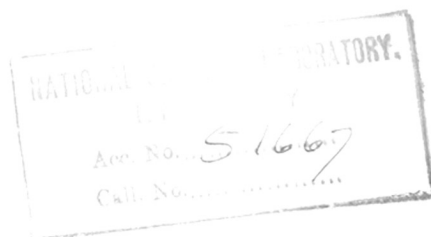


# KOLBE - SCHMITT CARBONATION OF 2-NAPHTHOL - A KINETIC ANALYSIS

COMPUTERISED



A THESIS SUBMITTED TO  
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FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY  
(Technology)  
BY

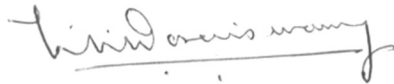
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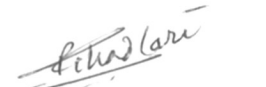
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The literature concerning the problem investigated has been surveyed, and all the necessary references are given in the thesis. The present work has been clearly indicated separately. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgment has been made wherever the work presented is based on the results of other workers.



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August 1967.



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SUMMARY AND CONCLUSIONS

The preparation of ... is a typical example of ... The so-called ... suffers from practical difficulties associated with heat transfer and agitation problems. Several workers have suggested modifications to overcome some of these inherent difficulties, and among these may be mentioned: (1) the use of a liquid ... (2) the elimination of the ... (3) the addition of ... (4) the use of ... (5) the use of ...

In view of its apparent advantages, the liquid dispersion method was taken up for detailed analysis in the present

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**SUMMARY AND**

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**CONCLUSIONS**

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## SUMMARY AND CONCLUSIONS

The preparation of BON acid from 2-naphthol is a typical example of Kolbe-Schmitt carbonation. The so-called dry method normally employed in industry suffers from practical difficulties associated with heat transfer and agitation problems. Several workers have suggested modifications to overcome some of these inherent difficulties, and among these may be mentioned : (1) the use of a liquid (solvent for dispersent) both during dehydration and carbonation; (2) the elimination of the dehydration step by using anhydrous  $K_2CO_3$  directly with 2-naphthol for carrying out the carbonation (Marasse method); (3) preparation of 2-hydroxy 1-naphthoic acid and its subsequent conversion to BON acid; and (4) the use of NaH during dehydration and carbonation.

In view of its apparent advantages, the liquid dispersent method was taken up for detailed analysis in the present investigation. For this

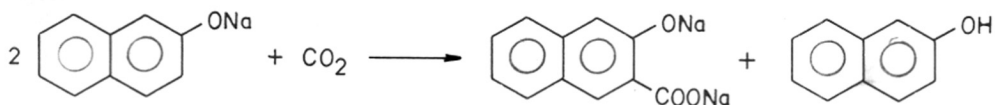
purpose, kerosene oil was chosen as the liquid dispersent for the following reasons : (1) it is a cheap and readily available solvent; (2) the use of kerosene oil has been reported in an industrial plant; and (3) it has a low dielectric constant (2.0 - 2.2).

The <sup>main</sup> reactions involved in the preparation of BON acid may be summarized as follows :

- (1) Preparation of the Na-salt of 2-naphtholate and its total dehydration by distillation along with kerosene :



- (2) Carbonation with  $\text{CO}_2$  at 30-100 psig. and  $230^\circ\text{-}270^\circ\text{C.}$  :



### Dehydration

Since total dehydration is essential prior to carbonation, this was first studied in great detail (Chapter - 3). A significant improvement has been introduced in this step by incorporating

trace quantities of an additive ( $\text{CaCl}_2$ ) which ensures complete dehydration in a short time. The final results of the experiments carried out show that with 2%  $\text{CaCl}_2$  (on 2-naphthol charged) and a dehydration time of about 6 hours, quantitative removal of water is possible without causing any deleterious effect on the carbonation reaction. Under these finalised conditions, finely divided grains of sodium 2-naphtholate form (a highly desirable condition), but the shape and size distribution of the particles were found to differ with slight changes in the dehydration conditions. Hence, during the entire study of carbonation, the conditions of dehydration established were strictly followed so that any variation in the physical state of the dehydrated naphtholate would be kept at the minimum.

### Carbonation

There are several variables which exercise direct or indirect influence on the carbonation reaction. Based on a knowledge of the reported literature, preliminary investigations were carried out to establish the significant variables of carbonation and also their effective ranges (Chapter - 3). Several studies on the mechanism



of the Kolbe-Schmitt reaction have been reported, but no theories have been advanced which might provide an engineering basis for the carbonation of 2-naphthol by the Kolbe-Schmitt (or modified) procedure.

The problem on hand was therefore investigated by two different approaches : (1) by evolving a mathematical equation for the principal reaction based on a conceptual model in order to understand the influence of the various physical factors controlling the reaction (Chapter - 4), and (2) by studying statistically (empirically) the effect of various changes in operating conditions to obtain the required optimum yield of BON acid (Chapter - 5).

#### Proposed reaction model

Two models were considered for Kolbe-Schmitt carbonation in the presence of kerosene oil as dispersent, one based on mass transfer control and the other on surface chemical reaction control. These models were then analysed in the light of the kinetic data collected (Appendix - A).

#### Mass transfer model :

Assuming that the Na-naphtholate is in a finely divided state and is well-suspended in the kerosene

medium, and that the chemical reaction between the naphtholate and  $\text{CO}_2$  is very fast (instantaneous), the rate of reaction will obviously depend on the diffusional rate of  $\text{CO}_2$  through an equivalent film of kerosene oil and a progressively increasing layer of the product crust. Based on this postulate and also making other justifiable assumptions, a mathematical model for the total disappearance of Na-naphtholate has been developed which is reproduced below :

$$\frac{3\theta}{A_M} = x + k_M \left[ 1.5 - x - 1.5 (1 - x)^{\frac{2}{3}} \right]$$

or

$$\frac{\theta}{x} = \frac{A_M k_M}{3} \left( \frac{\phi(x)}{x} \right) + \frac{A_M}{3}$$

where

$$A_M = \frac{2 \rho R}{k_L C_o}$$

$$\text{and } k_M = \frac{R}{Z_L \alpha}$$

If this model is to be acceptable, plots of  $\frac{\theta}{x}$  vs.  $\frac{\phi(x)}{x}$  should give straight lines and the values of  $A_M$  and  $k_M$  obtained from the intercepts and slopes of these lines should at least show order-of-magnitude agreement with those estimated from their

defining equations through an independent series of mass transfer experiments.

Chemical reaction model :

If it is assumed that the controlling step is the rate of chemical reaction at the reactant surface rather than the rate of mass transfer to it, then the reaction would be chemically controlled. For this the rate equation for a spherical particle given by Levenspiel (68) was considered :

$$k\theta = 1 - (1 - x)^{\frac{1}{3}}$$

Evidently a plot of reaction time  $\theta$  vs.  $(1 - (1 - x)^{\frac{1}{3}})$  should give a straight line passing through the origin.

Test of models :

Kinetic data at three levels of temperature and pressure and at different time intervals (from 15 to 180 min.) were collected. Based on these values plots of  $\frac{\theta}{x}$  vs.  $\frac{\phi(x)}{x}$  and  $\theta$  vs.  $(1 - (1 - x)^{\frac{1}{3}})$  were prepared, which are shown in Figs. (4.3) to (4.14). These plots clearly indicate that the reaction is controlled by mass transfer.  $A_M$  and  $k_M$  were then estimated from the linearised model by the method of least squares.

The constant  $A_M$  appearing in the model equation can be independently estimated from its defining equation provided the density of sodium naphtholate, particle size of the naphtholate, saturation concentration of  $CO_2$  in kerosene oil and the mass transfer coefficient ( $k_L$ ) are known. Thus a programme of work was organised from which these could be determined. The radius  $R$  was determined through the use of a high power microscope and the density was estimated by a procedure described in Appendix - B.1. The saturation solubility  $C_0$  and solubility  $C$  at different interval of time were determined (Appendix - B.2) by making use of a solubility apparatus constructed for this purpose (Chapter - 2). These data were subsequently used in estimating the mass transfer coefficient  $k_L''$  ( $\frac{1}{\text{min.}}$ ) which was converted to the specific mass transfer coefficient  $k_L$  ( $\frac{\text{gm.}}{\text{min.}}$ ) through the relationship

$$k_L = \frac{k_L''}{a}$$

In this equation  $a$  represents the interfacial surface area per unit volume and this was determined by the method of Danckwerts and Sharma (53) by employing an r.p.m. which was so small that the liquid surface could be assumed to be undisturbed. The location

of the stirrer was also altered to approach this condition. The determination of  $k_L^H$  and  $k_L$  is described in Appendix - B.3.

The values of  $A_M$  obtained by this method show more than an order-of-magnitude agreement with those calculated from the kinetic experiments. The average deviation of 70.0% obtained should be regarded as very satisfactory, considering the fact that the two methods of determining  $A_M$  are entirely unrelated.

The values of  $k_M$  could not be calculated from an independent series of experiments since the magnitude of the empirical constant  $\alpha$  is highly speculative. From the values of  $k_M$ ,  $\alpha$  was found to be of the order of 0.01, indicating that there is probably a high degree of compaction of the reaction products because of the bulkier nature of these products as compared to the reactant.

#### Statistical optimization

The kinetic data taken at three levels of temperature, pressure and time, were arranged in the  $3^3$  factorial design format and then analysed for the significance of the process variables (Chapter - 5). This analysis showed strongly that the maximum value

of the response (yield) present in this experimental set is close to the region of the optimum. Then, in order to obtain the optimum response, a 3-dimensional second degree equation was constructed and analysed by the method of Box and Wilson (66).

On transformation of the 3-dimensional second degree equation to the canonical form and determination of its coefficients, it was found that the response (yield) obtained at the center of the contour is at the optimum. Thus the estimated optimum conditions, and the corresponding optimum response (yield) and conversion, may be summarized as follows :

Estimated optimum temperature ..	250°C.
Estimated optimum pressure ..	69.8 psig.
Estimated optimum time ..	1.9 hr.
Yield of BON acid, % ..	79.65
Conversion to BON acid, % ..	34.8

## CHAPTER - 1

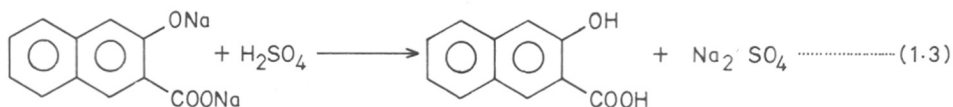
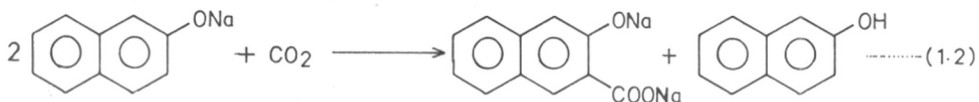
### LITERATURE SURVEY AND PROBLEM OUTLINE

#### 1.1 INTRODUCTION

Kolbe-Schmitt carbonation is a standard procedure for the preparation of aromatic hydroxy acids, in which the substitution generally occurs ortho to the phenolic hydroxy group. The intermediates thus prepared are used in the dyestuff and pharmaceutical industries. The preparation of 2-oxy 3-naphthoic acid, commercially known as BON acid, is a typical example of Kolbe-Schmitt carbonation. It is a valuable intermediate, particularly for the dyestuff and pigment industries. The aryl amides of BON acid (Naphthol AS series) have vastly extended the scope of azoic colours (65). The dyes produced on cotton fibre by these naphthols are comparable to anthraquinonoid vat dyes for their deep brilliant shades and all-round fastness properties. Metal complex dyes of BON acid are useful for the dyeing

of polymers, paper, synthetic fibres and tanned leather (50). BON acid also finds limited use in the pharmaceutical, bactericidal and plastic industries (57, 58).

The preparation of BON acid usually consists of the following stages : preparation of anhydrous sodium 2-naphtholate from 2-naphthol and aqueous caustic soda by vacuum dehydration, carbonation of the anhydrous salt with  $\text{CO}_2$  under pressure at  $230^\circ\text{--}270^\circ\text{C.}$ , recovery of 2-naphthol, and purification of the final product. The reaction scheme may be represented as follows :



Several workers have suggested modifications to overcome some of the inherent difficulties associated with this so-called dry process. One of these modifications, which employs a liquid dispersent, appears to offer certain advantages, in particular

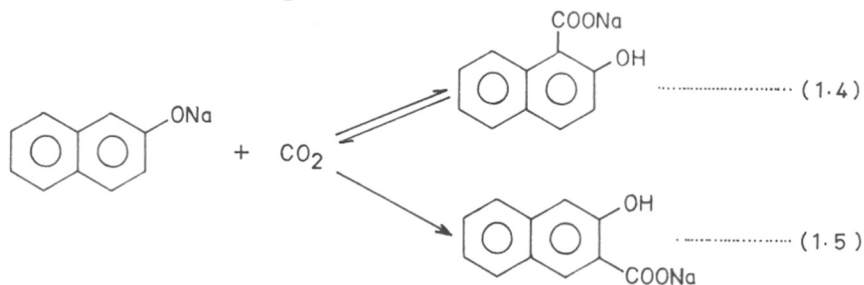


a possible reduction in power consumption.

In the following paragraphs a summary is presented of the reported literature on the preparation of BON acid, including the chemistry of the process and its technical aspects. Based on this review the scope of the present investigation is outlined in Section 1.4.

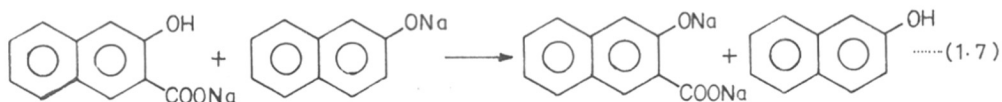
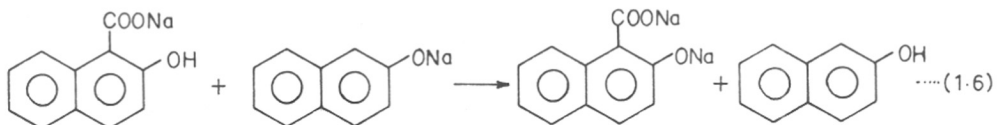
## 1.2 CHEMISTRY

The action of  $\text{CO}_2$  on dry sodium 2-naphtholate gives two isomeric acids (37, 38, 44). The salt of the valuable 2-hydroxy 3-naphthoic acid (BON acid) forms at temperatures above  $200^\circ\text{C}$ ., preferably in the range  $230^\circ\text{--}270^\circ\text{C}$ ., while the salt of 2-hydroxy 1-naphthoic acid forms between  $120^\circ$  and  $130^\circ\text{C}$ . and starts decomposing above  $130^\circ\text{C}$ .

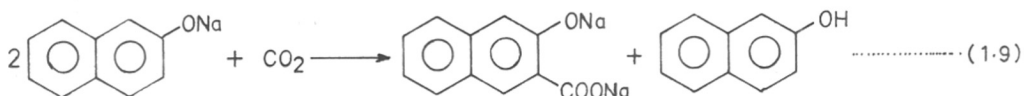
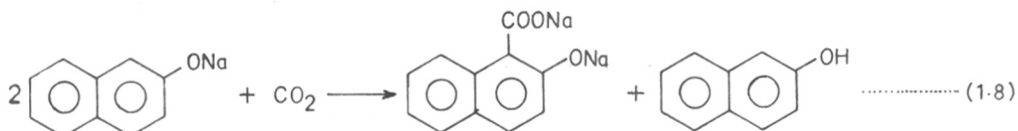


It has been proved experimentally that the two isomers can form by direct substitution (45). Both undergo further reaction with unreacted sodium

2-naphtholate readily to give the corresponding disodium salts.

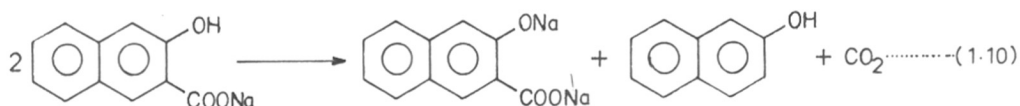


The overall reactions for the two isomers may then be represented as :



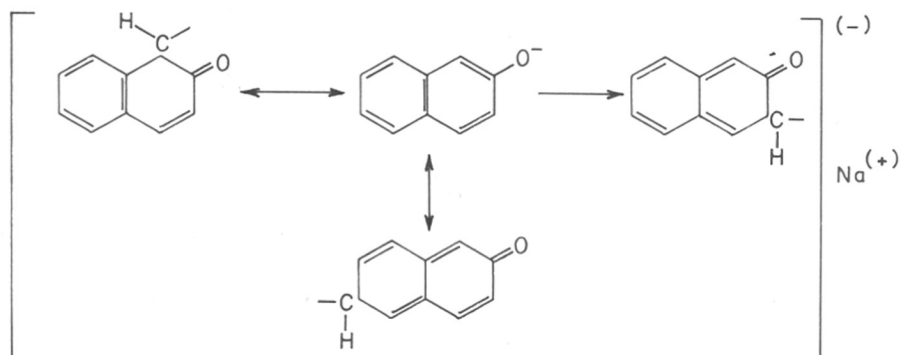
Thus the maximum theoretical conversion possible in both the cases is 50%.

The other probable reactions are the decomposition of the monosodium salts of 2 : 1 and 2 : 3 acids to the corresponding disodium salts, free 2-naphthol and  $\text{CO}_2$ . In the case of the 2 : 3 acid this reaction occurs only above  $275^\circ\text{C}$ . (44, 45).



It may therefore be seen that, since the carbonation temperature is less than  $275^{\circ}\text{C}$ ., the disodium salt is formed only according to reaction (1.7).

Tijmastra (32), Schwenk (34), Reimer Tiemann (39) and other workers (42, 46) have postulated mechanisms for the carbonation of sodium 2-naphtholate by  $\text{CO}_2$  (Kolbe-Schmitt reactions in general). But the theory put forward by Karpukhin and Khusid (35, 46) seems to be the most acceptable one. They pointed out that the products obtained by carbonation at different temperatures exist in tautomeric forms. Thus the reaction has to be considered as a Mesomeric system :



Depending on the temperature, the arrangement of  $\text{CO}_2$  may give an alkali salt, 2, 1-hydroxynaphthoic acid, or 2, 3-hydroxynaphthoic acid. This mechanism indicates that the reaction is solvent dependent, i.e. proton accepting solvents will favour carbonation

while proton donating solvents will inhibit it.

Seidel, Wolf and Krause (44) have graded the proton accepting solvents according to their relative effectiveness :

dioxane > pyridine > diphenylamine > toluol > butanol,  
phenol

### 1.3 TECHNOLOGY

#### 1.3.1 Kolbe-Schmitt process (dry)

Kolbe and Schmitt (2) prepared 2-hydroxy 1-naphthoic acid (m.p. 154° C.) by treating dry sodium 2-naphtholate with CO<sub>2</sub> at 120°-145° C. at atmospheric pressure. The sodium salt of hydroxynaphthoic acid formed was dissolved in water and acidified to give hydroxynaphthoic acid, but the acid was unstable and decomposed easily to 2-naphthol and CO<sub>2</sub>.

Later Schmitt (1, 3) obtained 2-hydroxy 3-naphthoic acid, a stable yellow compound (m.p. 216° C.), by carrying out the carbonation of dry sodium 2-naphtholate at 200°-250° C. under pressure. This method of manufacturing BON acid has since remained standard in the chemical industry. The manufacturing process as given in BIOS (31) is briefly described below.

Caustic soda as 50% liquor and 2-naphthol (in the molar ratio 1 : 1) are charged into a cast steel vessel heated by a coil using steam at 450 psi and provided with a Fredeking type stirrer through an adjustable gear box. The sodium 2-naphtholate formed is completely dehydrated under vacuum, first at 190°C. under 40 mm. Hg vacuum and finally at 220°-230°C. under 15 mm. Hg vacuum. The dehydration takes about 24 hours.

The dry sodium 2-naphtholate is then carbonated in three steps, starting at a temperature of 220°-230°C. and finishing at 260°C. with a final pressure of 4.5 atm. After each step (lasting for 5-6 hours) the free 2-naphthol formed is distilled at about 220°-230°C. under 15 mm. Hg vacuum. The total free 2-naphthol distilled in three distillations is nearly 42% of the charge, and the total time for carbonation and distillation is 28 to 30 hours.

