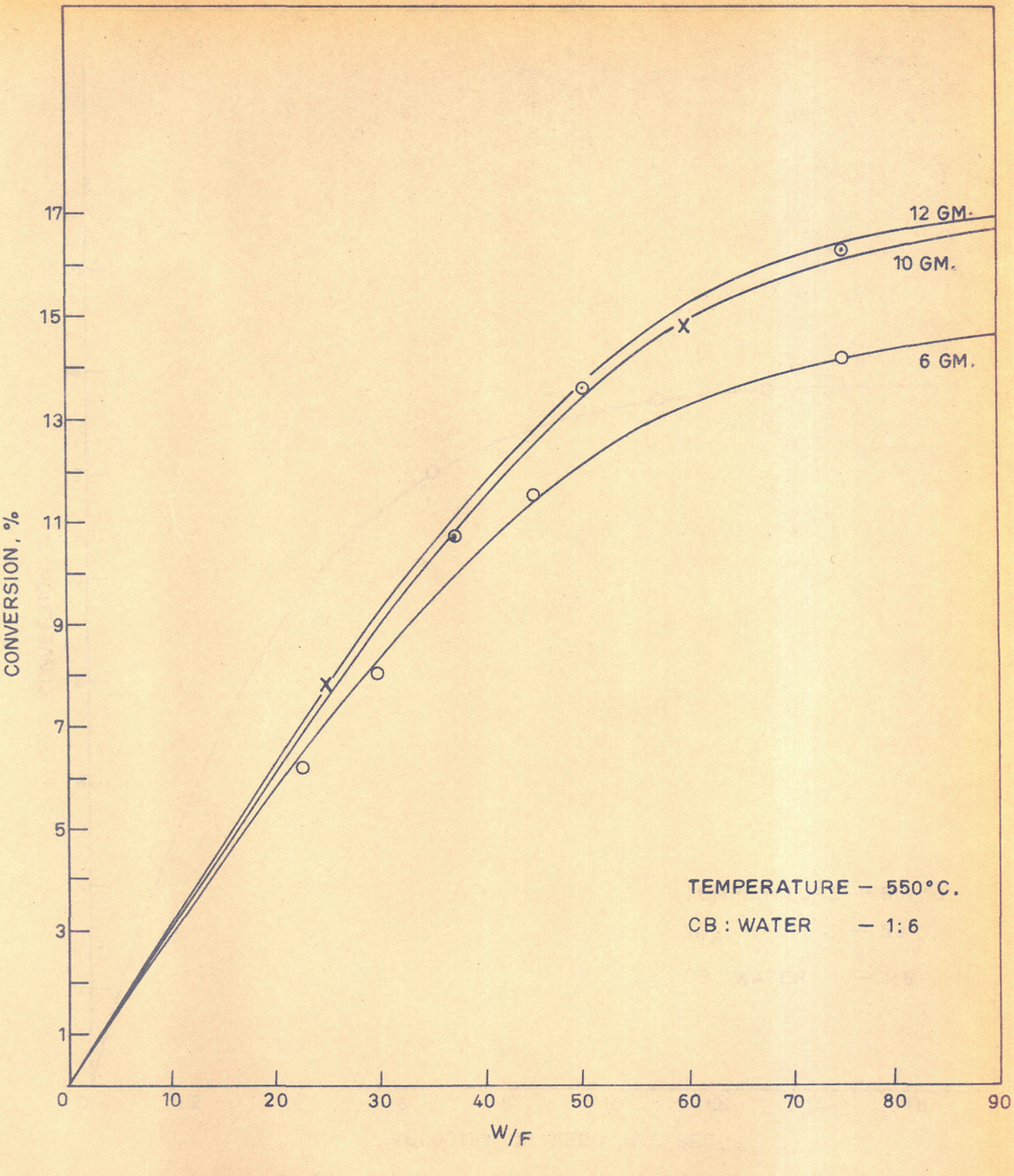


FIG. 5·3. MASS TRANSFER EFFECT: W/F VS CONVERSION FOR DIFFERENT CATALYST WTS.

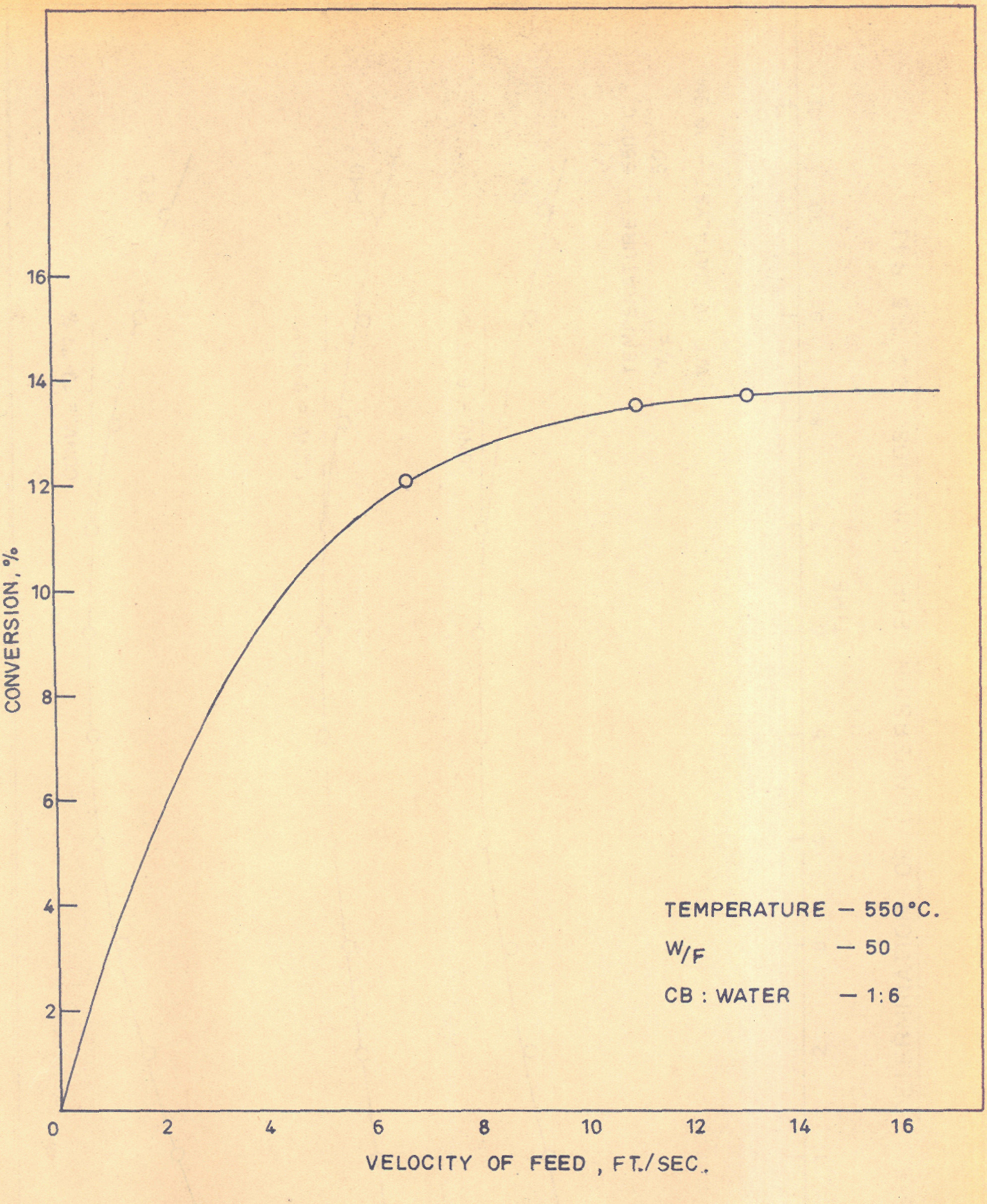


FIG. 5·4 . MASS TRANSFER EFFECT: FEED VELOCITY AS A FUNCTION OF CONVERSION

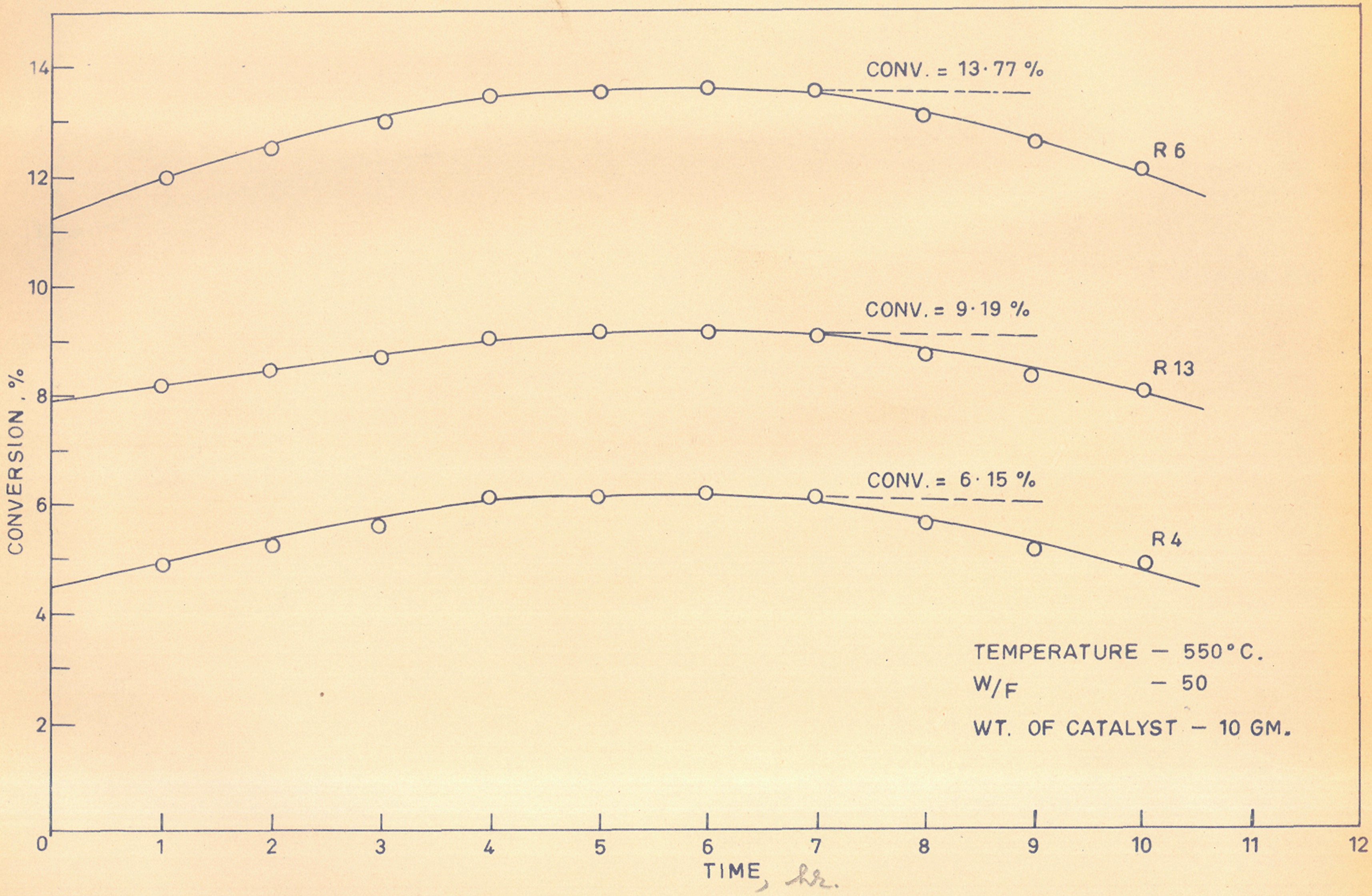


FIG. 5·5 . DETERMINATION OF CONVERSION FOR RUN NOS. R 4, R 6, R 13

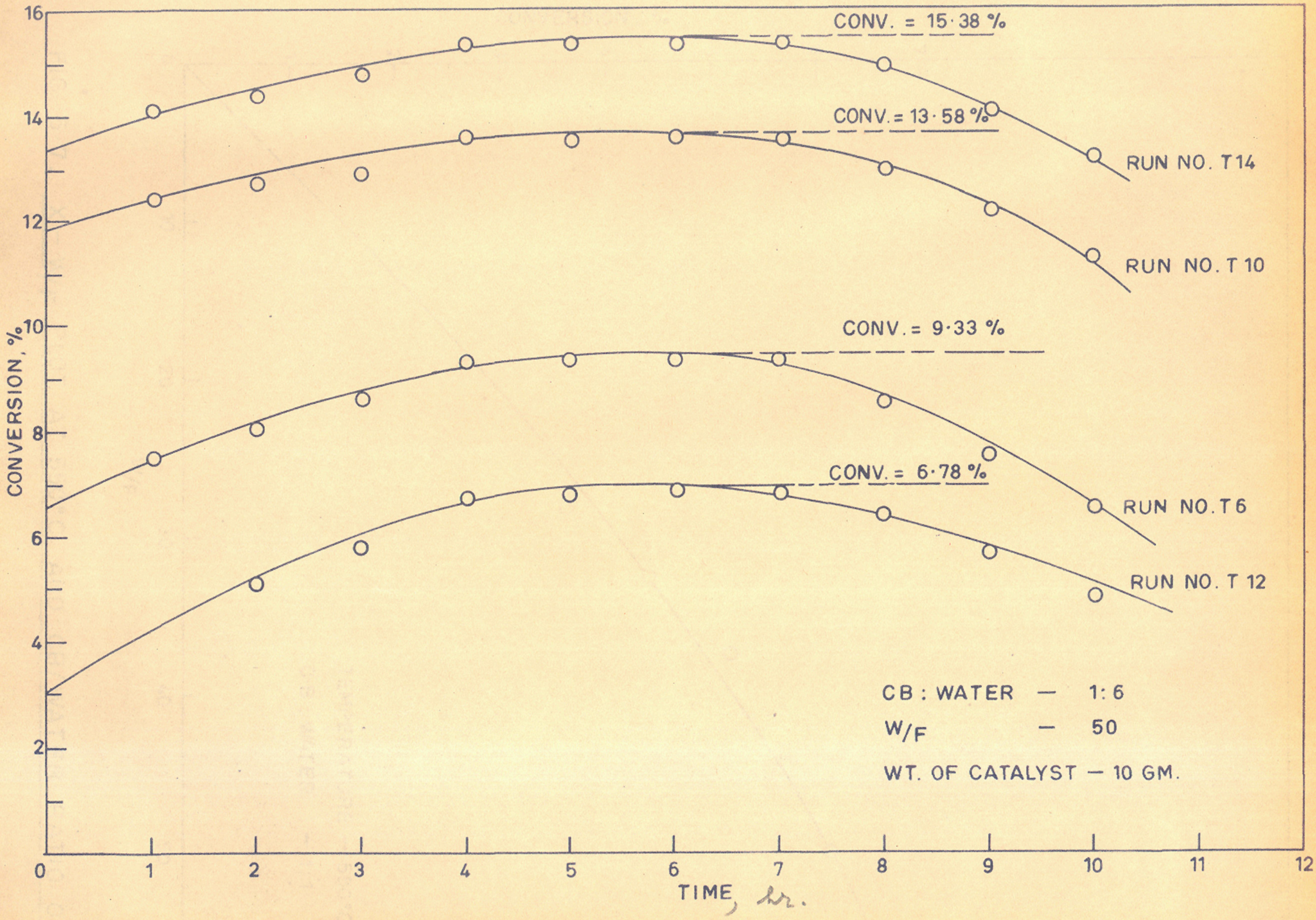