After the third distillation, water is introduced into the evacuated vessel and the reaction mass brought to about 145°C. The solution is then dumped in a neutralisation tank. Free 2-naphthol (nearly 9% of the charge) is precipitated at a pH of 6.8 and BON acid at a pH of 2. The following conversion and

yield are reported :

35.6% on 2-naphthol charged (conversion)

72.6% on 2-naphthol consumed (yield)

(See Chapter - 4, Chart-1, for definitions of conversion and yield.)

The total removal of water from the naphtholate is essential before carbonation. In this connection Hodges and Nadler (25) investigated the dehydration of hydrated sodium 2-naphtholate, and determined the minimum pressures (at different temperatures) required for attaining complete dehydration, which are as follows : 20, 165, 172, 175, 180, 186, 189, 195 and 200 mm. Hg at 250°, 300°, 307°, 310°, 315°, 320°, 325°, 330° and 335° C. respectively. They also claimed a conversion of 31.8% and a yield of 79.5% of BON acid by using a ball mill type reactor.

In the Kolbe-Schmitt method for the preparation of BON acid, the possibility of small quantities of the 2 : 1 acid forming can be eliminated by an appropriate choice of reaction pressure at a given temperature. For this purpose the data of Calcott, Hitch and Mahr (10) are useful. These investigators determined the dissociation pressures of the 2 : 1 acid at different temperatures in the range of interest

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for the production of BON acid. The data are as follows :

Temperature, °C.	Dissociation pressure, psi.
225	375
235	450
250	600

This shows that, for the temperatures indicated, at pressures higher than those mentioned, the 2 : 1 acid is stable, and at pressures lower than those mentioned, the 2 : 1 acid does not exist. Thus, at a temperature of 225°C., the pressure should not be allowed to reach 375 psi in order to avoid the existence of the 2 : 1 acid. This is necessary since any 2 : 1 acid present tends to form naphthoxanthone which constitutes the principal tary impurity in BON acid.

The use of nickel-clad mild steel has been recommended (31) as material of construction for the carbonation reactor instead of iron which tends to promote side reactions.

Alkali metals (9, 43, 46) influence the orientation in the Kolbe-Schmitt reaction because of their differences in chelation strengths. Lithium and sodium salicylates, for example, do not rearrange to

p-hydroxy benzoate, and are more strongly chelated than potassium, rubidium and cesium salicylates, which readily rearrange on heating.

Other methods described in the patent literature (5, 9, 11, 13, 14, 19, 24) on the dry process do not deviate significantly from the process briefly described above.

### 1.3.2 Marasse method

Marasse (4, 29, 40, 43) in 1893 proposed a simple modification to the Kolbe-Schmitt reaction in order to overcome the difficult and time consuming preparation of the hygroscopic naphthalate. The procedure involves heating 2-naphthol with an excess of anhydrous  $K_2CO_3$  at  $230^\circ C$ . under a high  $CO_2$  pressure (1200-2000 psi) to give the K-salt of 2-oxynaphthoic acid. Acidification releases the free acid in good yield, but there is also a likelihood of the formation of the isomer, 2-hydroxy 6-carboxynaphthalene.

This modification has been applied to approximately one hundred phenols (46) and has given good result in many cases. The excess of potassium carbonate acts as an extender and prevents the fusion of the mixture. Industrially this procedure is



expensive since only potassium, rubidium and cesium carbonates have been found to be suitable.

The failure of sodium, magnesium and calcium carbonates and of sodium bicarbonate may arise from their insolubility and consequent non-reactivity towards phenols, the formation of the metal aryl oxide being a necessary prelude to carbonation. Potassium, rubidium and cesium carbonates, on the other hand, readily react with phenols and carbonation then proceeds easily.

### 1.3.3 Use of liquids

#### (a) Solvents :

The possible use of free 2-naphthol as a solvent for this reaction arose out of the fact that reaction (1.7) leading to the formation of the disodium salt of 2 : 3 acid from its monosodium salt is actually an equilibrium reaction (44), and that the addition of 2-naphthol would shift the equilibrium towards the left. This would mean that a conversion greater than the theoretical 50% could be achieved; also there would be the added advantage of the solubility of the naphtholate in 2-naphthol leading to a more fluid reaction mass.

Hence many earlier workers (6, 8, 14, 30, 35) tried to exploit 2-naphthol as a solvent in this reaction, but without much success, because of the formation of large amounts of tar during the reaction. However, a recent British patent (29) has claimed 83% yield of BON acid in a continuous method using a considerable excess of 2-naphthol as solvent.

Organic liquids, which have a solvent action on 2-naphthol and alkali 2-naphtholate but do not dissolve the alkali salt of 2-naphthol carboxylic acids and which are stable and chemically inert, may be used as solvents (16, 17, 18, 20, 22, 27, 47). Dioxane, pyridine, their homologues and acid-soluble tar fractions fulfil these conditions and have been tried; for practical reasons dioxane has received greater consideration than other solvents.

In the solvent method, 2-naphthol is allowed to react with an equimolar or excess amount of NaOH in the solvent. Sodium 2-naphtholate is then dehydrated by azeotropic distillation using fresh dry solvent (for adjustment of volume). If an excess of NaOH is used, the mixture is refluxed for some time, the aqueous layer is separated, and the solvent layer dried over a dehydrating agent, e.g.

caustic soda, calcium oxide, barium oxide or calcium carbide. This procedure leads to efficient dehydration, but is time consuming. To shorten the time of azeotropic distillation (49), another solvent (e.g. benzene) which forms a minimum boiling mixture is used. After dehydration, carbonation proceeds smoothly under normal conditions.

The liquid method has a number of advantages. It ensures efficient drying of sodium 2-naphtholate, and no difficulties are encountered through local overheating or inadequate stirring. It reduces the formation of by-products such as xanthone or tar. As a result hydroxynaphthoic acids can be obtained in higher purity and yields. It enables carbonation to be carried out at the optimum temperature of  $250^{\circ}\text{C}$ . (from the beginning of the reaction) which is not possible in the dry process. The principal disadvantage of this method is the use of excessively large equipment and the additional investment for handling of solvents and their recovery.

(b) Dispersents :

Some organic liquids (e.g. paraffin, toluene, xylene, and tetralin) have been suggested (7, 15, 22, 24, 36) as dispersents (chemically

indifferent liquids) for carrying out this reaction. These do not dissolve the alkali metal naphtholate and do not react with the starting materials and intermediates or final products. Based on experimental data, Isemer (46) has concluded that the carbonation proceeds most readily in liquids (which are not necessarily solvents) having low dielectric constants (e.g. toluene, xylenes, dioxane, diisobutyl ketone). Thus, according to him, both protic and aprotic solvents (having low dielectric constants) are suitable.

The use of kerosene oil as a dispersent in an industrial plant is known. Such diluents facilitate the preparation of anhydrous naphtholate. However they tend to have an undesirable effect on the carbonation reaction because  $\text{CO}_2$  dissolves but sparingly in the dispersent (hydrocarbon); and the contact of  $\text{CO}_2$  with suspended and coated naphtholate particles might not be efficient. It is therefore necessary to use as little of the diluent as possible and also to get the naphtholate in a finely divided state for the carbonation to proceed smoothly and with the required reaction rate.

#### 1.3.4 Other methods

(a) Conversion of alkali salt of 2,1-hydroxynaphthoic acid to BON acid :

Dry sodium 2-naphtholate is subjected to the action of  $\text{CO}_2$  at a temperature of  $40^\circ\text{-}60^\circ\text{C}$ . (or in some cases at  $120^\circ\text{-}130^\circ\text{C}$ ) with or without a liquid medium under atmospheric pressure (12, 21, 23, 24, 26, 30). The product obtained is the disodium salt of 2,1-hydroxynaphthoic acid, in accordance with reaction (1.8). This is then processed in the usual manner. The conversion of 2,1-hydroxynaphthoic acid is practically quantitative, i.e. 50% on the 2-naphthol charged. This can be increased to 100% of the naphthol charged if an equivalent amount of metallic sodium is used.



This reaction is best carried out in an indifferent liquid, or preferably in a liquid which is a solvent for both naphthol and naphtholate.

The disodium salt of 2,1-hydroxynaphthoic acid, substantially free from naphthol and other materials

containing free hydroxyl groups, is heated to  $220^{\circ}$ - $360^{\circ}$ C. in a chemically indifferent solvent under  $N_2$  or  $CO_2$  pressure till the tautomerisation is complete. The conversion to BON acid is substantially quantitative. Krepelka and Karing (36) have reported the optimal temperature range as  $235^{\circ}$ - $240^{\circ}$ C. and also added that under pressures of 15-50 atm. the conversion is a linear function of pressure.

In another process (30) the disodium salt of 2,1-hydroxynaphthoic acid is heated to  $235^{\circ}$ - $245^{\circ}$ C. under a  $CO_2$  pressure of 4.5 atm. with intermittent addition of 2-naphthol. After the tautomerisation the free 2-naphthol is distilled out in vacuo and the product is separated in 65-70% yield.

These processes involve the additional cost of preparing 2,1-hydroxynaphthoic acid, and if a liquid medium is used the cost of solvent handling and recovery is also added up. Further there is no improvement in the conversion and yield as compared with the direct methods.

(b) Use of sodium hydride :

A patent (28) has described the preparation of dry sodium 2-naphtholate by using NaOH or NaH in a nitrogen atmosphere. The dry salt is then treated

with  $\text{CO}_2$  at a pressure of 5 atm. at  $230^\circ\text{-}250^\circ\text{C.}$ , preferably with the addition of more NaH. Higher yields are claimed by a further reaction of the carboxylation product with  $\text{CO}_2$  and additional NaH.

#### 1.4 PROBLEM OUTLINE

The review presented in the foregoing paragraphs has brought out the following points :

- (1) Dehydration is an extremely important step, and total dehydration is a "must" for achieving good and reproducible results.
- (2) Neither the dry method nor the methods employing liquids (dispersent or solvent) have been systematically investigated in terms of the effect of the process variables on yield and conversion.
- (3) When the reaction is carried out in the dry phase, it evidently forms a gas-solid system, and when it is carried out in the presence of a liquid dispersent, a gas-liquid-solid system is involved. No model has so far been proposed for either of these systems (as applied to this reaction).

In view of the apparent advantages of the liquid

dispersent method, the present investigation was undertaken with the following objectives :

- (1) To study the effect of process variables on the dehydration of sodium 2-naphtholate in the presence of a dispersent.
- (2) After finalising the dehydration conditions, to investigate systematically the effect of carbonation variables (temperature, pressure, time, 2-naphthol to kerosene oil ratio) on the conversion and yield of the reaction.
- (3) To propose a plausible model for the carbonation reaction in the presence of a dispersent.
- (4) Using the relevant process data from this study, to optimize the reaction conditions by a three level factorial design.

In this investigation kerosene oil was chosen as the dispersent for the following reasons :

- (a) it is a cheap and readily available solvent;
- (b) the use of kerosene oil has been reported in an industrial plant; and
- (c) it has a low dielectric constant, (2.0-2.2).



## CHAPTER - 2

### EXPERIMENTAL

The experimental apparatus for this investigation were set up with the objectives: to study the effect of process variables on the Haber-Bosch reaction leading to the formation of  $\text{NH}_3$  and to determine the pressure of hydrogen as a function of temperature and to determine the equilibrium constant for the reaction of  $\text{N}_2$  and  $\text{H}_2$  in excess of the amount of  $\text{NH}_3$  formed. The main features of the experimental technique are briefly described under the heads: (1) equipment, (2) principle of operation, (3) operation, and (4) analysis, following by a description of the results obtained.

#### 2.1 EQUIPMENT (FOR REACTION)

Experiments on the study of process variables were carried out in two reactor assemblies: reactor 1, in which the earlier part of the reaction was carried out, and the reactor 2, in which the

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## CHAPTER - 2

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### EXPERIMENTAL

## CHAPTER - 2

### EXPERIMENTAL

The experimental assemblies for this investigation were set up with two objectives : to study the effect of process variables on the Kolbe-Schmitt reaction leading to the formation of BON acid in the presence of kerosene oil as a dispersent, and to determine the solubility and mass transfer coefficient of  $\text{CO}_2$  in kerosene oil to provide the data for verifying the proposed model. The main features of the experimental technique are briefly described under the heads : (1) equipment, (2) principal raw materials, (3) operation, and (4) analysis, follow<sup>ed</sup>ing by a description of the solubility apparatus.

#### 2.1 EQUIPMENT (FOR REACTION)

Experiments on the study of process variables were carried out in two reactor assemblies : Reactor A, in which the earlier part of the investigation was carried out, was the smaller of the two and was not

provided with a sampling device. The latter part of the investigation was carried out in reactor B, which was not only larger but was also provided with an arrangement for sampling.

#### 2.1.1 Reactor A

A diagrammatic sketch of the reactor and accessories is shown in Fig.(2.1) and a photograph of the unit appears in Fig.(2.2). This consisted essentially of a stainless steel reactor, 8 cm. diameter x 19 cm. height, with a volumetric capacity of 850 ml. The reactor was provided with an anchor type stirrer which could be driven at 160 rpm. by a  $\frac{1}{2}$  h.p. motor through a suitable pulley arrangement. The stirrer stuffing box was provided with a jacket (for the portion inside the reactor) for water cooling. In the flanged lid of the reactor were openings for charging, vapour outlet (used during distillation of the solvent) and CO<sub>2</sub> inlet. A thermowell of appropriate length was also provided. The reactor was heated by electrical resistance wire wound over its outer surface, and the heat input was controlled through a variac and an ammeter. The entire reaction assembly was tested for a pressure of 300 psig at 350°C. and was found to be leak-proof.

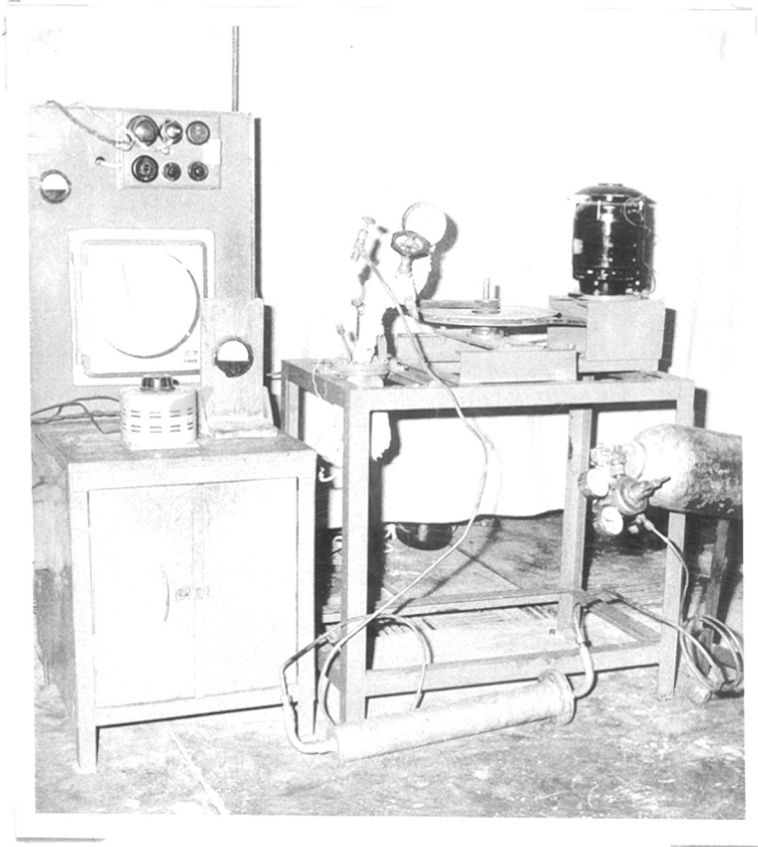


FIG. 2.2. PHOTOGRAPH OF REACTOR 'A' ASSEMBLY



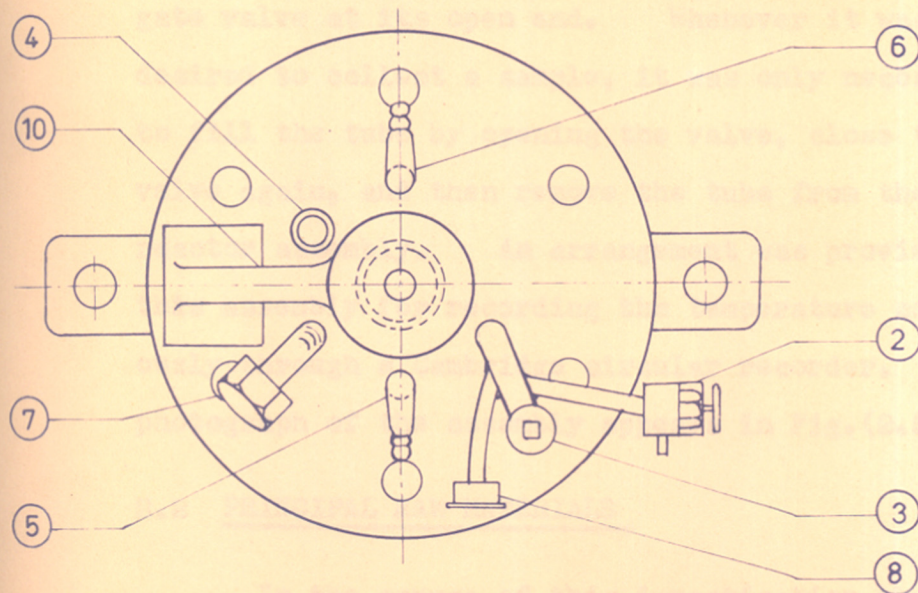
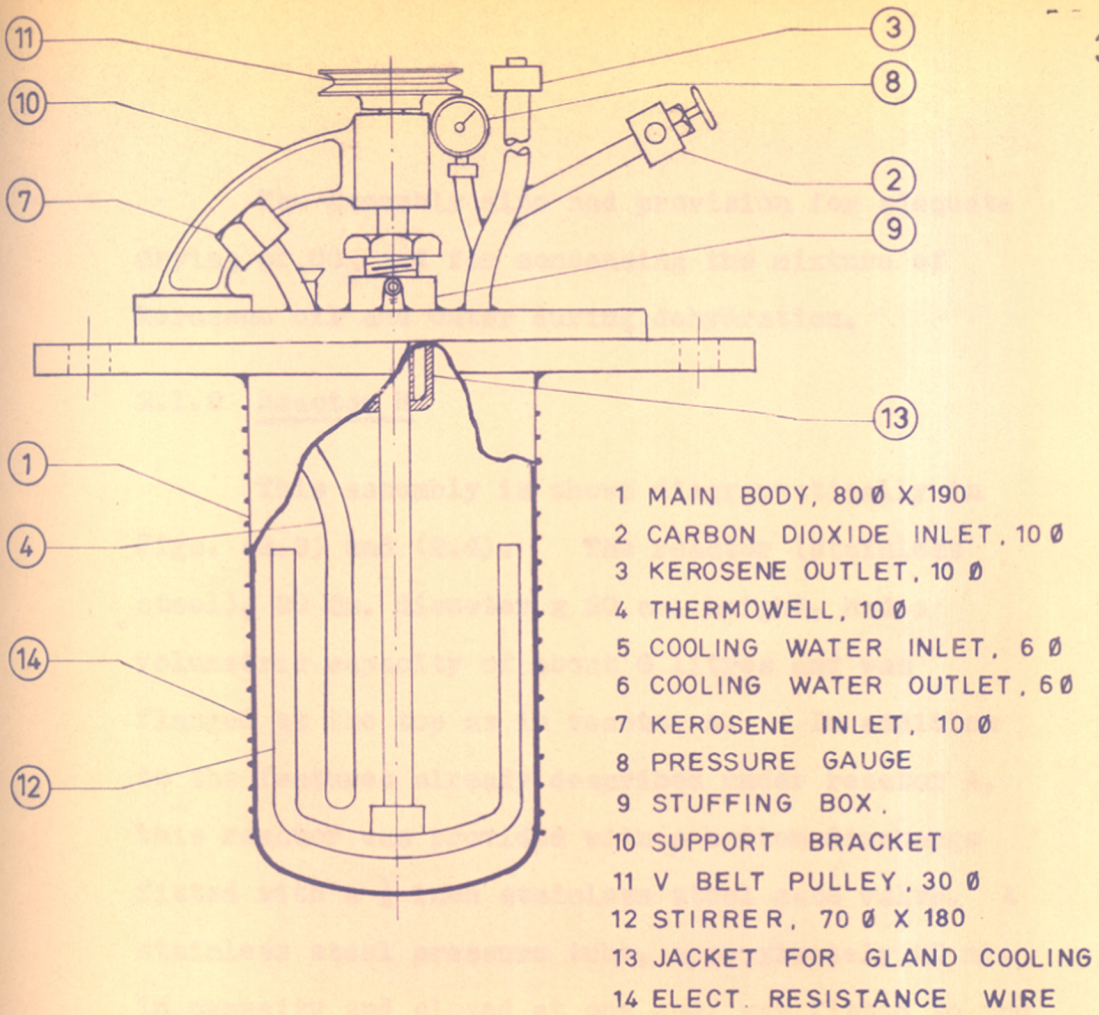


FIG. 2-1. REACTOR A

The assembly also had provision for adequate drying of  $\text{CO}_2$  and for condensing the mixture of kerosene oil and water during dehydration.