FIG. 5·6. DETERMINATION OF CONVERSION FOR RUN NOS. T2, T6, T10, T14

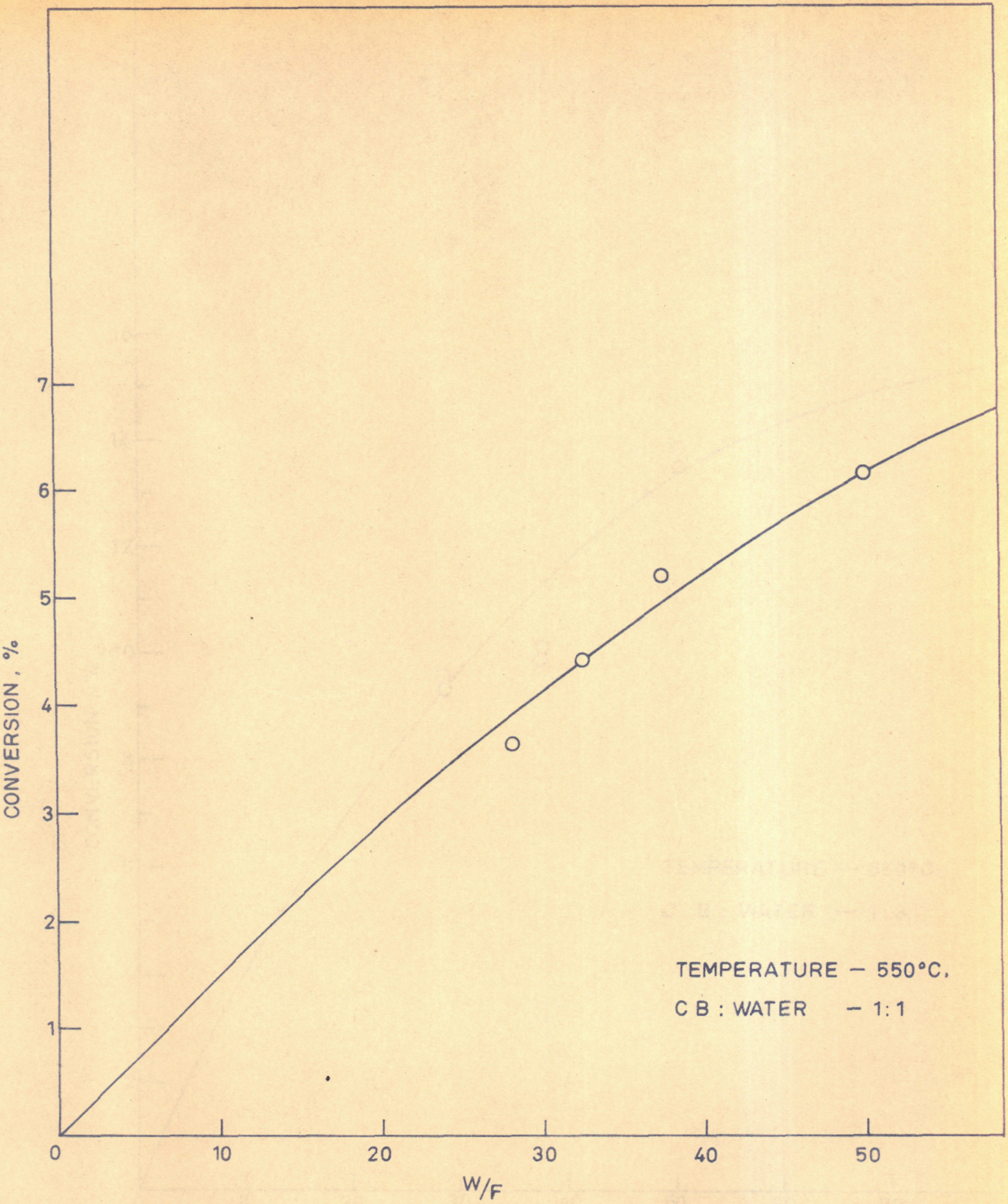


FIG. 5·7. X – W/F PLOT AT 550°C. AND CB/WATER RATIO OF 1:3

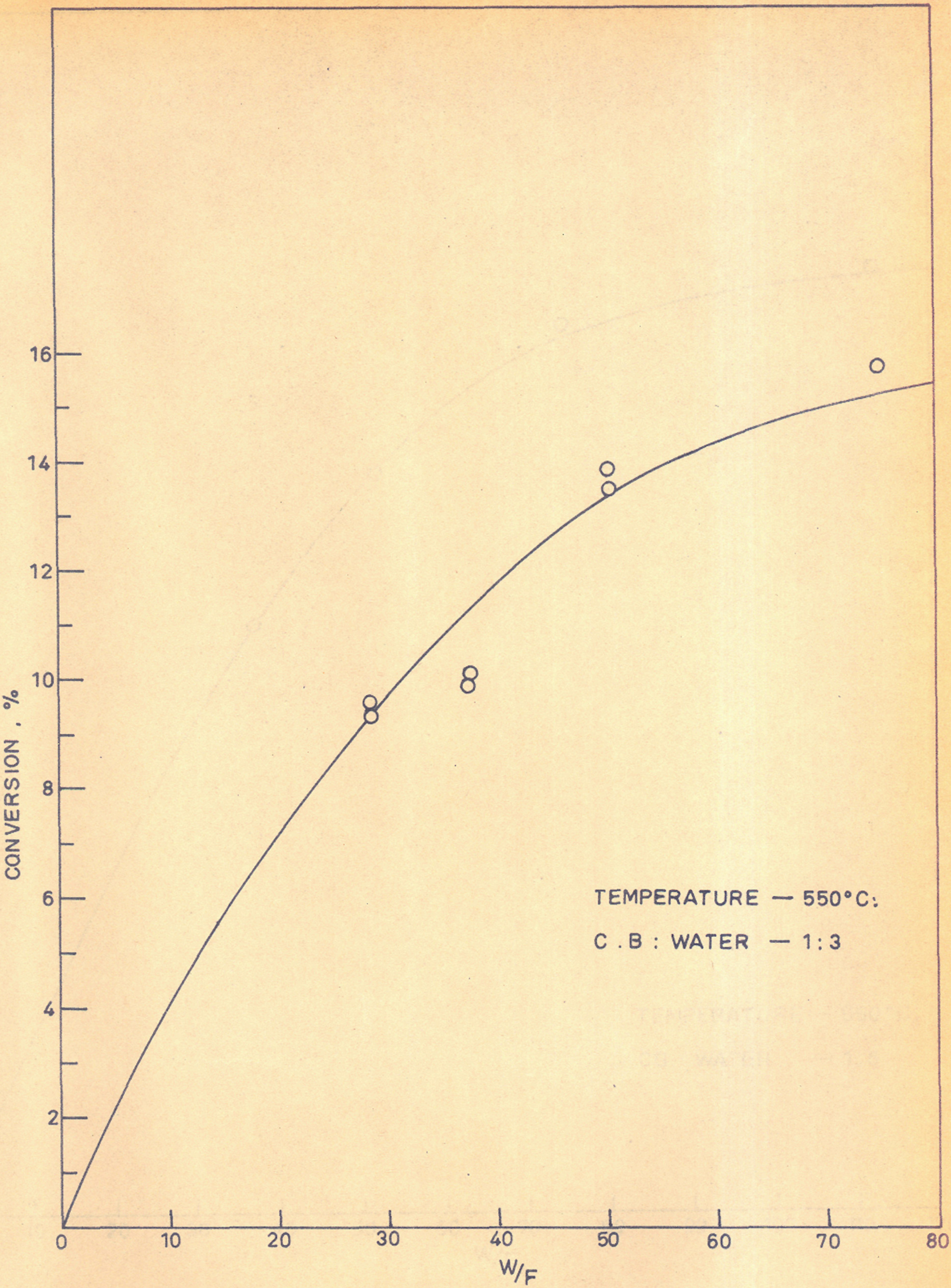


FIG. 5·8. X - W/F PLOT AT 550°C. AND CB / WATER RATIO OF 1:3