### 2.1.2 Reactor B

This assembly is shown diagrammatically in Figs. (2.3) and (2.4). The reactor (stainless steel), 20 cm. diameter x 20 cm. height, had a volumetric capacity of about 6 litres and was flanged at the top as in reactor A. In addition to the features already described under reactor A, this reactor was provided with a bottom discharge fitted with a  $\frac{1}{2}$  inch stainless steel gate valve. A stainless steel pressure tube, approximately 20 ml. in capacity and closed at one end, was fitted to the gate valve at its open end. Whenever it was desired to collect a sample, it was only necessary to fill the tube by opening the valve, close the valve again, and then remove the tube from the reactor assembly. An arrangement was provided in this assembly for recording the temperature continuously through a Cambridge circular recorder. A photograph of the assembly appears in Fig.(2.5).

## 2.2 PRINCIPAL RAW MATERIALS

In the course of this investigation the following

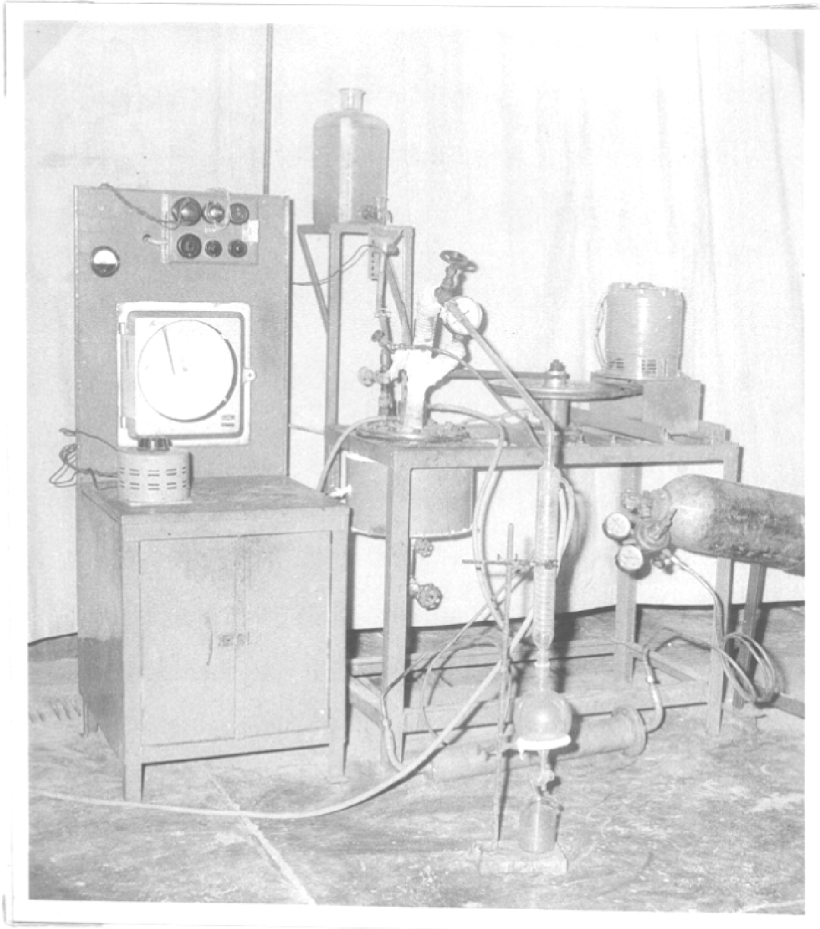


FIG. 2-5. PHOTOGRAPH OF REACTOR 'B' ASSEMBLY



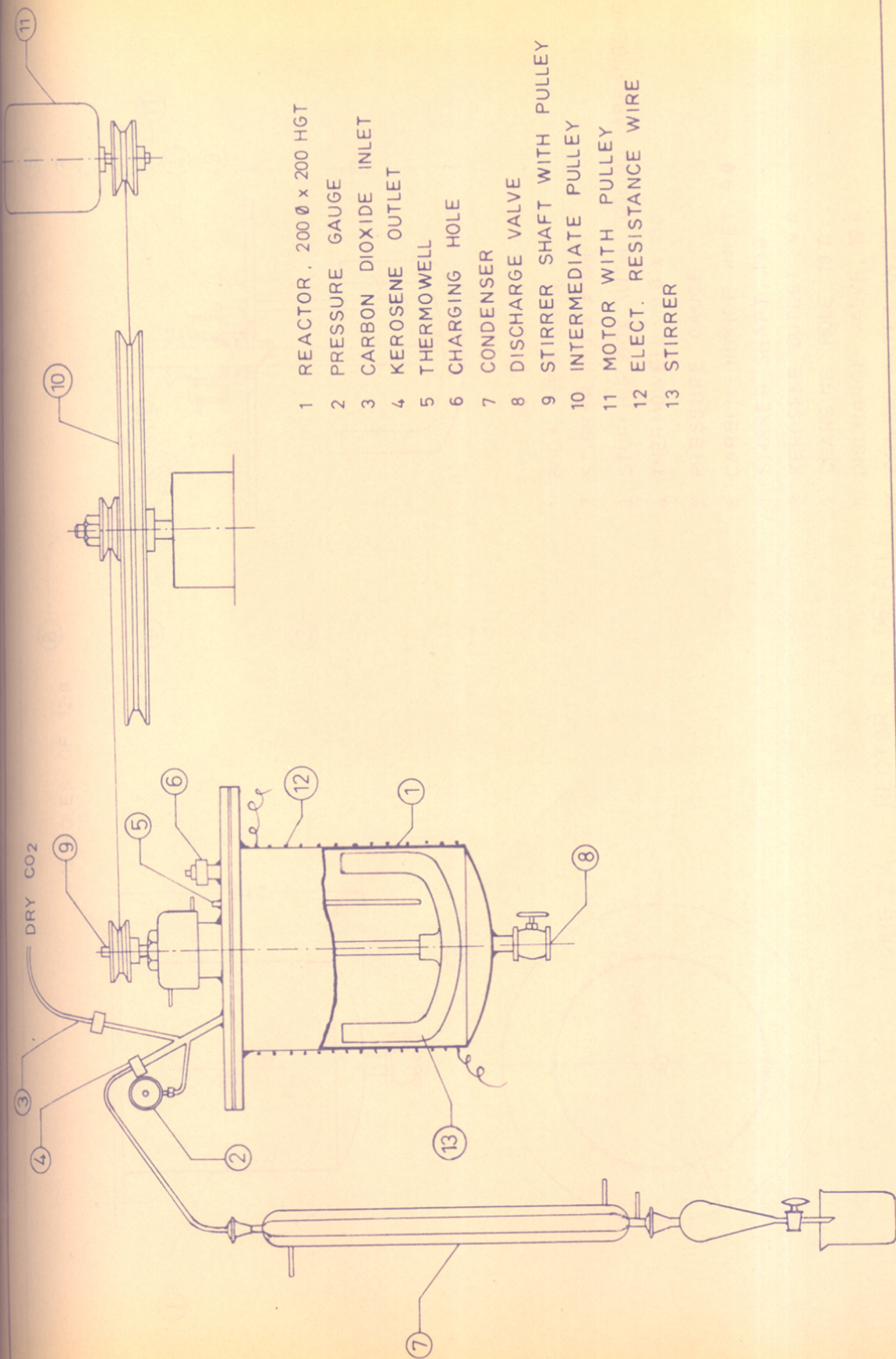
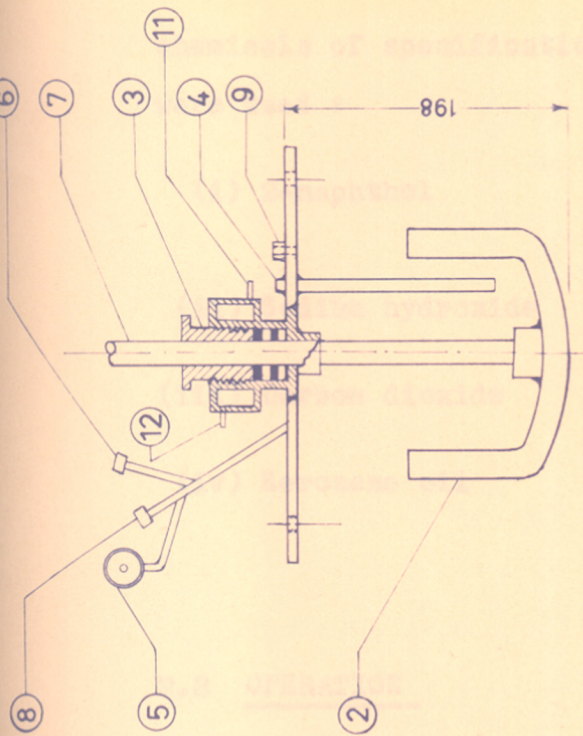
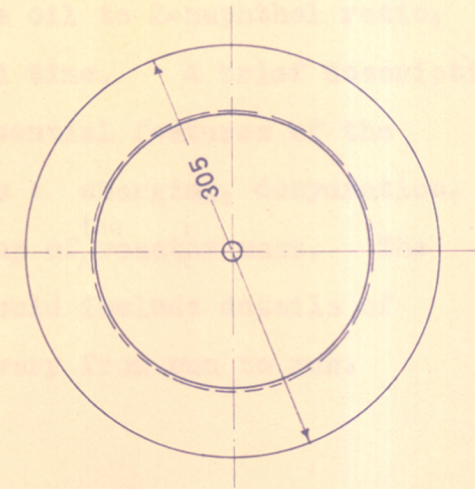
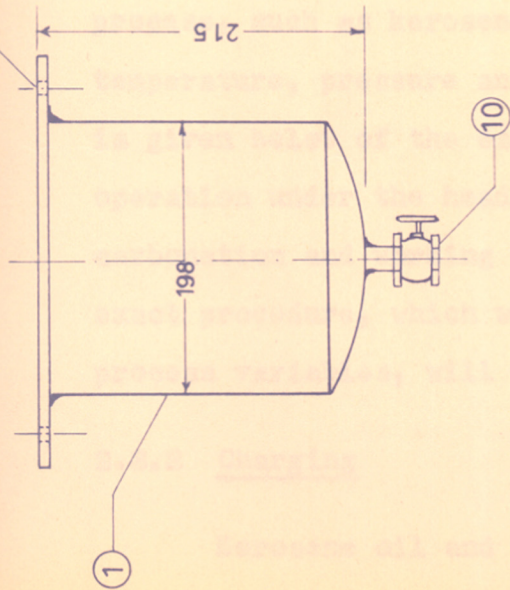


FIG. 2.3. REACTOR B ASSEMBLY



12 HOLES OF 12 Ø



1 BODY, 198 Ø X 215

2 STIRRER, 183 Ø X 198

3 STUFFING BOX WITH COOLING ARRANGEMENT

4 THERMOWELL, 19 Ø X 180

5 PRESSURE GAUGE

6 CARBON DIOXIDE INLET, 9 Ø

7 STIRRER SHAFT, 19 Ø

8 KEROSENE OUTLET, 9 Ø

9 CHARGING HOLE, 19 Ø

10 DISCHARGE VALVE, 19 Ø

11 COOLING WATER INLET

12 COOLING WATER OUTLET

FIG.2.4. RECTOR B - DETAILS

chemicals of specifications stated against them were used :

(i) 2-naphthol	Technical grade; brown grains; purity 96-97%.
(ii) Sodium hydroxide	Commercial grade; flakes; purity 93-94%.
(iii) Carbon dioxide	Commercial grade; dry CO <sub>2</sub> from cylinder.
(iv) Kerosene oil	Burmah-Shell superior grade kerosene oil; boiling range 160 <sup>o</sup> -265 <sup>o</sup> C.; 60% distilled below 200 <sup>o</sup> C.

## 2.3 OPERATION

### 2.3.1 Reactors A and B

The operation of the reactor assembly was carried out essentially according to a pre-determined procedure. Several factors were varied in the process, such as kerosene oil to 2-naphthol ratio, temperature, pressure and time. A brief description is given below of the essential features of the operation under the heads : charging, dehydration, carbonation and working up of <sup>the</sup> <sub>^</sub> reactor <sup>i</sup> <sub>^</sub> mass. The exact procedure, which would include details of process variables, will vary from run to run.

### 2.3.2 Charging

Kerosene oil and 2-naphthol were charged in

the reactor in a pre-determined ratio. Stirring was then started and the stoichiometric quantity of NaOH was added as 50% liquor. Heating was commenced and the temperature brought to about  $60^{\circ}\text{C}$ . in an  $\frac{1}{2}$  hour. An accurately weighed quantity of an additive was then added to the reaction mass.

### 2.3.3 Dehydration

An air condenser and a water condenser (along with a separating funnel as receiver) were connected in series with the distillation arm of the reactor. The feed hole of the reactor was connected to a graduated reservoir of fresh kerosene oil. Heat input was then increased and the temperature raised to  $90^{\circ}\text{C}$ . in another  $\frac{1}{2}$  hour. At this temperature a mixture of kerosene oil and water started to distill over. In order to ensure a constant ratio of kerosene oil to 2-naphthol in the reactor, kerosene oil was introduced into the reactor through a graduated reservoir at the same rate at which it distilled over from the reactor. In order also to ensure that moisture was not introduced along with the kerosene oil, carefully dried kerosene oil was used. (In the later part of the investigation it was found unnecessary to dry the kerosene oil before use since the water content of the oil was found to

be negligible as determined by Karl Fischer reagent.)

By this distillation almost all the water (water added with caustic soda plus water formed during the reaction) could be removed in the first two to three hours. The last traces of moisture came out in the form of droplets in the distilling kerosene oil. The quantitative removal of water was ascertained in each run by measuring the water removed. Dehydration was considered to be complete only when the water removed was equal to the water added and that formed during the reaction. In order to make sure that the last traces of moisture were completely removed, distillation and addition of kerosene oil were continued, till there were three complete change-overs of kerosene oil from the reactor. This meant the addition of 6 litres of kerosene oil to the reactor during distillation.

The next step in the dehydration cycle was the adjustment of 2-naphthol to kerosene oil ratio in the reactor to a pre-determined value, either by adding or removing kerosene oil. At the end of this adjustment, the temperature in the reactor reached a stable value of  $240^{\circ}$ - $250^{\circ}$ C. in the majority of runs. The total time of dehydration was then defined as the time required to reach this stage.

#### 2.3.4 Carbonation

The condensers and the feeding line were disconnected and these openings in the reactor were closed. The needle valve fixed to the reactor was then connected to the CO<sub>2</sub> cylinder through a trap filled with silica gel.

CO<sub>2</sub> was introduced inside the reactor at a slow, regulated rate at the desired temperature. The pressure and temperature were then varied according to a pre-determined plan. It was found that at the beginning of carbonation the control of the carbonation temperature was difficult. Also an appreciable consumption of CO<sub>2</sub> was noticed in the first-1-2 hours, after which there was practically no consumption till the end of the reaction. The reaction was stopped after the desired time interval, and the products of reaction were worked up.

#### 2.3.5 Working up

After carbonation the heating was cut off and CO<sub>2</sub> was released slowly. The reactor mass was allowed to cool down under stirring to 90°C. Water was added to  $\frac{1}{4}$ th capacity of the reactor along with the required amount of caustic soda. The mass was heated to about 125°C. for ensuring complete dissolution.

It was cooled and discharged through the bottom valve and further diluted by water to 8.6 to 10.2 Tw. This solution, which varied from dark brown to dark red in colour, was stirred for about 10 minutes and allowed to separate into two layers. The upper oily layer containing kerosene oil plus dissolved tar was removed. Activated charcoal (1% on 2-naphthol charged) was added to the aqueous layer and heated to 70°-80°C. by steam for 15 minutes, after which steam was stopped but stirring was continued for one hour; this was then allowed to settle for  $\frac{1}{2}$  hour. This procedure helped to separate the tar efficiently.

The tar was removed by filtration. The filtrate consisted of two layers, the aqueous layer containing BON acid and 2-naphthol and the small residual organic layer containing kerosene oil plus dissolved tar. The residual organic layer was removed and the aqueous layer was worked up for the isolation of 2-naphthol and BON acid in the following manner.

The aqueous layer was heated to 55°-60°C. and the pH brought down to 6.3 by 50% sulfuric acid when 2-naphthol precipitated out. The complete precipi-



tation of 2-naphthol was ensured by the following test: a sample filtered through a dry filter should remain clear with further dilution with water. The precipitated 2-naphthol was then filtered and the filtrate worked up for BON acid. The content of 2-naphthol in the crude wet cake was estimated by completely redissolving to a known volume. In a few test cases, the wet cake was distilled under high vacuum in a specially constructed distillation unit to determine the total recovery of 2-naphthol (pure).

The filtrate was heated to  $70^{\circ}$ - $80^{\circ}$  C. and the pH brought down to 2 with 50% sulfuric acid when BON acid precipitated out. The slurry was then cooled to  $50^{\circ}$  C., filtered, and washed free of acid. The BON acid thus obtained was dried in a vacuum dryer at  $60^{\circ}$ - $70^{\circ}$  C.

## 2.4 ANALYSIS

### 2.4.1 Estimation of 2-naphthol and BON acid

Primary aromatic amine salts are quantitatively diazotised by nitrous acid at low temperature ( $0^{\circ}$ - $5^{\circ}$  C.). The resulting diazonium salts are very soluble in water, and couple rapidly and quantitatively with

naphthols in alkaline solution. This forms the basis for the estimation of naphthols. The iodometric method (59, 60, 61) was also tried for the estimation of naphthols but did not give satisfactory results; all the naphthols estimations were therefore carried out by diazo titration.

#### Preparation of standard diazo solution

Sodium nitrite solution (0.5 N) was prepared, and its exact strength was determined by sulfanilic acid and also by oxidation with potassium permanganate (59, 60, 64). This standardised sodium nitrite solution was used in determining the content of p-chloroaniline in a prepared solution (0.25 N in excess HCl). Standardised p-chloroaniline solution (50 ml.) was then taken in an amber coloured volumetric flask (250 ml. capacity) and was diazotised at  $0^{\circ}$ - $5^{\circ}$ C. with sodium nitrite solution; a small amount of potassium bromide was used for stabilizing the diazo solution. This standard diazo solution was used in the estimation of naphthols as given below.

#### Estimation by standard diazo solution

##### 2-NAPHTHOL :

1.44 gm. of 2-naphthol was dissolved in 10 ml. of 2 N NaOH and 400 ml. water, and then made upto 500 ml.



50 ml. of this solution was transferred to a beaker containing 20 ml. of 2 N  $\text{Na}_2\text{CO}_3$  (buffer) plus some ice pieces and cold water (total volume about 200 ml.). Standard diazo solution from a jacketted burette (cooled by ice cold water circulation) was added to the naphthol solution in stages of 0.5 ml. each with efficient stirring. After each addition a drop of the mixture was spotted on a clean filter paper. The clear outer ring was tested by spotting with diazo solution and with a fast coupler (H acid or J acid) solution. In the beginning the clear outer ring gave a coloured rim with diazo solution which became faint and then vanished with further addition of diazo solution from the burette indicating exhaustion of 2-naphthol in the titrating mixture. At this stage the clear outer ring was tested by spotting with H acid solution indicating the presence of excess diazo solution in the titration mixture. The end point was taken as the mean of the last spot with diazo and the first spot with the H acid solution.