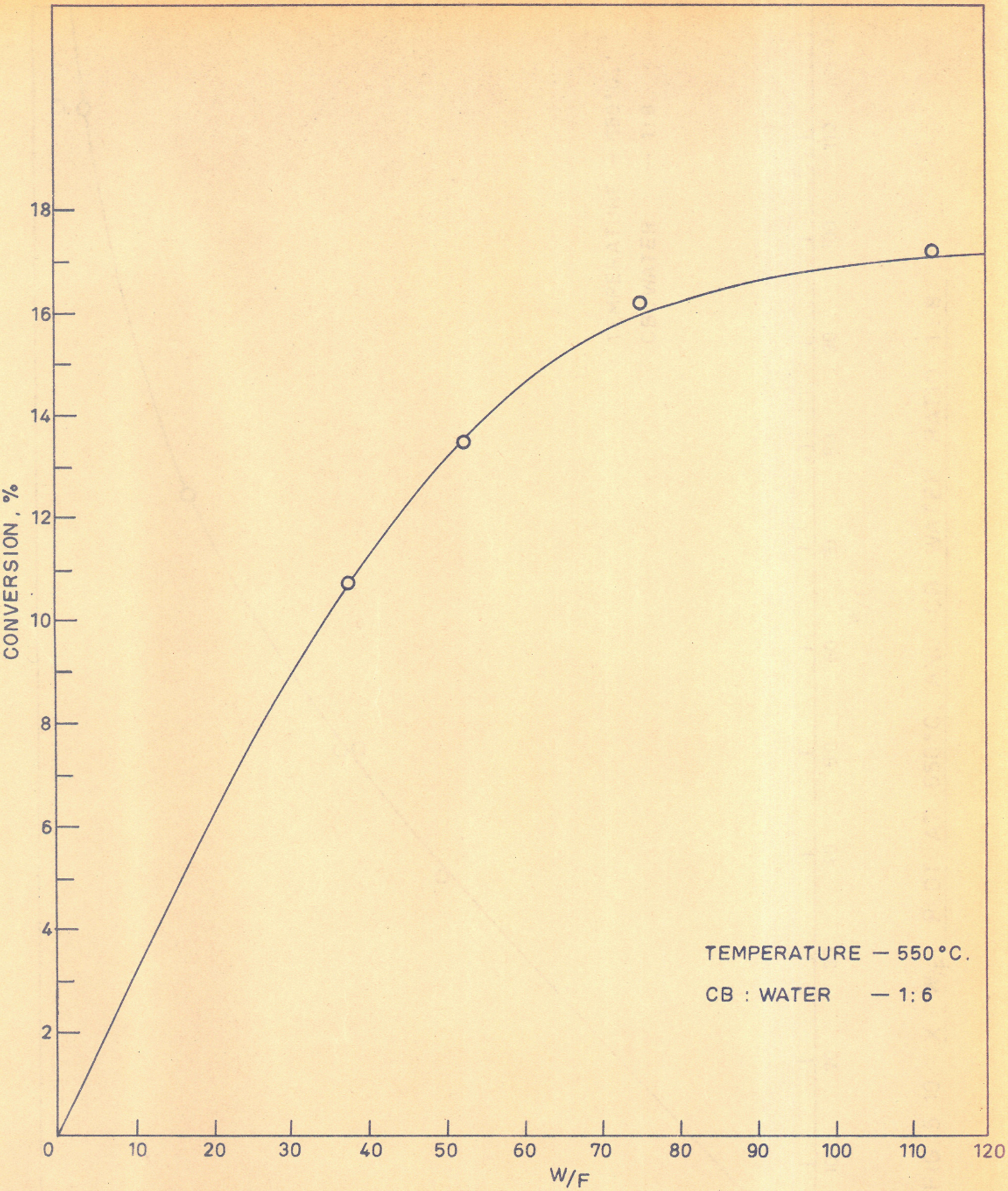


FIG. 5·9. X-W/F PLOT AT 550°C. AND CB/WATER RATIO OF 1:6

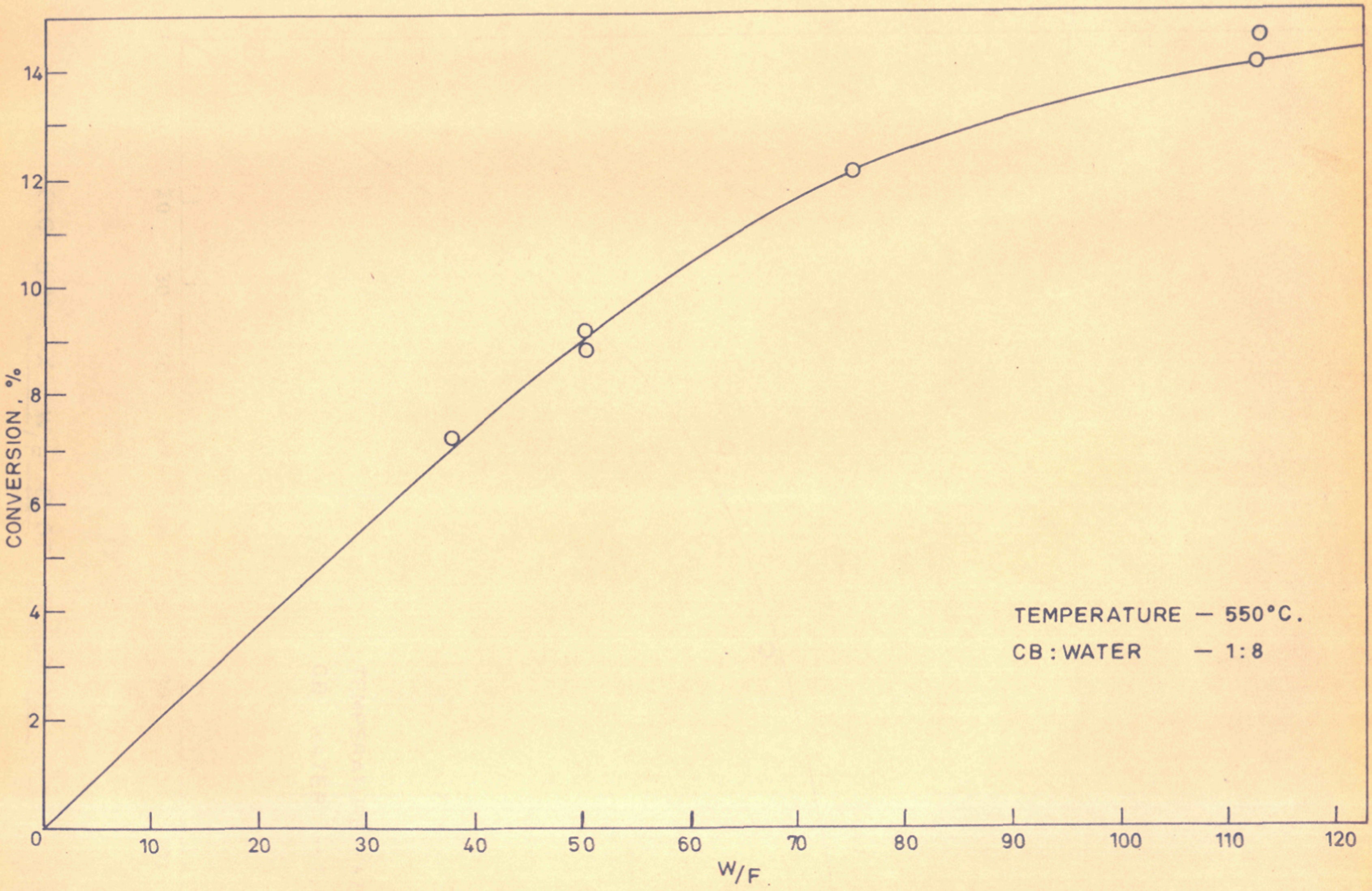


FIG. 5·10. X - W/F PLOT AT 550°C. AND CB : WATER RATIO 1 : 8

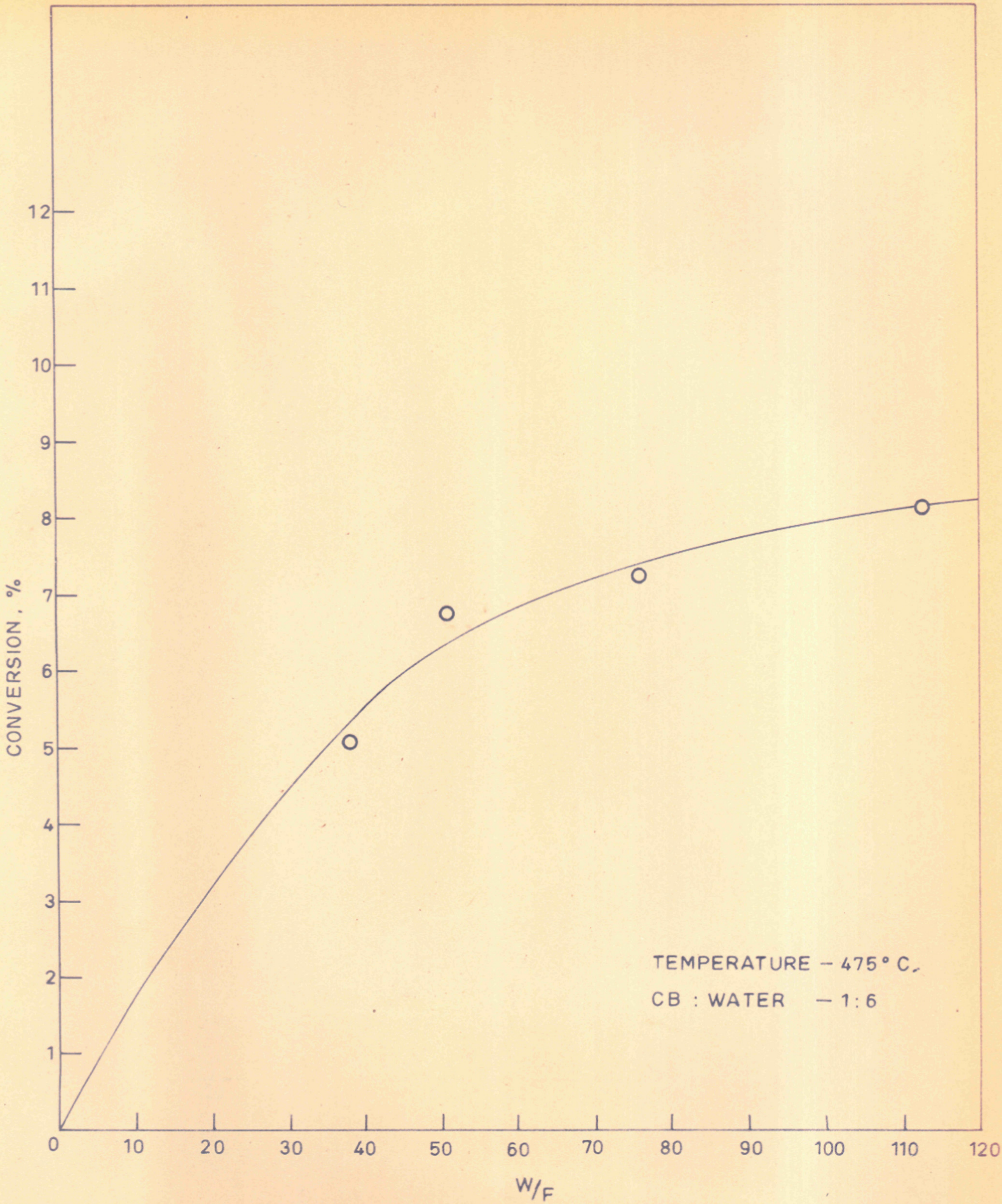


FIG. 5·11 X – W/F PLOT AT 475°C.