Calculation :

$$\text{2-Naphthol, \%} = \frac{X \times N \times 72 \times 100}{50 \times W}$$

where

- X = volume in ml. of diazo solution added;  
N = normality of diazo solution; and  
W = weight in gm. of 2-naphthol (500 ml.).

BON ACID :

The estimation of BON acid was carried out by a similar procedure. The starting solution was prepared by dissolving 1.88 gm. of BON acid in 10 ml. of 2 N NaOH and 400 ml. water and then making up to 500 ml.

Determination of 2-naphthol in BON acid (31)

18.8 gm. of BON acid was creamed with 50 ml. water and dissolved in the cold with 110 ml. NaOH (0.1 N) solution. This solution was treated with 5 gm. pure ammonium sulfate. The separated free 2-naphthol was then extracted with ether three times taking 25 ml. ether for each extraction. The total ether extract was filtered through a small dry filter paper and evaporated. The residue was dissolved in the minimum amount of NaOH (0.1 N) solution and transferred to a 500 ml. iodine flask using 200 ml. water. The solution was made acidic to Congo red by adding dilute HCl. To this 10 gm.

$\text{NaHCO}_3$  was added and shaken till effervescence stopped. Starch solution was added and titrated against iodine solution (0.1 N) till blue colour was obtained. 10 ml. excess of standard iodine solution (0.1 N) was then added and the flask was stoppered well and allowed to stand for 10 minutes with occasional shaking. Excess of iodine was back titrated with 0.1 N solution of arsenious acid.

Calculation :

$$\text{2-Naphthol content, \%} = (a - b) \times 0.0383$$

where

a = volume in ml. of 0.1 N iodine solution added; and

b = volume in ml. of 0.1 N arsenious acid (back titrated reading).

The ether extract residue was also analysed by the diazo titration method as mentioned above.

#### 2.4.2 Sodium hydroxide (59, 62)

Approximately 45-50% caustic soda solution was used during charging. For convenience a carefully analysed stock of caustic soda solution was preserved during the investigation. It was regularly analysed by titrating samples against standard potassium hydrogen phthalate solution.

### 2.4.3 Determination of water in kerosene oil (63)

In the course of this investigation it was necessary to determine the amount of water in kerosene oil. This was done by the following method.

About 25 ml. of the reagent methanol was transferred to the titration flask and was titrated to the end point with the Fischer reagent. To this 25 ml. of kerosene oil (from the distillate sample) was added quickly. The solution was stirred vigorously and was titrated with the Fischer reagent.

## 2.5 CARBON DIOXIDE SOLUBILITY APPARATUS (33)

### 2.5.1 Description

A diagrammatic sketch of the apparatus is shown in Fig. (2.6). The apparatus consisted essentially of two glass burettes (1, 2) both of which had a capacity of 75 ml. with 0.1 ml. graduations. Burette (1), or kerosene oil burette, was connected through its bottom end to a tee, one opening of which was connected to a levelling bulb ( $L_1$ ) filled with kerosene oil saturated with  $CO_2$  at room temperature, and the other opening to a high

pressure needle valve ( $V_1$ ). The levelling bulb line was provided with a stopcock ( $S_1$ ) so that the oil level inside the oil burette (1) could be adjusted to any mark. From valve ( $V_1$ ) a  $\frac{1}{8}$  inch diameter pressure copper tubing (T) was connected to the discharge valve of the reactor B. This pressure line was also provided with a branch line with another pressure valve ( $V_2$ ) so that it could be purged when desired.

Burette (2), or carbon dioxide burette, was also provided with a stopcock ( $S_2$ ) and a levelling bulb ( $L_2$ ) filled with kerosene oil saturated with  $CO_2$  at room temperature. The two burettes were connected at the top to a glass tee that led to a two-way stopcock ( $S_3$ ). One opening of the stopcock ( $S_3$ ) connected the burette system to the atmosphere while the other opening connected it to a mercury manometer (M).

#### 2.5.2 Operation

4 litres of kerosene oil of  $220^{\circ}$ - $265^{\circ}$  C. cut was charged into reactor B. It was heated to the desired temperature and maintained steady at that temperature ( $\pm 2^{\circ}$ C.) during an entire measurement. The bottom discharge valve was then connected through

1/8" thick copper tubing to two identical solubility units described above through a tee connection.

The solubility units were next prepared for measurement. The saturated kerosene oil level in burette (1) was adjusted to the zero mark by means of the levelling bulb ( $L_1$ ). Stopcock ( $S_3$ ) was positioned to connect the burette system to the atmosphere. The saturated kerosene oil bulb ( $L_2$ ) was then raised to a position such that the oil would flow into the gas burette (2) to a reading of 45 to 50 ml. Stopcock ( $S_3$ ) was then turned to connect the burette system to the mercury manometer (M). The saturated kerosene oil levelling bulb ( $L_2$ ) was readjusted, if necessary, so that the manometer would be at the atmospheric pressure. The same procedure was used for the second identical solubility apparatus. Atmospheric pressure and room temperature were then recorded. With these manipulations both the solubility units were ready to receive the sample.

CO<sub>2</sub> gas was introduced into reactor B to the desired pressure in about 30 seconds, and maintained at that pressure during an entire measurement. The procedure given below is for any one of the solubility units, the valves of the second unit being kept closed during this period. The connecting line was flushed

through valve ( $V_2$ ) with 20-30 ml. of oil from reactor B before introducing the solution sample in the apparatus. Valve ( $V_2$ ) was then closed, and valve ( $V_1$ ) was momentarily opened to allow a small sample of solution to flow from the reactor to the oil burette (1). The sample size varied between 15 and 20 ml. As soon as the required volume of solution was admitted, valve ( $V_1$ ) was closed,  $CO_2$  began flashing immediately from the oil, and the pressure increased inside the burette system. In order to eliminate leaks, the saturated kerosene oil bulb ( $L_2$ ) was lowered at a rate such that essentially atmospheric pressure was maintained in the burette system as indicated by the mercury manometer (M).

When no more  $CO_2$  bubbles were seen in the oil phase, the saturated kerosene oil levelling bulb ( $L_2$ ) was adjusted to a final position that indicated exactly atmospheric pressure in the apparatus. About 2 minutes were necessary for the  $CO_2$  to flash completely. The levels of oil in both the burettes were recorded simultaneously. About 3-4 minutes were necessary to perform this entire operation in one unit.

The procedure described above is adequate if the saturation solubility of  $CO_2$  in kerosene oil is to be determined. For this purpose it is only necessary to ensure that the kerosene oil in the



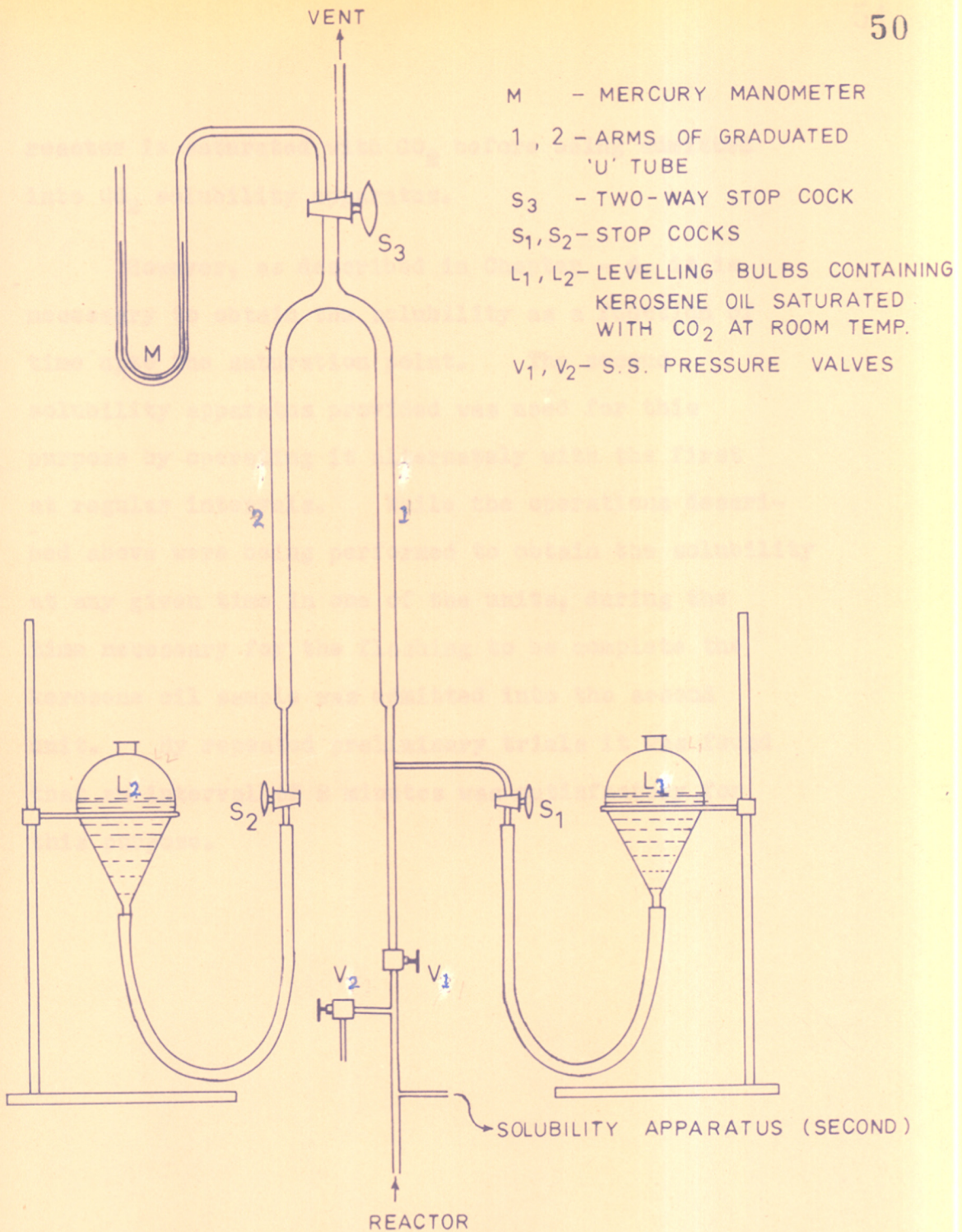


FIG. 2.6. SOLUBILITY APPARATUS



reactor is saturated with  $\text{CO}_2$  before being admitted into  $\text{CO}_2$  solubility apparatus.

However, as described in Chapter - 4, it is necessary to obtain the solubility as a function of time upto the saturation point. The second solubility apparatus provided was used for this purpose by operating it alternately with the first at regular intervals. While the operations described above were being performed to obtain the solubility at any given time in one of the units, during the time necessary for the flashing to be complete the kerosene oil sample was admitted into the second unit. By repeated preliminary trials it was found that an interval of 2 minutes was satisfactory for this purpose.

## CHAPTER - 3

### PRELIMINARY STUDY OF PROCESS VARIABLES

Experimental investigations were carried out to determine the effective range of the different process variables that influence the conversion and yield in tube-sheet conversion. The results obtained are discussed in this chapter with the object goals, objectives and objectives.

Details of the experimental procedure and working up of the reaction products have already been described in Chapter - 2, and will be specifically stated if any be added that this procedure has been adopted in obtaining the data presented and discussed below.

#### 3.1 INTRODUCTION

In the experiments designed to study conversion, a wide range of initial conversion (10% to 100%) was used (with the initial conversion constant) and the effect of conversion on the yield of the product was studied as far as possible.

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## CHAPTER-3

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### PRELIMINARY STUDY OF PROCESS VARIABLES

## CHAPTER - 3

### PRELIMINARY STUDY OF PROCESS VARIABLES

Experimental investigations were carried out to determine the effective ranges of the different process variables that influence the conversion and yield in Kolbe-Schmitt carbonation. The results obtained are discussed in this chapter under the broad heads, dehydration and carbonation.

Details of the experimental procedure and working up of the reaction products have already been described in Chapter - 2, and unless specifically stated it may be assumed that this procedure has been adopted in obtaining the data presented and discussed below.

#### 3.1 DEHYDRATION

In the experiments designed to study dehydration, a close range of distilled kerosene oil (low dielectric constant) was used as entrainer in nitrogen atmosphere so as to keep away oxygen coming into

contact with the naphtholate. The conditions of carbonation were fixed on the basis of the data reported in the literature, thus ensuring that any variation in conversion would be due to changes in dehydration conditions only.

### 3.1.1 Importance of total dehydration

A few preliminary runs were carried out in reactor A maintaining the reaction conditions generally as described in the literature. The conditions used were as follows :

Charge :

<u>Chemical</u>	<u>Amount</u>	<u>Specification</u>
2-Naphthol	144 gm.	97%
Caustic soda	42.5 gm.	94%
Water	92 ml.	Distilled water
Kerosene oil	450 ml.	180°-210° C. close range; (distilled)

Dehydration :

4.0 litres of kerosene oil were continuously added during distillation in order to maintain a ratio of 1 : 3 (2-naphthol to kerosene) over the entire dehydration period. A slow stream of N<sub>2</sub> gas was maintained inside the reactor during this period.

Dehydration time	24 hr.
Total water recoverable	Water added (192 ml.) plus reaction water (18 ml.) - 110 ml.

Carbonation :

2-naphthol to kerosene ratio	1 : 1.3
Temperature	230°-250°C.
Pressure	0-150 psig.
Time	24 hr.

CO<sub>2</sub> was introduced at 230°C., the pressure and temperature were raised gradually to 150 psig and 250°C. respectively in the course of five hours, and maintained there for 19 hours. Several runs were carried out under these conditions, and they are recorded in Table-3.1. In all these runs the conversion to BON acid was found to be poor, varying generally from 5 to 10%, against the theoretical conversion of 50%. The total water recovered was never 100% and, as can be seen from the table, varied from 90.0 to 95.5%, even though the final temperature attained during dehydration was 200°C.

The complete exclusion of water before carbonation is essential since it inhibits carbonation and leads to side reactions resulting in the loss of

TABLE - 3.1

RESULTS OF PRELIMINARY RUNS ON DEHYDRATION AND CARBONATION

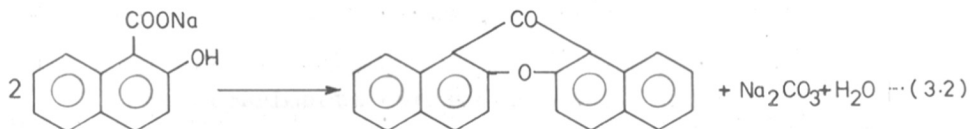
Dehydration time ..	24 hr.	2-naphthol to kerosene ratio :		
Expected recovery of water ..	110 ml.	During dehydration .. 1 : 3		
Carbonation time ..	24 hr.	During carbonation .. 1 : 1.3		
No.	Final temperature °C.	Water recovery		Conversion to BON acid %
		ml.	%	
1	190	99.0	90.0	2
2	190	101.0	92.0	2
3	195	103.0	93.5	8
4	205	103.0	93.5	4
5	200	103.5	94.0	4
6	200	104.0	94.5	6
7	200	103.0	93.5	8
8	195	102.0	92.5	negligible
9	200	105.0	95.5	10
10	200	103.0	93.5	8

2-naphtholate. Water forms strong chelation with sodium 2-naphtholate, thus preventing the addition of  $\text{CO}_2$  to give BON acid. In the presence of  $\text{CO}_2$  the hydrolysis of this complex gives free 2-naphthol and sodium carbonate.



The free 2-naphthol does not form sodium naphtholate again, since in its fused form it is inert to alkali.

In another side reaction one mole of water is formed for every mole of xanthone (1,2,7,8-dibenzoxanthone), which is the main constituent of by-product tar.



In other words, for every mole of xanthone formed, four moles of sodium 2-naphtholate are lost.

Hence it is essential to ensure the total absence of moisture during the reaction and also to avoid the side reactions which result in the formation of water.

### 3.1.2 Effect of temperature on dehydration

In all the runs discussed earlier, the recovery of water was poor. It is likely that under the distillation conditions used the water present in combination (chemical and physical) with the naphtholate may not have been removed. It was therefore thought that the combined water could be removed by heating the naphtholate to a high temperature ( $270^{\circ}$ - $320^{\circ}$ C.) in the final stages of dehydration. Temperatures above  $307^{\circ}$ C. might be more effective as sodium 2-naphtholate melts at that temperature, thus facilitating the removal of bound water. It is known that there is no deleterious effect on sodium 2-naphtholate of temperatures as high as  $320^{\circ}$ C. even if it is held at these temperatures over a prolonged period under inert atmosphere.

The experiments carried out for investigating the effect of temperature were divided into four groups : (1) experiments at  $200^{\circ}$ C.; (2) at  $240^{\circ}$ C.; (3) at  $280^{\circ}$ C.; and (4) at  $320^{\circ}$ C. The experimental technique involved in group (1) where the temperature did not exceed  $220^{\circ}$ C. (which is within the boiling range of kerosene) was in accordance with the procedure described earlier. For groups (2), (3) and (4), where the final dehydration temperatures



were  $240^{\circ}$ ,  $280^{\circ}$  and  $320^{\circ}$  C. respectively, this procedure could not be followed since it would not be possible to obtain the temperatures involved by the open distillation method adopted at the lower temperature. The following procedure was used. Distillation was carried out by the usual method up to  $200^{\circ}$  C. at which stage the reactor was closed and heating continued. The water (along with kerosene) from the reactor was then discharged intermittently by opening the valves. It was observed that after five such discharges there were no visible droplets of water in the kerosene discharge.

The results of these experiments are summarized in Tables-3.2 and 3.3. The runs recorded in Table-3.2 were carried to completion, while those recorded in Table-3.3 were stopped after dehydration in order to observe the physical state of the naphtholate. It will be observed that in the first two groups the recovery of water was of the order of 95%. This recovery figure is in consonance with the values recorded in Table-3.1 for the scouting experiments which were also carried out under similar conditions. Observations about the physical state of the sodium 2-naphtholate showed that it was in the form of finely divided grains well suspended in kerosene oil.

TABLE - 3.2

## EFFECT OF DEHYDRATION TEMPERATURE ON CARBONATION

Dehydration time .. 24 hr. 2-naphthol to kerosene ratio :  
 Expected recovery of water .. 110 ml. During dehydration .. 1 : 3  
 Carbonation time .. 24 hr. During carbonation .. 1 : 1.3

No.	Final temperature ° C.	Water recovery		Conversion to BON acid %
		ml.	%	
1	200	103.0	93.5	8.0
2	200	104.0	95.0	11.0
3	240	103.5	94.0	9.0
4	240	104.0	95.0	13.0
5	280	107.0	97.5	3.0
6	280	108.0	98.0	3.5
7	320	108.0	98.0	1.0
8	320	107.5	98.0	negligible

TABLE - 3.3

## EFFECT OF DEHYDRATION TEMPERATURE ON THE PHYSICAL STATE OF 2-NAPHTHOLATE

Dehydration time .. 20 hr.  
 Expected recovery of water .. 110 ml.  
 2-naphthol to kerosene ratio .. 1 : 3

No.	Final temperature ° C.	Water recovery		Remarks
		ml.	%	
1	200	103.0	93.5	Finely divided grains
2	200	103.5	94.0	-do-
3	240	104.0	94.5	-do-
4	240	103.5	94.0	-do-
5	280	108.0	98.0	Lumps which became very hard on cooling
6	280	108.0	98.0	-do-
7	320	107.5	98.0	-do-
8	320	108.0	98.0	-do-

Contrary to expectations, the conversions to BON acid obtained in groups (3) and (4) were lower than at the lower dehydration temperatures. It will be observed from Tables-3.2 and 3.3 that in both these cases the recovery of water was over 98%, which is higher than that at lower temperatures. The physical form of sodium naphtholate provides a possible clue to the low conversions in spite of superior water recovery. At both these temperatures (280° and 320°C.), the sodium naphtholate was observed to be in the form of lumps which were probably not accessible to carbonation to the same extent as finely divided grains. Kerosene oil does not have solvent action on the sodium salt of 2-naphthol which remains in the oil as suspension. Thus a proper physical shape and size (finely divided grains) of sodium 2-naphtholate is essential. On the other hand, at the lower temperatures studied (200° and 240°C.), although the physical state was satisfactory, the temperature was not high enough to ensure total dehydration.

The obvious conclusion follows that, although increasing the temperature of dehydration might enhance the recovery of water, a necessary pre-condition for efficient carbonation, the conversion to BON acid

is still poor in view of the unfavourable physical state of the sodium naphtholate. The effect of 2-naphthol/kerosene oil ratio on the physical state of the naphtholate is discussed in Section 3.2.2.

### 3.1.3 Use of additives

In an alternative method for the complete removal of moisture, a search was made for suitable additives which could be used along with the normal charge. The properties desirable in such an additive would be : (i) capacity to extract water which is in combination with the naphtholate particle without destroying its physical shape and size and (ii) absence of any deleterious effect on carbonation and on the quality of the carbonation products.

Chemicals normally used as dehydrants (together with a few others) were screened for this purpose :  $\text{CaCl}_2$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{ZnCl}_2$ , silica gel, bauxite and Kieselguhr. Dehydration runs were carried out using these materials (independently) to the extent of 1 to 5% (on 2-naphthol charged), and the results were examined in the light of the properties mentioned above. The data on dehydration are summarized in Table-3.4.

The results show that  $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ , bauxite,  $\text{NaOH}$ , and  $\text{KOH}$  give a water recovery of 99 to 100%

TABLE - 3.4

## DEHYDRATION DATA SHOWING THE EFFECT OF ADDITIVES ON TOTAL WATER RECOVERY

Dehydration time .. 12 hr.  
 Final dehydration temperature .. 190°-200° C.  
 2-naphthol to kerosene ratio .. 1 : 3

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Remarks
			ml.	%	
1	Caustic soda	1	108.0	98.5	-
2	Caustic soda	2	109.5	100.0	-
3	Potassium hydroxide	1	108.0	98.0	-
4	Potassium hydroxide	2	109.0	99.5	-
5	Calcium chloride	1	109.0	99.5	Quick water recovery
6	Calcium chloride	2	110.0	100.0	-do-
7	Calcium chloride	4	110.0	100.0	-do-
8	Calcium chloride	6	110.0	100.0	-do-
9	Bauxite	1	109.0	99.5	Quick water recovery but distillate turbid
10	Bauxite	2	110.0	100.0	-do-

TABLE - 3.4 (contd.)

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Remarks
			ml.	%	
11	Bauxite	4	110.0	100.0	Quick water recovery but distillate turbid
12	Potassium carbonate	1	103.0	93.5	0.5 gm. 2-naphthol came out
13	Potassium carbonate	2	106.0	96.0	Water droplets were recovered over longer period
14	Potassium carbonate	4	104.0	94.5	Lump formation
15	Calcium carbonate	1	106.0	96.0	Water was recovered over longer period
16	Calcium carbonate	4	106.0	96.0	Lump formation
17	Silica gel	1	107.0	97.5	Water was recovered over longer period
18	Silica gel	4	107.0	97.5	-do-
19	Kieselguhr	1	104.0	94.5	-do-
20	Kieselguhr	4	105.0	95.5	-do-

TABLE - 3-4 (contd.)

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Remarks
			ml.	%	
21	Sodium sulphate	1	107.0	97.5	Water was recovered over longer period
22	Sodium sulphate	4	107.0	97.5	--do--
23	Zinc chloride	1	109.0	99.5	-
24	Zinc chloride	4	108.0	98.0	0.5 gm. 2-naphthol came out
25	Alumina	1	108.0	98.0	-
26	Alumina	4	108.0	98.0	-



when used along with the normal charge (to the extent of 1 to 2% on 2-naphthol) without affecting the fine grain structure of the naphtholate. In other cases the recovery of water is not satisfactory.

Using these additives ( $\text{CaCl}_2$ ,  $\text{ZnCl}_2$ , bauxite,  $\text{NaOH}$ ,  $\text{KOH}$ ) both dehydration and carbonation were then carried out in order to observe the effect of these additives on the conversion of 2-naphthol to BON acid, keeping dehydration and carbonation times as 12 and 14 hours respectively and maintaining the other conditions as described in Section 3.1.1. The results obtained are summarized in Table-3.5. It will be observed that in the case of  $\text{CaCl}_2$ , the recovery of water as well as conversion to BON acid are superior to those obtained with the other chemicals. In the case of bauxite and  $\text{ZnCl}_2$  the 2-naphthol recovered was greenish in colour.

#### 3.1.4 Further studies on dehydration

From Table-3.5 it may be observed that the use of about 2%  $\text{CaCl}_2$  (on 2-naphthol charged) is adequate to ensure quantitative removal of water. In all the runs discussed so far, distilled kerosene oil ( $180^\circ$ - $210^\circ\text{C}$ .) was used keeping the dehydration time fixed at 12 hours. It is known that  $\text{CaCl}_2$  loses water

TABLE - 3.5

DATA SHOWING THE EFFECT OF DIFFERENT ADDITIVES ON CARBONATION

Dehydration time .. 12 hr. 2-naphthol to kerosene ratio :  
 Expected water recovery .. 110 ml. During dehydration .. 1 : 3  
 Final temperature of dehydration .. 200°C. During carbonation .. 1 : 1.3  
 Carbonation time .. 14 hr.

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Conversion to BON acid %	Remarks
			ml.	%		
1	Sodium hydroxide	1	109.0	99.5	24.0	-
2	Sodium hydroxide	2	109.5	100.0	23.0	-
3	Potassium hydroxide	1	109.0	99.5	22.0	-
4	Potassium hydroxide	2	109.0	99.5	22.5	-
5	Calcium chloride	1	110.0	100.0	27.0	Water recovery was rapid
6	Calcium chloride	2	110.0	100.0	28.5	-do-
7	Bauxite	1	110.0	100.0	22.0	Recovered 2-naphthol was greenish
8	Bauxite	2	110.0	100.0	21.0	-do-

TABLE - 3.5 (contd.)

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Conversion to BON acid %	Remarks
			ml.	%		
9	Zinc chloride	1	109.0	99.5	20.5	Reaction products found greenish
10	Zinc chloride	4	109.5	100.0	22.0	-do-
11	Alumina	1	108.0	98.0	21.0	-
12	Alumina	4	109.0	99.5	23.5	-

of hydration completely above  $200^{\circ}\text{C}.$ ; so kerosene oil of a higher range was considered to be better. A few experiments were carried out using commercial kerosene oil (superior grade,  $160^{\circ}$ - $265^{\circ}\text{C}.$ ). The removal of water was observed to be quite fast as compared with the previous closer range of the oil.

A series of runs, using commercial grade kerosene oil ( $160^{\circ}$ - $265^{\circ}\text{C}.$ ), was then organized in which the amount of water removed was determined as a function of time. This was done in the following way. During distillation the separable water removed with kerosene was measured, and the water content of kerosene was also determined by the Karl Fischer reagent (Chapter - 2, Section 2.4.3). Separable water ceased to come out after three hours. Fig. (3.1) shows the water content of kerosene oil as a function of time. The water content evidently levels off after about 6 hours at a value of 8 mg. of water for 100 ml. of kerosene oil, which corresponds to the normal solubility of water in the oil. The higher proportion of water in kerosene at lower dehydration <sup>times</sup> ~~temperatures~~ is due to the physically bound moisture in the oil as evidenced by its turbidity. Although the separable water is removed within 3 hours, it is evidently necessary to continue the dehydration

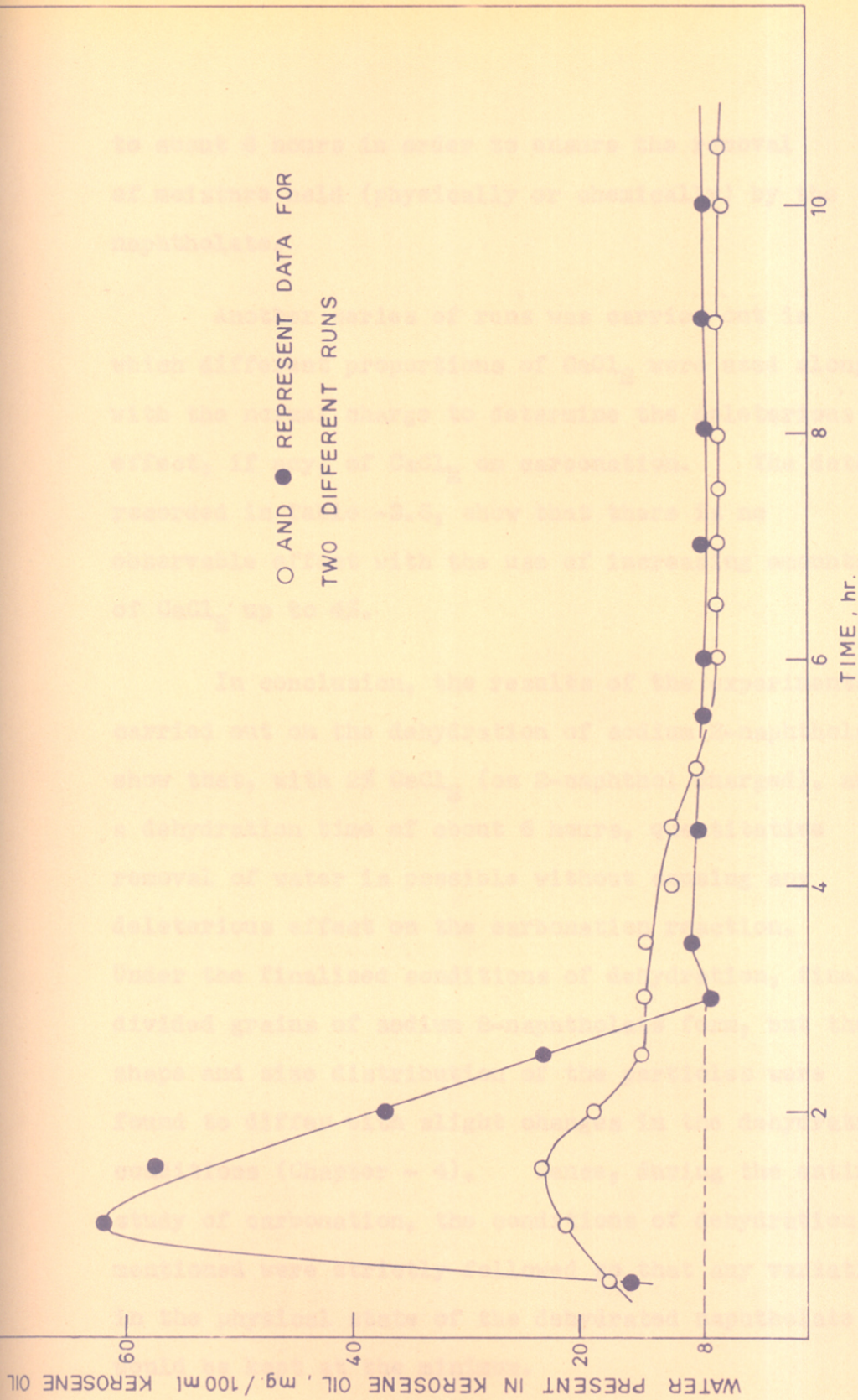


FIG. 3.1. WATER PRESENT IN KEROSENE OIL DURING DISTILLATION

to about 6 hours in order to ensure the removal of moisture held (physically or chemically) by the naphtholate.

Another series of runs was carried out in which different proportions of  $\text{CaCl}_2$  were used along with the normal charge to determine the deleterious effect, if any, of  $\text{CaCl}_2$  on carbonation. The data, recorded in Table 3.6, show that there is no observable effect with the use of increasing amounts of  $\text{CaCl}_2$  up to 4%.

In conclusion, the results of the experiments carried out on the dehydration of sodium 2-naphtholate show that, with 2%  $\text{CaCl}_2$  (on 2-naphthol charged), and a dehydration time of about 6 hours, quantitative removal of water is possible without causing any deleterious effect on the carbonation reaction. Under the finalised conditions of dehydration, finely divided grains of sodium 2-naphtholate form, but the shape and size distribution of the particles were found to differ with slight changes in the dehydration conditions (Chapter - 4). Hence, during the entire study of carbonation, the conditions of dehydration mentioned were strictly followed so that any variation in the physical state of the dehydrated naphtholate would be kept at the minimum.

EFFECT OF  $\text{CaCl}_2$  (ADDITIVE) ON CARBONATION

Charge :		Carbonation :	
2-naphthol ..	5 moles	Temperature ..	250° C.
Dehydration ..	8 hr. time	Pressure ..	70 psig.
2-naphthol ..	1 : 2.5 to kerosene ratio	Time ..	4 hr.
No.	Additive $\text{CaCl}_2$ 2-naphthol % on <del>2.5</del> charge	Conversion to BON acid %	Yield of BON acid %
1	1	33.4	71.0
2	2	34.6	74.5
3	4	33.0	73.2
4	6	29.4	65.1
5	8	26.8	61.0



### 3.2 CARBONATION

There are several variables which exercise direct and indirect influence on the carbonation reaction. Of these the following four variables, 2-naphthol to kerosene oil ratio, temperature, pressure and time, are evidently the most significant. These were studied in some detail to determine the conditions for obtaining high conversions and yields.

In the present kerosene oil dispersent system, it was found possible to carry out the carbonation at any fixed temperature and pressure without introducing any (significant) variations in temperature and pressure during the entire period. Kerosene oil acts as a diluent and hinders the attack of  $\text{CO}_2$  on sodium naphtholate. So the minimum practicable ratios of 2-naphthol to kerosene oil, having no apparent bad effect on the physical state of naphtholate, were chosen for the study.

It is known from the literature that the 2 : 1 acid predominates at carbonation temperatures below  $200^\circ\text{C}$ ., above which it decomposes. It becomes



stabilised at pressures higher than its dissociation pressure at any temperature. This acid shows a strong tendency for side reactions leading to the formation of tar. At the outset, therefore, it was decided to use temperatures above  $220^{\circ}\text{C}$ . and pressures much lower than the dissociation pressures of the 2 : 1 acid corresponding to the different temperature employed.

### 3.2.1 Variables and their ranges

The variables studied, together with the ranges covered, are listed below.

Temperature	$230^{\circ}$ - $270^{\circ}\text{C}$ .
Pressure	20 - 150 psig.
Carbonation time	4 - 16 hr.
2-naphthol to kerosene oil ratio	1 : 0.6 to 1 : 1.5

### 3.2.2 Effect of naphthol to kerosene oil ratio

In the present dispersent system, kerosene oil imparts a physical hindrance to the rate of the reaction. The major role of kerosene oil (or any dispersent) is that it dissolves the  $\text{CO}_2$ , and the reaction between sodium naphtholate and  $\text{CO}_2$  then proceeds by the transfer of  $\text{CO}_2$  across a film of the dispersent surrounding the solid particles of the

naphtholate. Details of the mass transfer mechanism associated with the reaction will be discussed in a separate chapter.

For the selection of suitable ratios for study, the physical state of the dehydrated naphtholate was actually observed at various ratios by opening the lid of the reactor after the adjustment of the ratio. Below a ratio of 1 : 0.6 finely divided grains were found transforming into compact lumps, probably due to high agglomeration. The ratio range 1 : 0.6 to 1 : 1.5 was chosen for the study to see if any systematic trends could be observed. Experiments were carried out in reactor A under the following conditions :

Charge :

<u>Chemical</u>	<u>Amount</u>
2-naphthol	149 gm.
Caustic soda (45%) solution	89 gm.
Kerosene oil	450 ml.
Calcium chloride	3 gm.

Dehydration :

Additional kerosene oil (used during distillation)	4 l.
--	------

Average time	6 hr.
Final temperature	200°-205°C.
Total water recovery	100%

#### Carbonation :

Carried out at different 2-naphthol to kerosene oil ratios (1 : 0.6, 1 : 1, 1 : 1.5) and pressures (20, 50, 100, 150 psig.) keeping temperature (250°C.) and time (14 hr.) fixed.

The data obtained are summarized in Table-3.7. Plots of conversion and yield vs. pressure at the three ratios are shown in Figures (3.2) and (3.3) respectively. It will be observed that there is a general tendency for the conversion to decrease with increase in the ratio of 2-naphthol to kerosene oil. In other words, the lesser the quantity of the dispersent used, the higher is the conversion. On the other hand, the yield shows a tendency to rise with increase in the ratio, even though the conversion exhibits a decreasing tendency. This is because of the decreased formation of tar with increasing ratio. The data clearly suggest a ratio of 1 : 1 as the most suitable in the range studied.