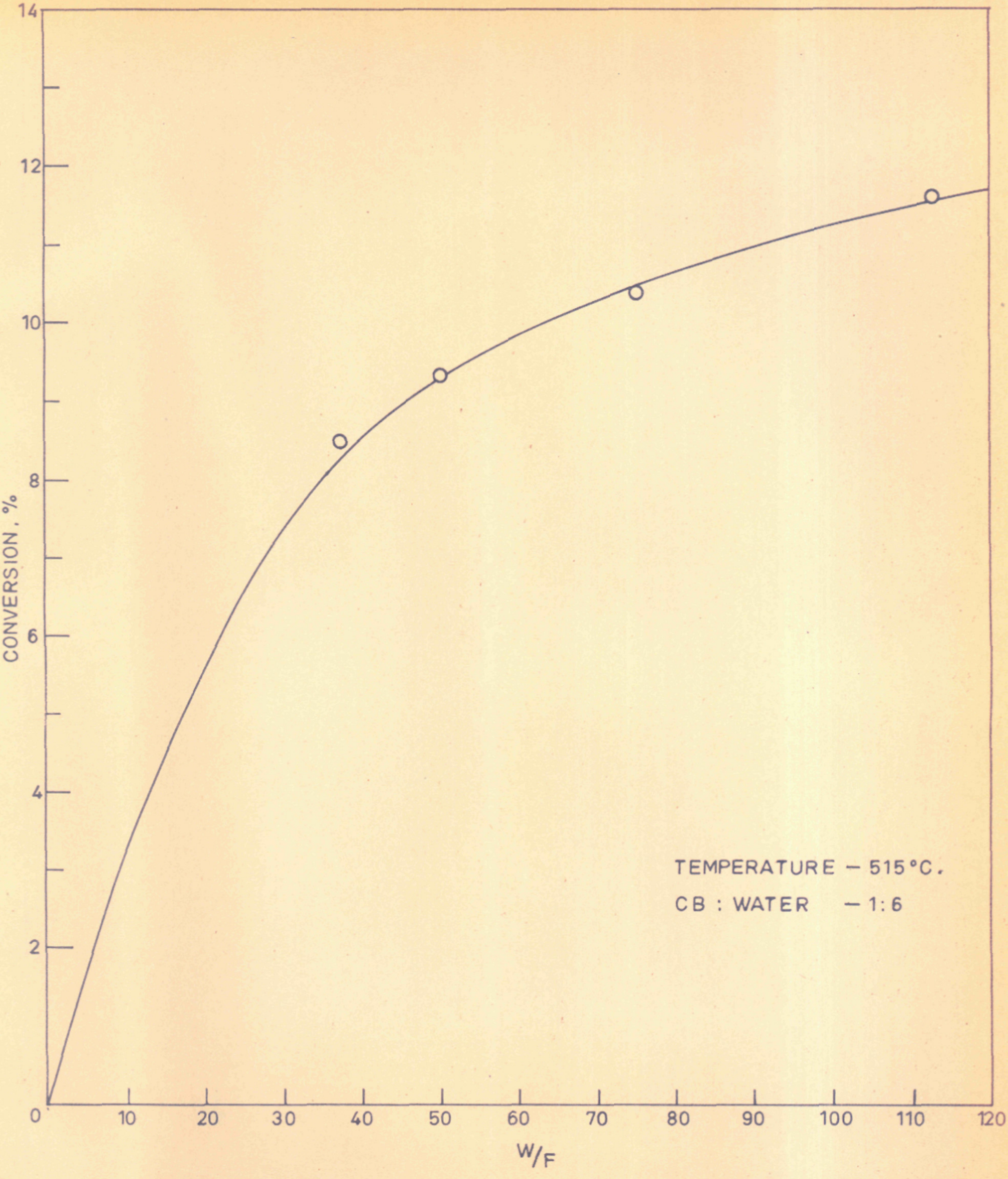


FIG. 5·12. X – W/F PLOT AT 515 °C.

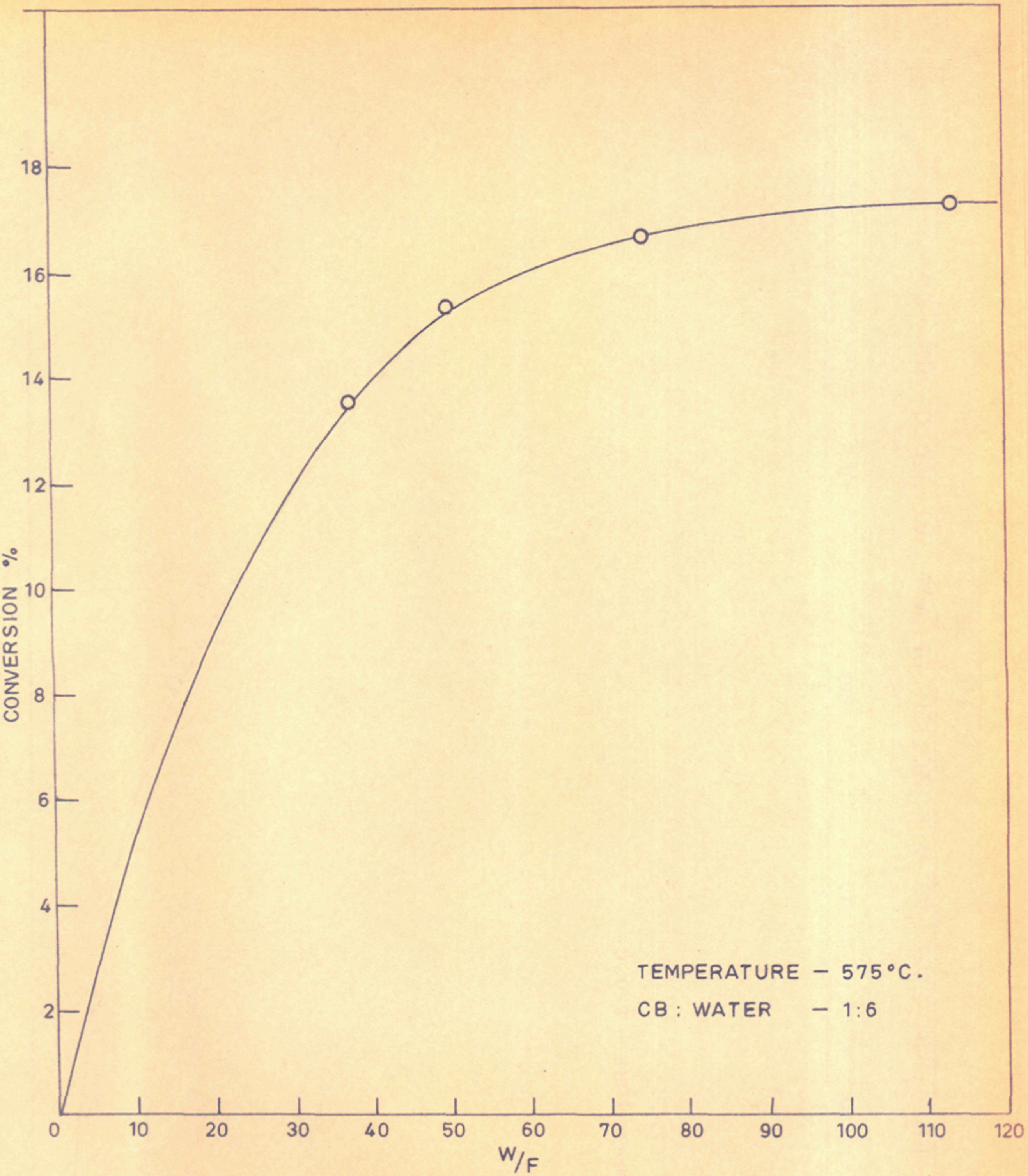


FIG. 5·13. X – W/F PLOT AT 575°C.