#### 3.2.3 Effect of temperature, pressure, and carbonation time

This series was carried out in reactor B as it

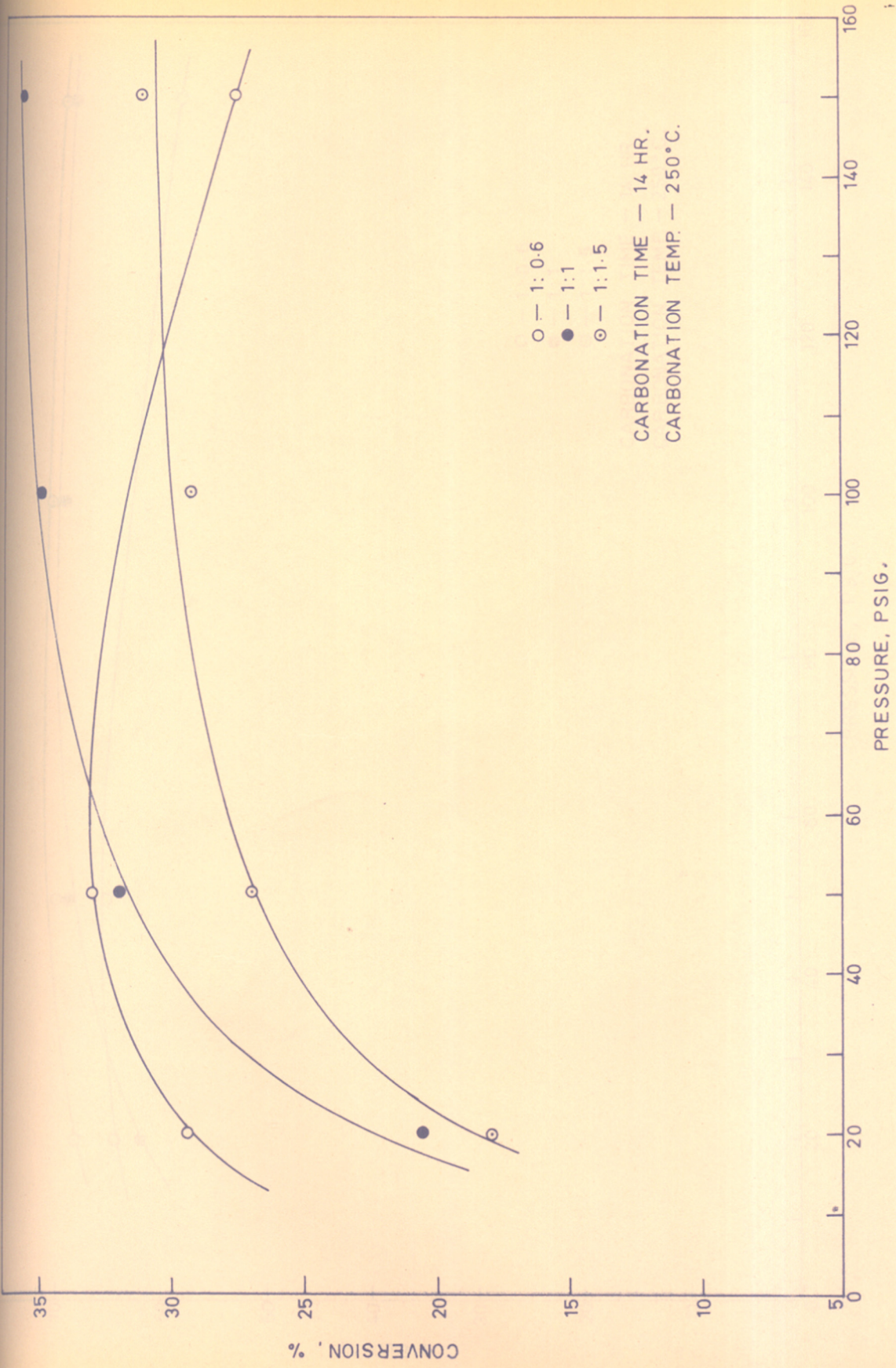


FIG. 3.2. EFFECT OF 2-NAPHTHOL : KEROSENE RATIO ON CONVERSION



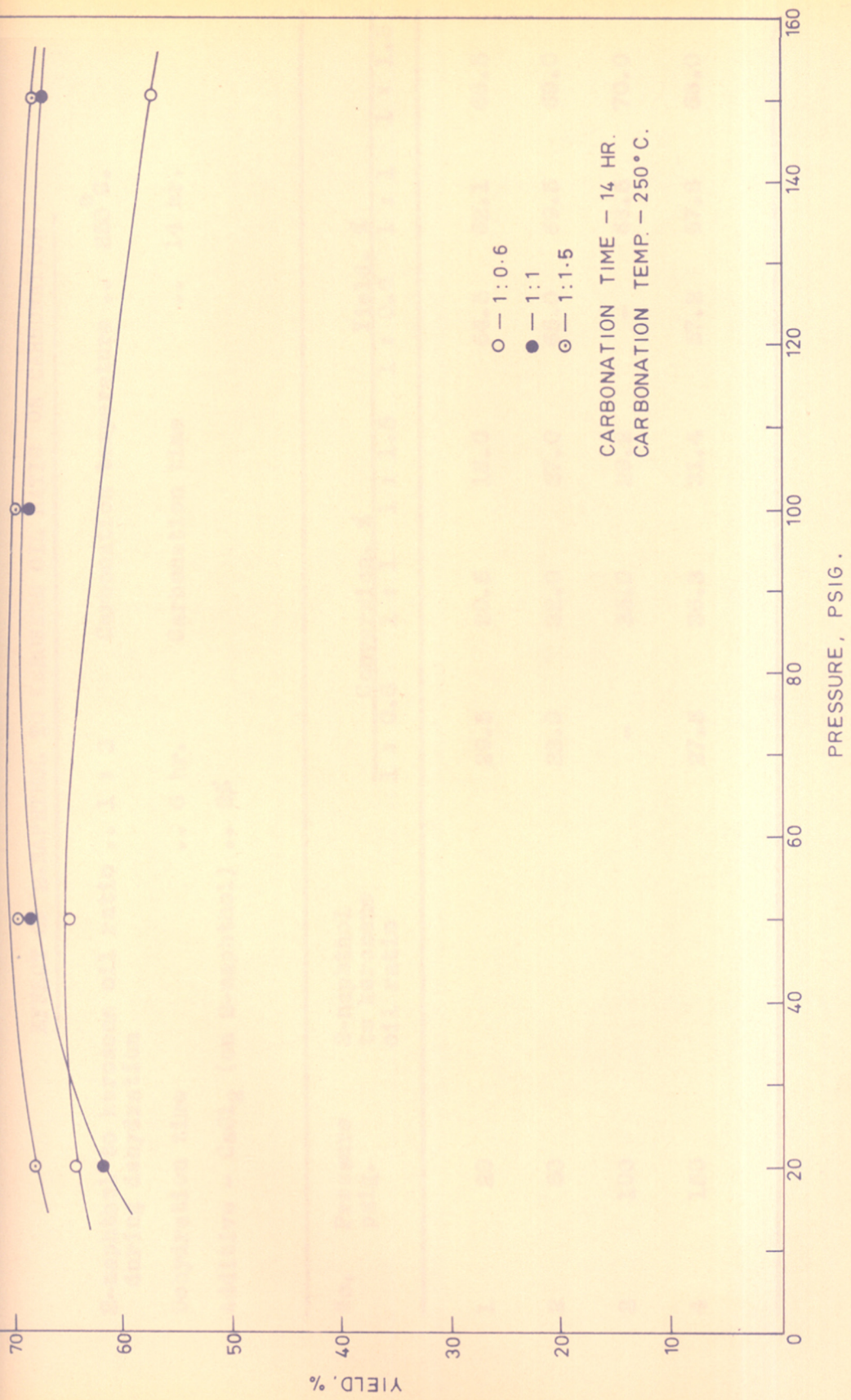


FIG. 3.3. EFFECT OF 2-NAPHTHOL: KEROSENE RATIO ON YIELD

TABLE - 3.7

EFFECT OF 2-NAPHTHOL TO KEROSENE OIL RATIO ON CARBONATION

2-naphthol to kerosene oil ratio .. 1 : 3      Carbonation temperature .. 250°C.  
 during dehydration

Dehydration time .. 6 hr.      Carbonation time .. 14 hr.

Additive - CaCl<sub>2</sub> (on 2-naphthol) .. 2%

No.	Pressure psig.	2-naphthol to kerosene oil ratio	Conversion, %		Yield, %			
			1 : 1	1 : 1.5	1 : 0.6	1 : 1		
1	20		29.5	20.5	18.0	64.5	62.1	68.5
2	50		33.0	32.0	27.0	65.0	69.5	69.0
3	100		-	35.0	29.2	-	68.5	70.0
4	150		27.5	36.3	31.4	57.2	67.8	68.0

was provided with a bottom discharge (Chapter - 2). While it was possible to operate this arrangement with difficulty, it was considered desirable to discharge the entire mass after a specified carbonation time rather than analyse the reaction products by sampling through the bottom discharge. A few test runs showed that the analysis of a sample at a particular carbonation time was some what different from that of the entire reaction mass when it was discharged at that carbonation time. The results discussed below are based on runs for which analyses were carried out by discharging the entire mass. The experimental conditions employed were :

Charge :

<u>Chemical</u>	<u>Amount</u>
2-naphthol	760 gm.
Caustic soda solution (45%)	444.5 gm.
Kerosene oil	2000 ml.
Calcium chloride	15 gm.

Dehydration :

Additional kerosene oil (used during dehydration)	6 l.
Average time	8 hr.
Final temperature	230 <sup>o</sup> -250 <sup>o</sup> C.
Total water recovery	100%.

EFFECT OF TEMPERATURE, PRESSURE AND TIME ON CARBONATION

2-naphthol to kerosene oil ratio : Dehydration time .. 8 hr.

during dehydration .. 1 : 2.5  
 during carbonation .. 1 : 1

CaCl<sub>2</sub> (on 2-naphthol charged) .. 2%

No.	Time of Temperature, °C. →		230		250		270				
	carbonation, hr.	Pressure, psig.	20	50	20	50	20	50			
1	4		25.10	29.86	26.79	24.34	34.20	34.36	14.62	28.22	30.40
2	8		30.88	31.81	29.35	22.09	33.40	29.35	12.37	14.20	21.47
3	12		30.10	27.71	30.47	15.14	30.20	28.32	8.18	13.29	8.69
4	16		-	-	-	-	22.00	23.31	-	-	-
<u>YIELD, %</u>											
1	4		66.0	70.5	65.6	67.0	74.0	74.0	51.0	64.0	67.0
2	8		70.4	71.8	66.0	61.0	70.5	67.6	43.6	45.7	54.1
3	12		67.0	66.5	62.7	58.0	67.0	63.8	31.2	28.4	30.4
4	16		-	-	-	-	55.5	56.5	-	-	-



### Carbonation :

Carried out under different conditions of temperature ( $230^{\circ}$ ,  $250^{\circ}$ ,  $270^{\circ}\text{C.}$ ), pressure (20, 50, 100 psig.), and carbonation time (4, 8, 12, 16 hr.), keeping the ratio of 2-naphthol to kerosene oil fixed at 1 : 1.

The results of this investigation, summarized in Table-3.8, show in general that higher temperatures and pressures are detrimental to the reaction. A further conclusion is that higher carbonation times are also detrimental to the reaction. There is a steep fall in yield as the carbonation time increases, and it appears that a carbonation<sup>time</sup> of about 4 hours gives favourable results. In Fig. (3.4) conversion has been plotted as a function of pressure at  $230^{\circ}$ ,  $250^{\circ}$ , and  $270^{\circ}\text{C.}$  at a carbonation time of 4 hours. Similarly in Fig. (3.5) yield has been plotted as a function of pressure at  $230^{\circ}$ ,  $250^{\circ}$  and  $270^{\circ}\text{C.}$  at a carbonation time of 4 hours. These two plots suggest a temperature of  $250^{\circ}\text{C.}$  and a pressure of 70 psig as being the most favourable. This investigation has shown that the principal carbonation reaction comes to a stop at or before a reaction time of 4 hours.

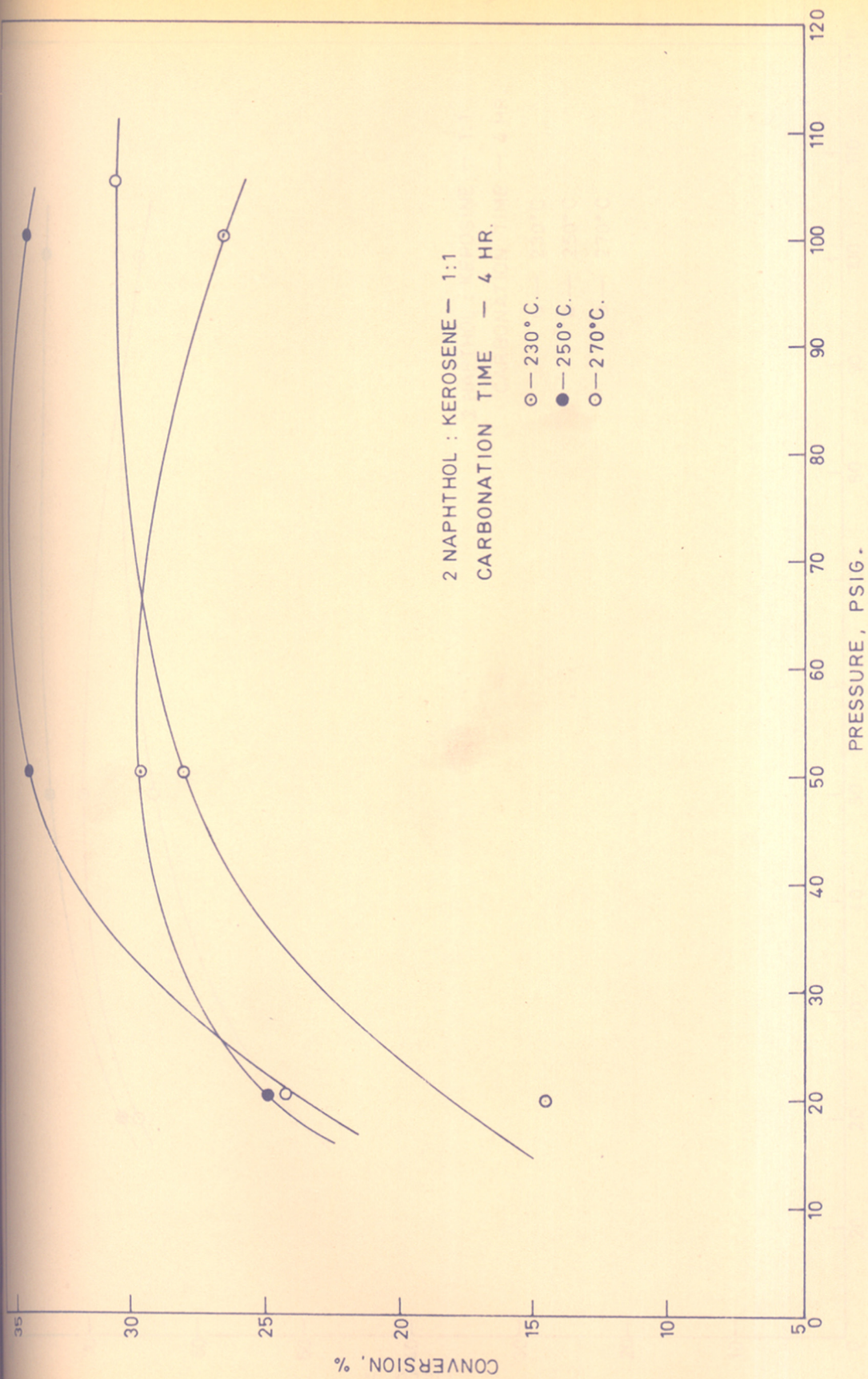


FIG. 3.4. PRELIMINARY EVALUATION OF THE EFFECT OF TEMPERATURE AND PRESSURE ON

CONVERSION



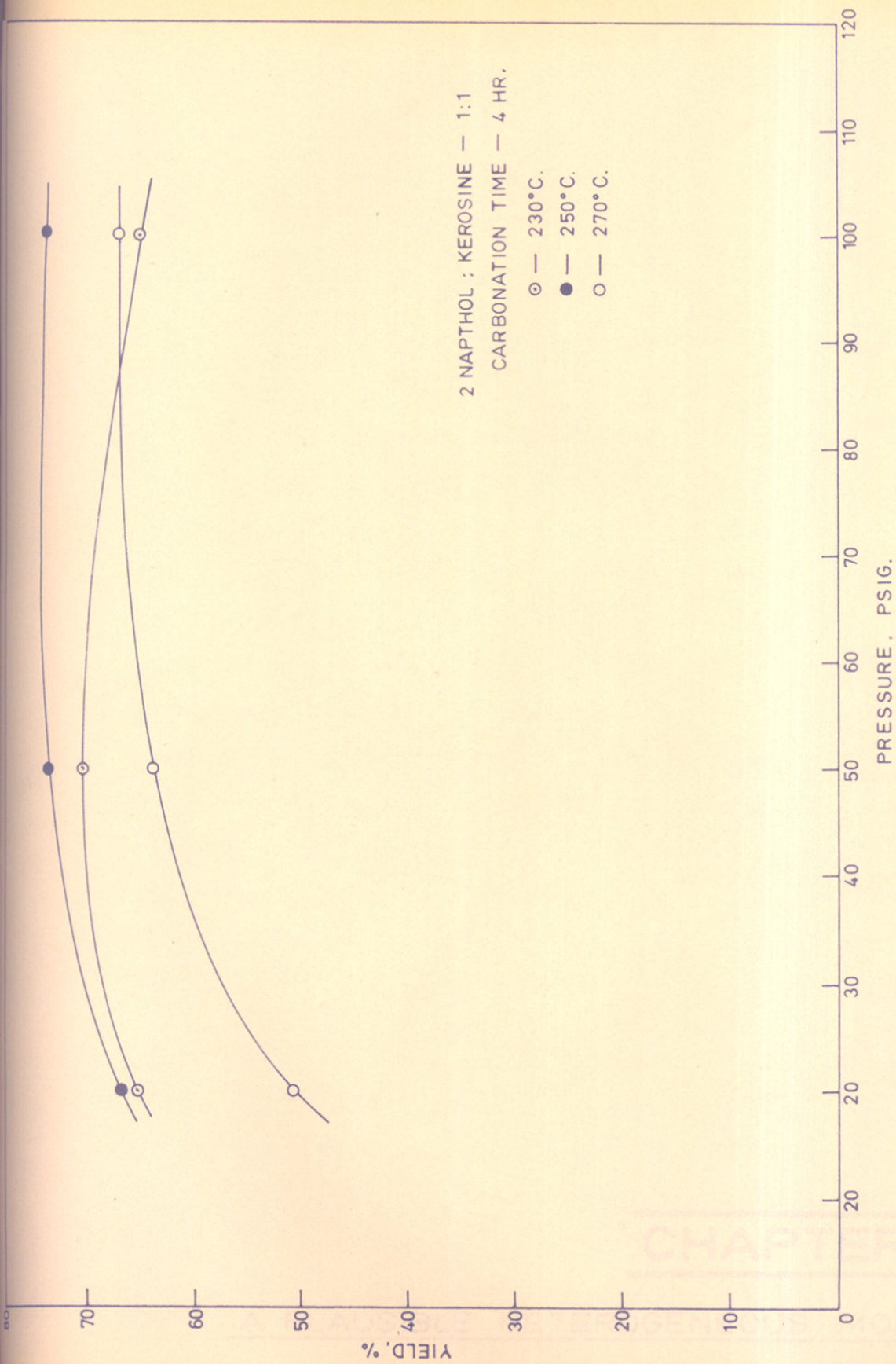


FIG. 3-5. PRELIMINARY EVALUATION OF THE EFFECT OF TEMPERATURE AND PRESSURE ON YIELD.

CHAPTER



CHAPTER - 4

A PLAUSIBLE HETEROGENEOUS MODEL

The dry process for Kalbe-Sonjice substitution involves a gas-solid system in which  $\text{CO}_2$  reacts with dry solid 2-ampholene to give 205 and 206 products. The fact that in this process the 2-ampholene, which is one of the products formed, has to be intermediately removed by distillation suggests that the removal of this product facilitates the reaction of  $\text{CO}_2$  with unreacted solid 2-ampholene. From this it may be concluded that the rate-determining step is that due to the diffusion of  $\text{CO}_2$  through the outer layer of the product formed. Although 205 and 206 will remain in the crust, the removal of 2-ampholene product increases the rate which increases the diffusion rate.

In the liquid method, on the other hand, one is concerned with a three phase system, gas-liquid-solid. This system can be regarded as a two phase system.

**CHAPTER-4**

A PLAUSIBLE HETEROGENEOUS MODEL

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### A PLAUSIBLE HETEROGENEOUS MODEL

The dry process for Kolbe-Schmitt carbonation involves a gas-solid system in which the  $\text{CO}_2$  reacts with dry sodium 2-naphtholate to give BON acid and side products. The fact that in this process the 2-naphthol, which is one of the products formed, has to be intermittently removed by distillation suggests that the removal of this product facilitates the reaction of  $\text{CO}_2$  with unreacted sodium naphtholate. From this it may be concluded that the resistance eliminated is that due to the diffusion of  $\text{CO}_2$  through the outer layer of the product formed. Although BON acid and tar still remain in the crust, the removal of 2-naphthol perhaps creates voids in the crust which enhance the diffusion rate.

In the liquid method, on the other hand, one is concerned with a three phase system, gas-liquid-solid. This system can be reduced to a two phase liquid-solid

system if the gas side resistance is made insignificant. In the present case, since the partial pressure of  $\text{CO}_2$  in the gas phase is almost unity (it is not exactly equal to unity in view of the vapour pressure of kerosene), the gas side resistance can be neglected without serious error.

In this chapter two models are considered for Kolbe-Schmitt carbonation in the presence of kerosene oil as dispersent, one based on mass transfer and the other on chemical reaction. These models are then analysed in the light of the kinetic data collected. The mass transfer model, which was finally selected as the plausible one, has then been verified by estimating the model constants by an independent series of mass transfer experiments.

#### 4.1 THEORETICAL MODELS

##### 4.1.1 The main reactions

Before undertaking the development of models, the reactions to be considered should be clearly defined. If the dehydration step is carried out efficiently, ensuring the removal of the entire theoretical water formed, it can safely be assumed that at the commencement of carbonation no free

2-naphthol is present and that the only reactant (other than  $\text{CO}_2$ ) is the sodium salt of 2-naphthol. Several reactions are possible in the Kolbe-Schmitt carbonation of sodium 2-naphtholate, giving BON acid with an equivalent amount of free naphthol, and involving the subsequent conversion of BON acid, naphthol and naphtholate to a variety of compounds which together may be termed as tar.

The proportion of products formed will depend on the rates of the different reactions involved. The principal overall reaction can, however, be easily recognized : the disappearance of sodium 2-naphtholate by reaction with  $\text{CO}_2$ . Whatever the nature of the side products formed, it is possible to visualize the diffusion of  $\text{CO}_2$  through a mixture of products as one of the steps in the reaction.

The following reaction mechanisms are considered based on models generally used for gas-solid reactions (51, 52, 68). A comprehensive theoretical development of models for fluid-solid reactions has been presented by Levenspiel (68), and by Narsimhan (51) for the decomposition of calcium carbonate.

#### 4.1.2 Mass transfer model

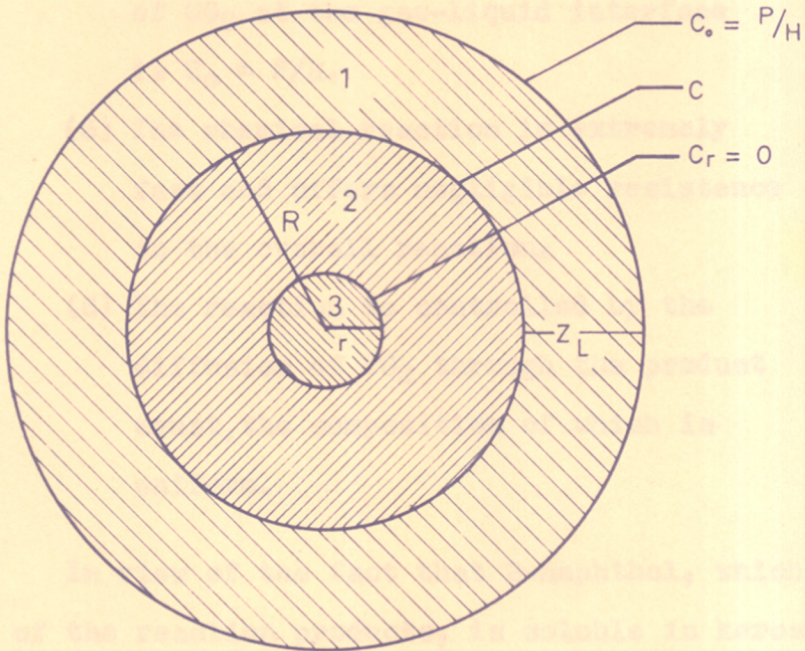
A diagrammatic sketch of the proposed reaction

model is presented in Fig. (4.1). It shows a sphere of naphtholate of radius  $R$ , on whose surface the reaction is initiated by the diffusion of  $\text{CO}_2$  across an equivalent kerosene film of thickness  $Z_L$ . As the reaction progresses, the reaction plane retreats inside the sphere, leaving an outer crust of products surrounding an unreacted sphere of the naphtholate. Thus, if at any time  $\theta$ , the reaction plane is situated at a distance  $r$  from the centre, the thickness of the product shell is given by  $(R - r)$ . The shell can be visualized as a mixture of products and kerosene oil. The rate of diffusion of  $\text{CO}_2$  through this shell will depend on its effective diffusivity.

The following assumptions will be made :

- (1) The naphtholate particles are in a state of suspension in the reaction mass.
- (2) The particle is spherical in shape and remains unchanged in size during reaction.
- (3) The reaction takes place by the diffusion of  $\text{CO}_2$  across an equivalent kerosene film on the particle surface.
- (4) The concentration difference of  $\text{CO}_2$  while diffusing through the gas phase





- 1 EQUIVALENT KEROSENE FILM
- 2 OUTER PRODUCT SHELL
- 3 UNREACTED SODIUM NAPHTHOLATE

FIG. 4-1. IDEALISED SKETCH OF PROPOSED MODEL

is negligible and the concentration of  $\text{CO}_2$  at the gas-liquid interface is  $C_0 = P/H$ .

- (5) The chemical reaction is extremely fast and offers negligible resistance to the overall reaction.
- (6) The reaction is controlled by the diffusion of  $\text{CO}_2$  through the product crust, the composition of which is uniform.

In view of the fact that 2-naphthol, which is one of the reaction products, is soluble in kerosene oil at the reaction temperature, and part of the tar is also soluble at this temperature, the product crust consists of the sodium salt of BON acid and undissolved tar. Since the total volume of the product is reduced due to the dissolution of 2-naphthol and part of the tar, it is likely that the void fraction (i.e. fraction occupied by the liquid) of the solid crust would be more than that of the unreacted core. Thus the product layer covering the reactant core can be regarded as a dispersion of BON acid and tar in a medium of kerosene oil. The diffusion coefficient of  $\text{CO}_2$  through this crust would then be the diffusion coefficient through kerosene oil multiplied by a factor which would depend on the voidage and a

tortuosity factor. This will be further discussed during the development of the equation.

Based on these concepts, an appropriate equation can be derived for the rate of disappearance of sodium naphtholate. At any time  $\theta$ , the rate of diffusion of  $\text{CO}_2$  across an equivalent film of kerosene outside the product shell may be written as

$$n_A = k_L (C_0 - C) \quad \dots (4.1)$$

where

$$k_L = \frac{D}{Z_L} \quad \dots (4.2)$$

and  $n_A$  = diffusional flux

The number of moles diffusing per unit time is then given by

$$N_A = k_L 4 \pi R^2 (C_0 - C) \quad \dots (4.3)$$

where

$R$  = radius of the original naphtholate particle

The rate of diffusion of  $\text{CO}_2$  across the product layer is given by

$$n_A = k_L' (C - C_r) \quad \dots (4.4)$$

where  $k_L'$  represents the mass transfer coefficient through the product shell which is assumed to be a dense dispersion of the product in kerosene, dense enough to be held together as an outer shell. Assuming the reaction to be very fast, i.e.  $C_T = 0$

$$n_A = \frac{D_e}{R - r} \cdot C \quad \dots (4.5)$$

where

$$k_L' = \frac{D_e}{R - r} \quad \dots (4.6)$$

$D_e$  in Equation (4.6) represents the effective diffusion coefficient of  $CO_2$  in the product shell. The number of moles diffusing per unit time is given by

$$N_A = \frac{4 \pi r R D_e}{(R - r)} \cdot C \quad \dots (4.7)$$

where  $4 \pi R r$  represents the geometric mean of the two surfaces,  $4 \pi R^2$  and  $4 \pi r^2$ .

The effective diffusivity  $D_e$  appearing in the equations may be written as

$$D_e = \alpha D \quad \dots (4.8)$$

$\alpha$  in Equation (4.8) is an overall constant with which

the diffusion coefficient ( $D$ ) should be multiplied to give the effective diffusion coefficient. In view of the presence of solids in the shell, the available area for mass transfer is reduced. Assuming the area void fraction to be the same as the volume void fraction, this can be expressed in terms of the volume void fraction,  $\epsilon$ . Further the passage of the diffusing gas will not be linear due to the presence of the solids. Considering these factors,  $\alpha$  is defined as

$$\alpha = \frac{\epsilon}{\tau} \quad \dots (4.9)$$

where  $\tau$  is a tortuosity factor ( $>1$ ). The tortuosity factor in the case of solid catalysts is usually between 1 and 5, but in this case would probably be higher. The void fraction would be lower than in a catalyst, thus leading to a considerably low value of  $\alpha$

Combining Equations (4.7) and (4.8)

$$N_A = \frac{k_L 4 \pi r R Z_L \alpha}{(R - r)} C \quad \dots (4.10)$$

From a consideration of mass balance it is clear that

the moles of  $\text{CO}_2$  diffusing across the kerosene film should be equal to the moles diffusing across the product layer. Thus from Equations (4.3) and (4.10), Equation (4.11) may be derived by appropriate rearrangement

$$C = \frac{R C_0 (R - r)}{\alpha Z_L r + R(R - r)} \quad \dots (4.11)$$

Substituting Equation (4.11) in (4.3) and simplifying,

$$N_A = \frac{k_L 4 \pi R^2 C_0 \alpha Z_L r}{\alpha Z_L r + R(R - r)} \quad \dots (4.12)$$

or

$$N_A = \frac{k_L 4 \pi R^2 C_0 r'}{r' + k_M (1 - r')} \quad \dots (4.13)$$

where

$$r' = \frac{r}{R} \text{ (fraction unreacted), } \dots (4.14)$$

and

$$k_M = \frac{R}{Z_L \alpha} \quad \dots (4.15)$$

For every mole of  $\text{CO}_2$ , 2 moles of naphtholate react. Keeping this in mind, the rate of diffusion

of  $\text{CO}_2$  can be equated to the instantaneous rate of disappearance of the naphtholate.

$$N_A = -2 \rho 4 \pi r^2 \frac{dr}{d\theta} \quad \dots (4.16)$$

where the right hand side represents the rate of the chemical reaction. Using the parameter  $r'$  as defined earlier, Equation (4.16) may be written as

$$N_A = -8 \rho \pi R^2 r'^2 R \frac{dr'}{d\theta} \quad \dots (4.17)$$

From Equations (4.13) and (4.17), we may write,

$$-d\theta = \frac{2 R \rho}{k_L C_0} \cdot r' [r' + k_M(1 - r')] dr' \dots (4.18)$$

The reduced co-ordinate  $r'$  represents the fraction of sodium naphtholate unreacted. If  $x$  is the overall conversion of the naphtholate then  $(1-x)$  represents the fraction unreacted. For spherical geometry it has been shown by Levenspiel (63) that  $r'$  is related to  $(1-x)$  by the equation

$$r' = (1 - x)^{\frac{1}{3}} \quad \dots (4.19)$$

Equation (4.18) can now be integrated if the boundary conditions are fixed. Since at any time  $\theta$  Equation



(4.19) holds, and at initial conditions  $r'$  is unity, the following boundary conditions can be written :

$$\begin{aligned}\theta &= 0, \quad r' = 1 \\ \theta &= \theta, \quad r' = (1-x)^{\frac{1}{2}}\end{aligned}$$

Integration within these limits gives

$$\frac{3\theta}{A_M} = x + k_M \left[ 1.5 - x - 1.5 (1-x)^{\frac{3}{2}} \right] \dots (4.20)$$

where

$$A_M = \frac{2rR}{k_L C_0} \dots (4.21)$$

Equation (4.20) contains two constants  $k_M$  and  $A_M$  defined respectively by Equations (4.15) and (4.21). These constants are independent of chemical reaction, and can be estimated exclusively from the particle diameter and certain physical properties of the system. For simple reactions involving solid particles of predictable geometry and crust composition, these can be accurately evaluated and Equation (4.20) then used to estimate the overall conversion at any time. In the present system, however, these constants cannot be estimated from their defining equations very accurately. Hence they have to be determined from kinetic data by statistical methods. However, if



this model is to be acceptable, there should at least be an order-of-magnitude agreement between the kinetically determined values of the constants and those determined from the defining equations.

#### 4.1.3 Chemical reaction model

If it is assumed that the controlling step is the rate of the chemical reaction at the reactant surface rather than the rate of mass transfer to it, then the reaction would be chemically controlled, and a suitable rate equation can be written. It should be pointed out, however, that such models appear to be more reasonable for reactions where the products are in the gaseous state at the reaction temperature. A typical example of this is the chlorination of  $\text{Fe}_2\text{O}_3$  in Ilmenite which has been studied by Bijawat, Kunte and Doraiswamy (48). In this system the reaction product is  $\text{FeCl}_3$  which is a vapour at the temperature involved ( $700^\circ\text{-}900^\circ\text{C.}$ ). Thus the chemical reaction between  $\text{Cl}_2$  and  $\text{Fe}_2\text{O}_3$  (and CO which was also used as a reactant in the study) would appear to be the controlling step, as was indeed found to be the case.

Although the chemical reaction model does not, on a preliminary consideration of the reaction

system, seem plausible, nevertheless it cannot be rejected without suitable verification. Levenspiel (68) has given the rate equation for a spherical particle for the case where chemical reaction is controlling. This equation can be written as

$$K\theta = 1 - (1 - x)^{\frac{1}{3}} \quad \dots (4.22)$$

Evidently a plot of reaction time  $\theta$  vs.  $(1 - (1 - x)^{\frac{1}{3}})$  should give a straight line passing through the origin.

Both the models presented above are examined in the light of the kinetic data obtained in the following section.

#### 4.2 TEST OF MODELS FROM KINETIC DATA

##### 4.2.1 Effect of agitation

Before making kinetic measurements for examining the models it is necessary to eliminate the effect of external agitation on the reaction. According to the film theory, the eddy transport in a fluid bulk can be expressed as the product of molecular diffusion and concentration gradient in an equivalent film. With increased agitation, the eddy diffusivity increases, reaching a near-constant

value at a certain agitation. This will correspond to a certain equivalent film thickness. In order to apply Equation (4.20), which has been derived on the basis of the film theory, the film thickness contained in the constant  $k_M$  should obviously be independent of agitation. The first step in the study was therefore to examine the effect of stirrer r.p.m. on the reaction.

The response chosen in this case was the conversion  $x''$  of 2-naphthol to BON acid (see Chart - 1 which is explained in the next section) and the results at three stirrer speeds are shown in Fig.(4.2). Beyond 150 r.p.m. the effect of agitation does not appear to be significant. In all the kinetic runs an r.p.m. of 160 was maintained to eliminate the effect of external agitation.

#### 4.2.2 Kinetic data

In the preliminary studies reported in Chapter - 3, it was observed that the most satisfactory results could be obtained by maintaining the ratio of 2-naphthol to kerosene oil at 1 : 1 throughout the carbonation. During the kinetic runs this ratio was held constant at 1 : 1, and an experimental programme was organised to obtain data

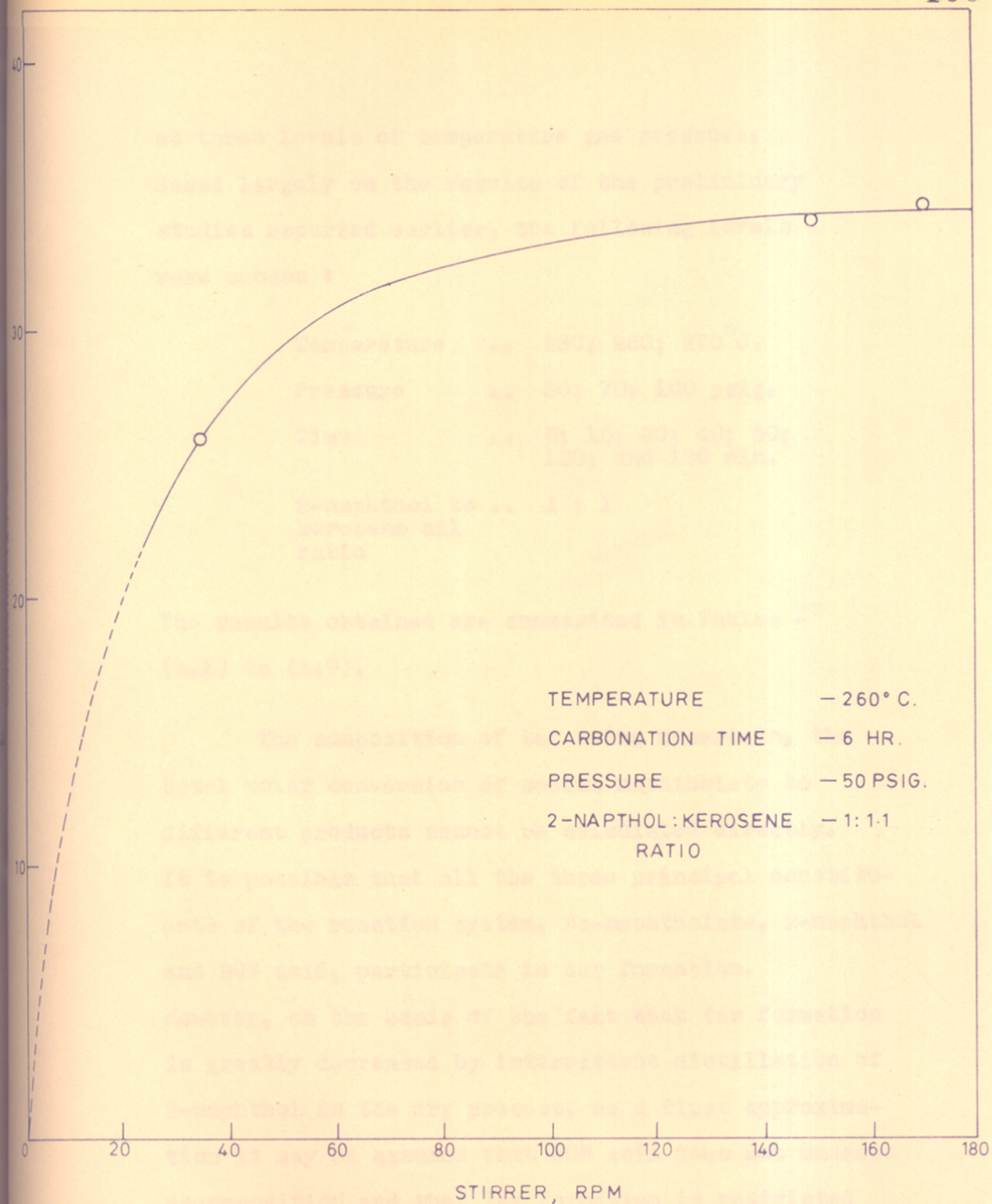


FIG. 4.2. EFFECT OF AGITATION ON CARBONATION

at three levels of temperature and pressure. Based largely on the results of the preliminary studies reported earlier, the following levels were chosen :

Temperature	..	230; 250; 270°C.
Pressure	..	30; 70; 100 psig.
Time	..	5; 15; 30; 40; 60; 120; and 180 min.
2-naphthol to kerosene oil ratio	..	1 : 1

The results obtained are summarized in Tables - (A.1) to (A.9).

The composition of tar being uncertain, the total molar conversion of sodium naphtholate to different products cannot be calculated directly. It is possible that all the three principal constituents of the reaction system, Na-naphtholate, 2-naphthol and BON acid, participate in tar formation. However, on the basis of the fact that tar formation is greatly decreased by intermittent distillation of 2-naphthol in the dry process, as a first approximation it may be assumed that BON acid does not undergo decomposition and that tar formation is restricted to reactions involving 2-naphthol (and its Na-salt). The overall conversion of 2-naphthol can then be

calculated as shown in Chart - 1 which also includes other definitions of conversion.

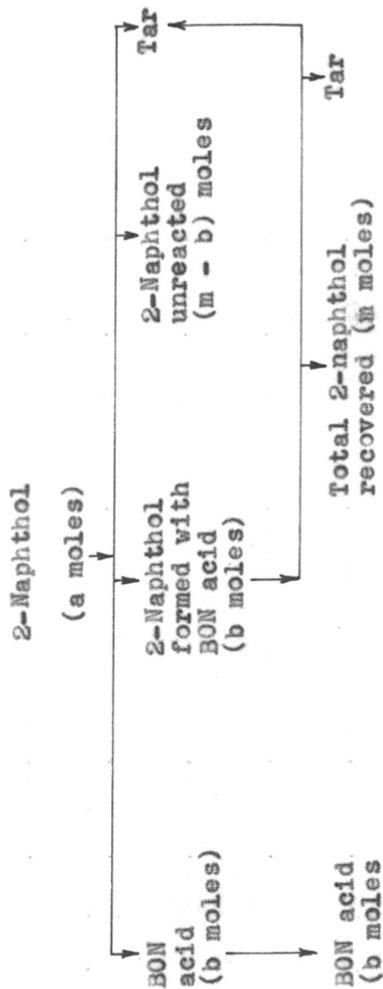
The best dehydration conditions (Chapter - 3) were used during all the kinetic runs. Under these conditions it was possible to remove the theoretical quantity of water formed due to reaction (1.1), thus ensuring (a) total conversion of naphthol to its sodium salt and (b) total dehydration of Na-naphtholate, which is a necessary pre-condition for a high yield of BON acid and which therefore justifies to a large extent another assumption in the proposed model calling for uniform product composition. The proportion of the total quantity of tar in the product may be taken as an approximate index of crust uniformity. In all the runs carried out in the present kinetic programme, tar formation was found to be quite low during the carbonation, and for any given set of operating condition the amount of tar formed was reasonably uniform for reaction times up to 3 hours.

#### 4.2.3 Mass transfer model

The mathematical equation for the rate of disappearance of sodium naphtholate based on the conceptual mass transfer model given by Equation (4.20)

CHART - 1

PRODUCT COMPOSITION AND CONVERSIONS



1. Total conversion,  $x = \frac{a - (m - b)}{a}$
2. Conversion of 2-naphthol to BON acid,  $x' = \frac{2b}{a}$
3. Conversion expressed as moles BON acid formed per mole 2-naphthol,  $x'' = \frac{b}{a}$
4. Yield on 2-naphthol consumed =  $y = \frac{b}{a - m}$

can be put in the following linear form.\*

$$\frac{\theta}{x} = \frac{A_M k_M}{3} \left( \frac{\phi(x)}{x} \right) + \frac{(A_M)}{3} \quad \dots (4.23)$$

$$\text{where } \phi(x) = \left[ 1.5 - x - 1.5 (1 - x)^{\frac{2}{3}} \right] \quad \dots (4.24)$$

From the plot of  $\frac{\theta}{x}$  vs.  $\frac{\phi(x)}{x}$  the values of  $A_M$  and  $k_M$  can be determined, provided the model is valid and a straight line is consequently obtained. The constants can be calculated from the slope and intercept of this line

$$\text{Slope, } S = \frac{A_M k_M}{3} \quad \dots (4.25)$$

$$\text{Intercept, } I = \frac{A_M}{3} \quad \dots (4.26)$$

The values of  $\frac{\theta}{x}$  and  $\frac{\phi(x)}{x}$  were calculated from the kinetic data (Tables - A.1 to A.9) as shown in Tables - A.10 to A.12. Plots of  $\frac{\theta}{x}$  vs.  $\frac{\phi(x)}{x}$  at three temperatures and pressures considered are shown in Figures (4.3) to (4.11). It is evident from all these plots that reasonably good straight lines can be drawn at all the nine conditions considered up to a carbonation time of about 60 minutes. It can also be seen from the kinetic data tables that the

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\* The suggestion of Massoth (54, 55) in this connection is acknowledged.