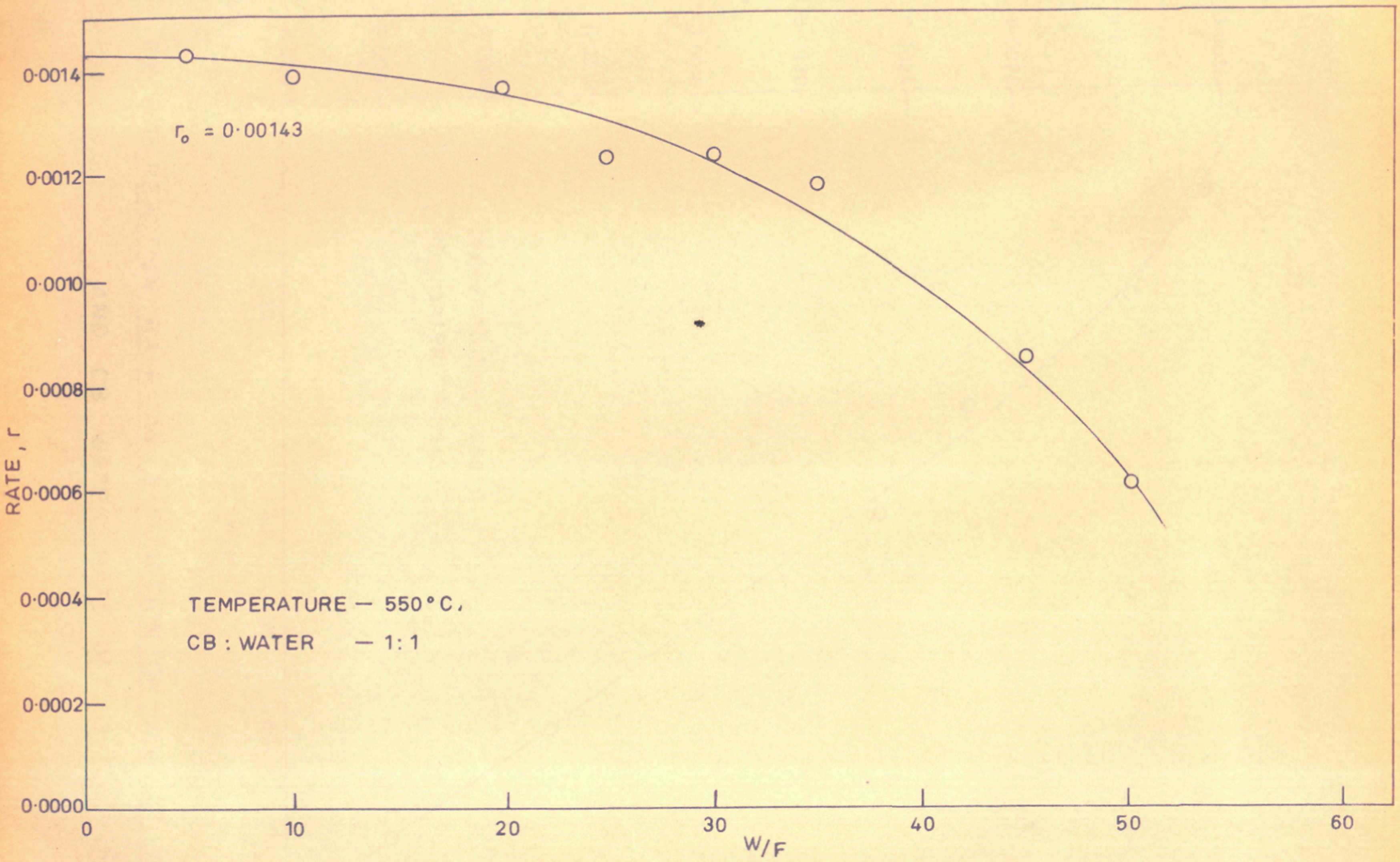


FIG. 5·14. REACTION RATE AS A FUNCTION OF W/F AT 550°C. AND CB:WATER RATIO OF 1:1

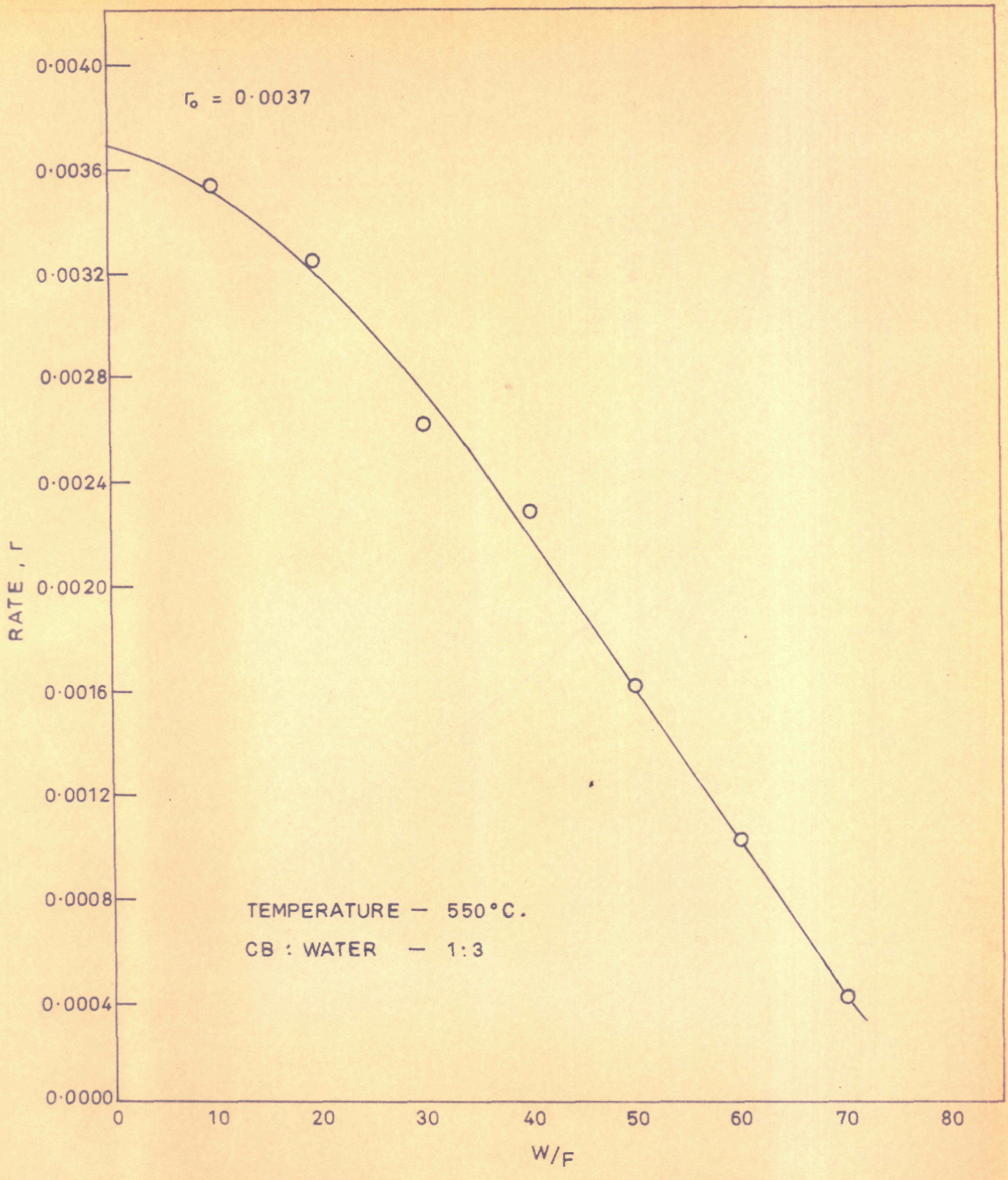


FIG. 5·15. REACTION RATE AS A FUNCTION OF W/F AT 550°C. AND CB WATER RATE OF 1:3

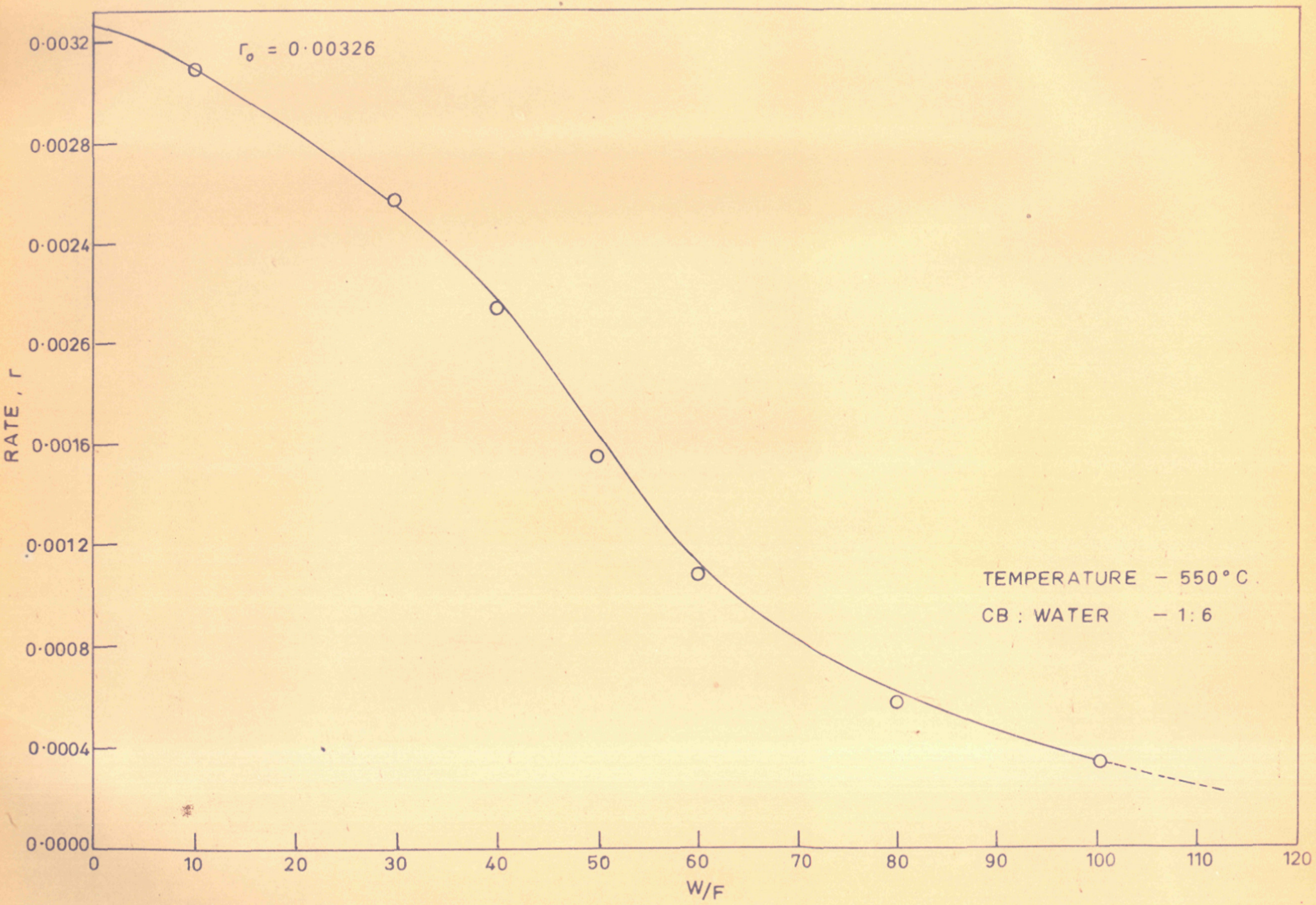


FIG. 5·16. <u>REACTION RATE AS A FUNCTION OF W/F AT 550 °C. AND CB / WATER</u>

RATIO 1:6

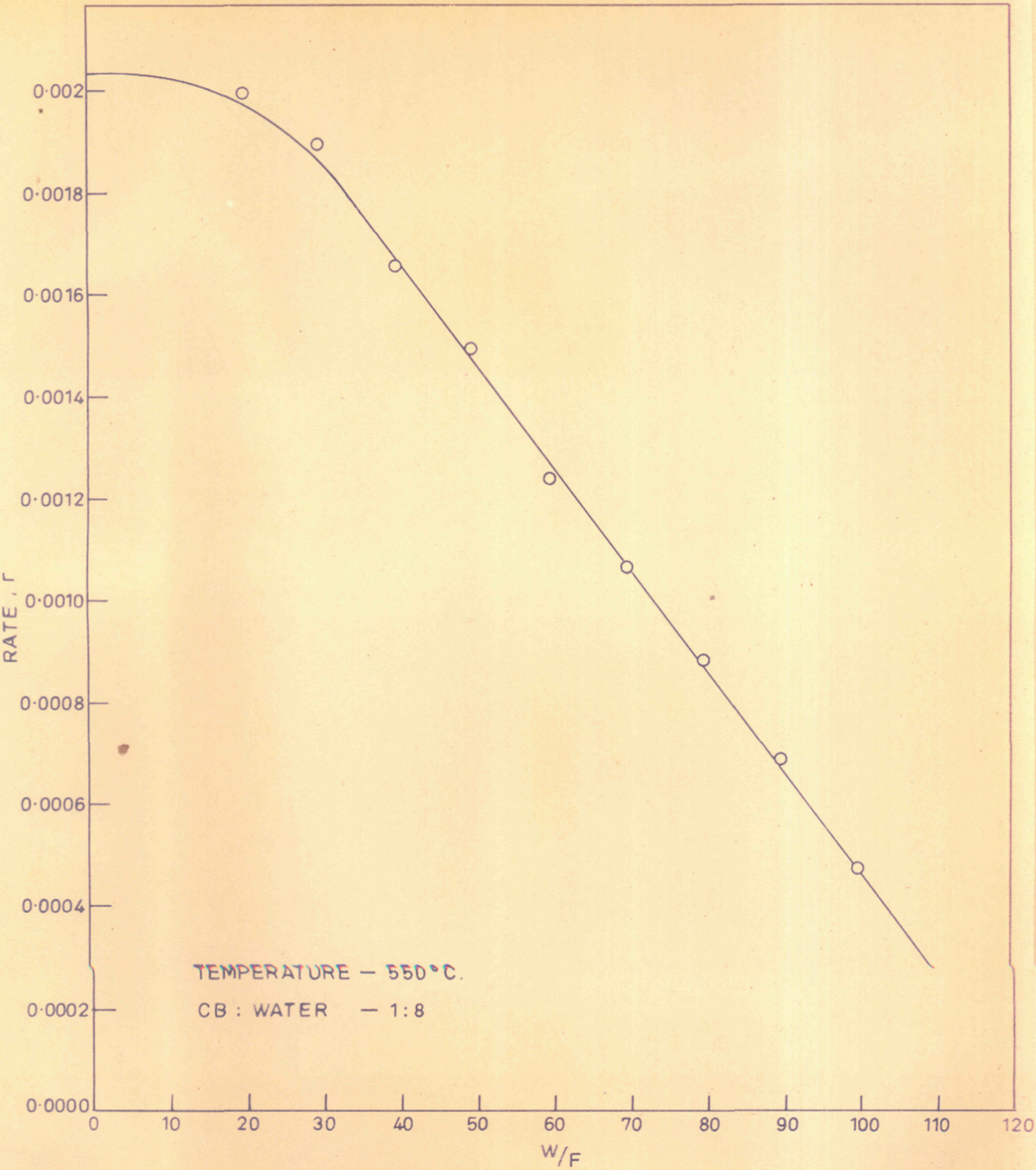


FIG. 5·17. REACTION RATE AS A FUNCTION OF W/F AT 550°C.

CB/WATER RATIO OF 1:8

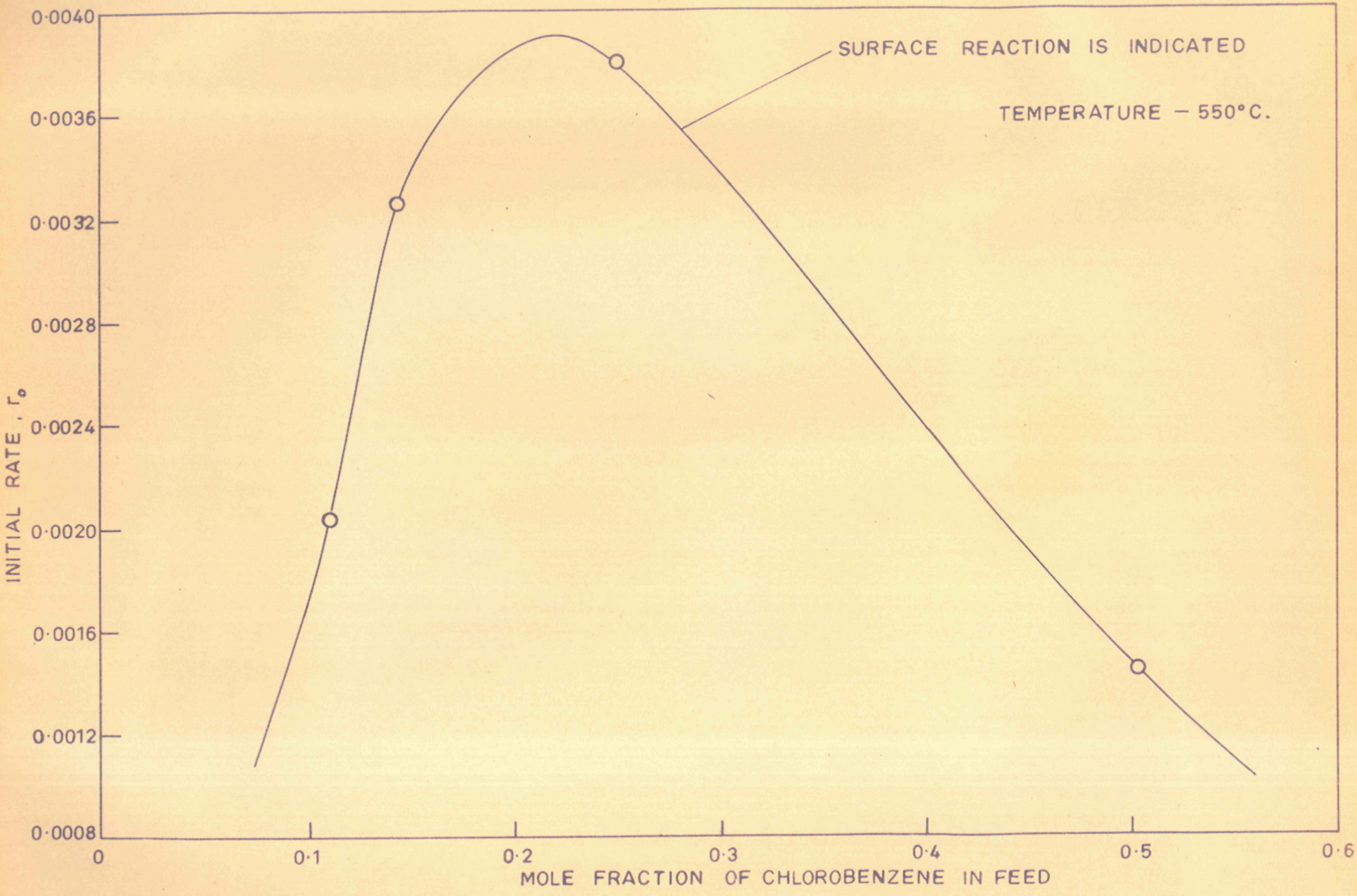


FIG. 5·18 VARIATION OF INITIAL RATE WITH MOLE FRACTION OF CB IN FEED

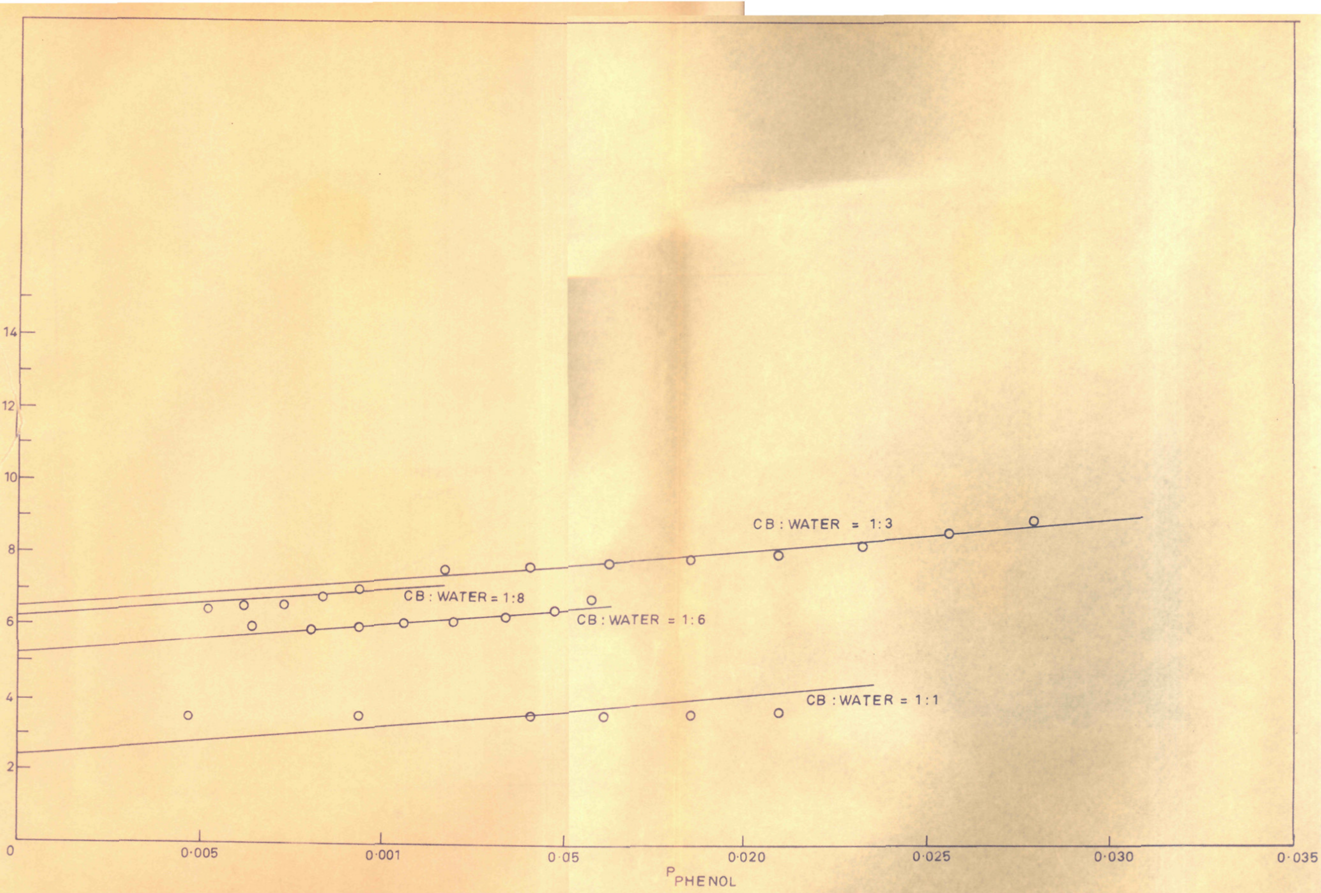


FIG. 5·19. VARIATION OF RATE FUNCTION R WITH PARTIAL PRESSURE OF PHENOL

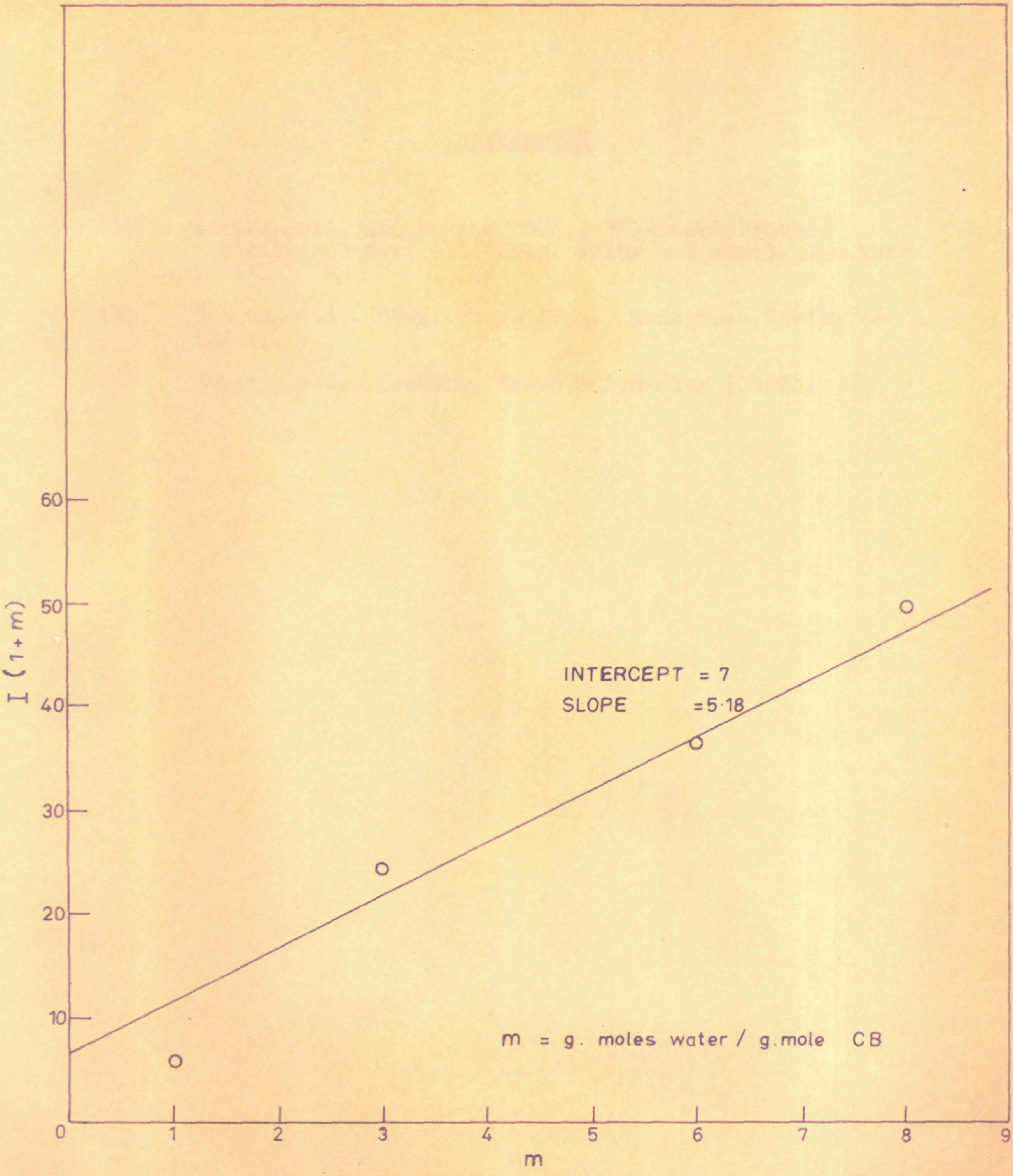


FIG. 5·20. VARIATION OF INTERCEPT FUNCTION WITH m.

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