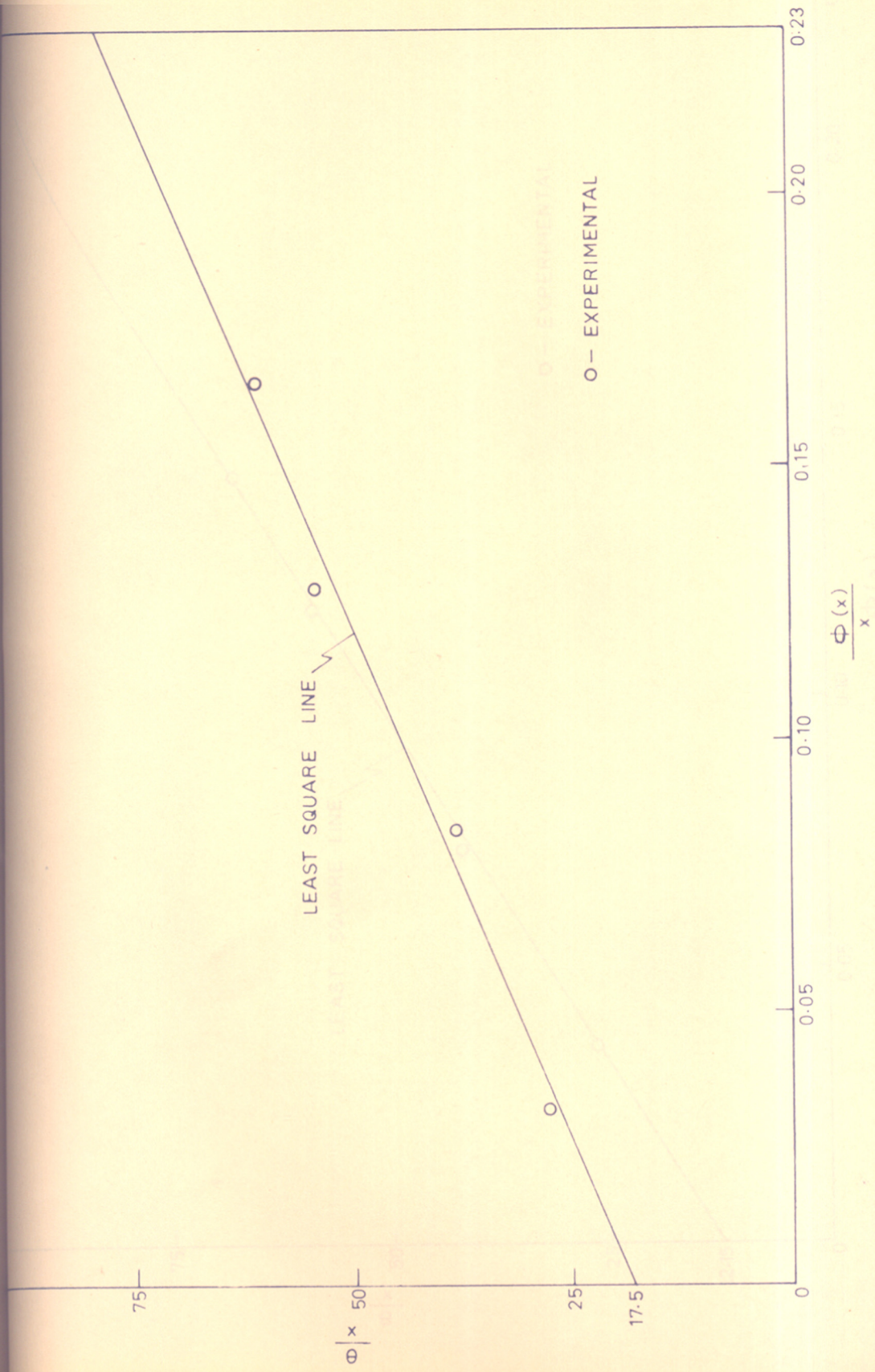


FIG. 4.3. TEST OF MASS TRANSFER MODEL AT 230°C., 30 PSIG.



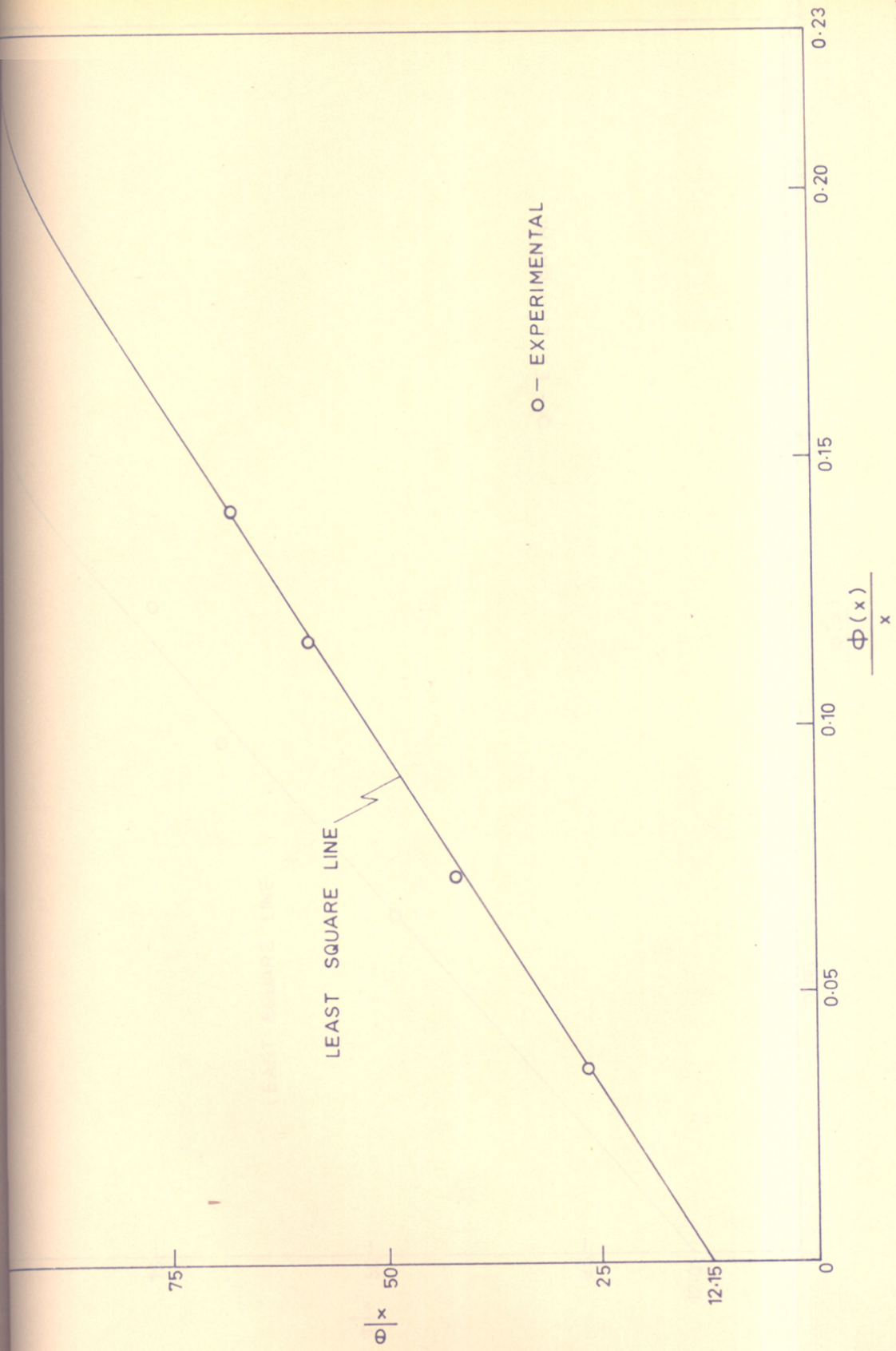


FIG. 4.4. TEST OF MASS TRANSFER MODEL AT 230°C., 70 PSIG.



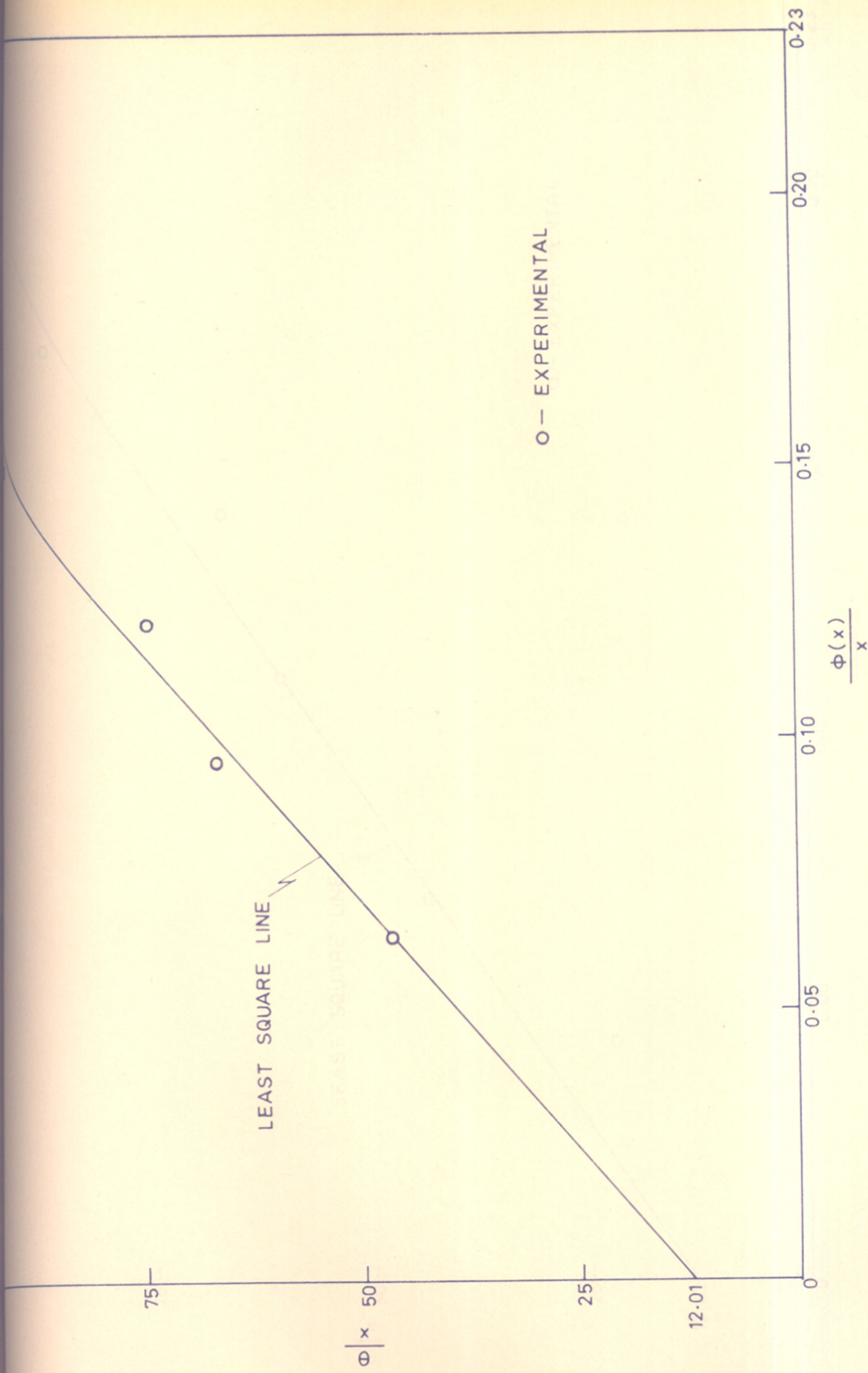


FIG. 4.5 . TEST OF MASS TRANSFER MODEL AT 230°C., 100 PSIG.



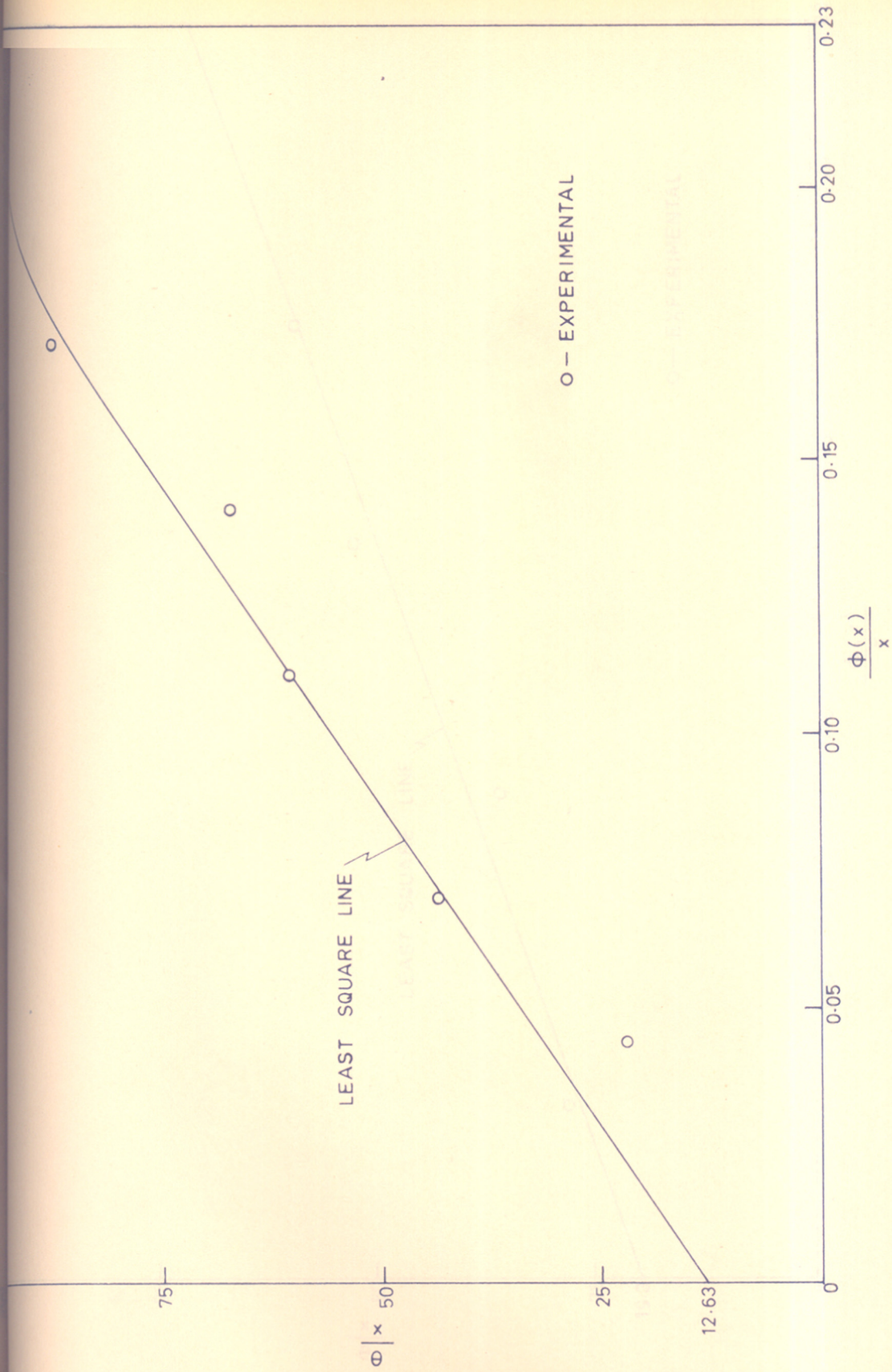


FIG. 4.6. TEST OF MASS TRANSFER MODEL AT 250°C., 30 PSIG.

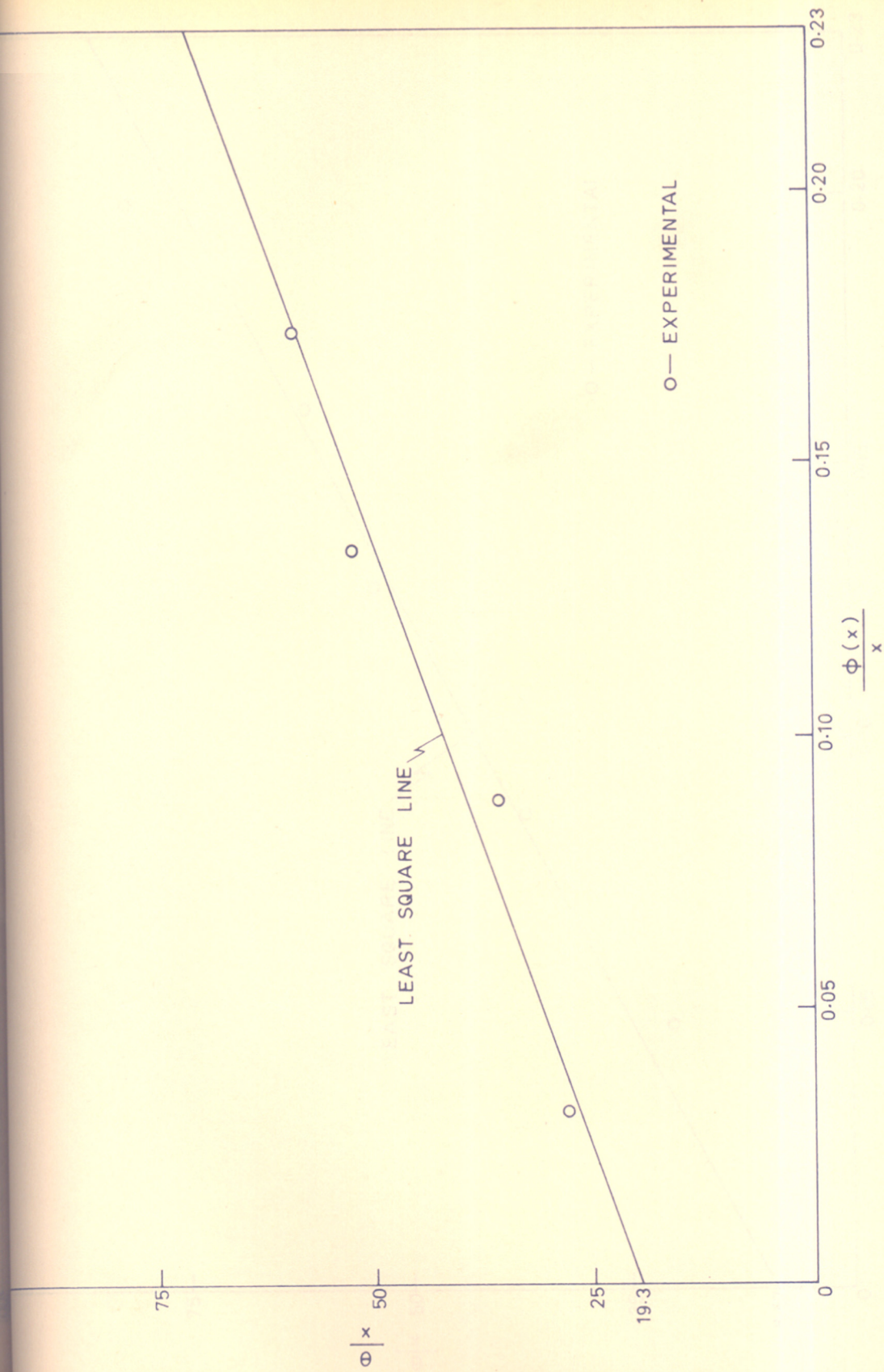


FIG. 4.7. TEST OF MASS TRANSFER MODEL AT 250° C., 70 PSIG.



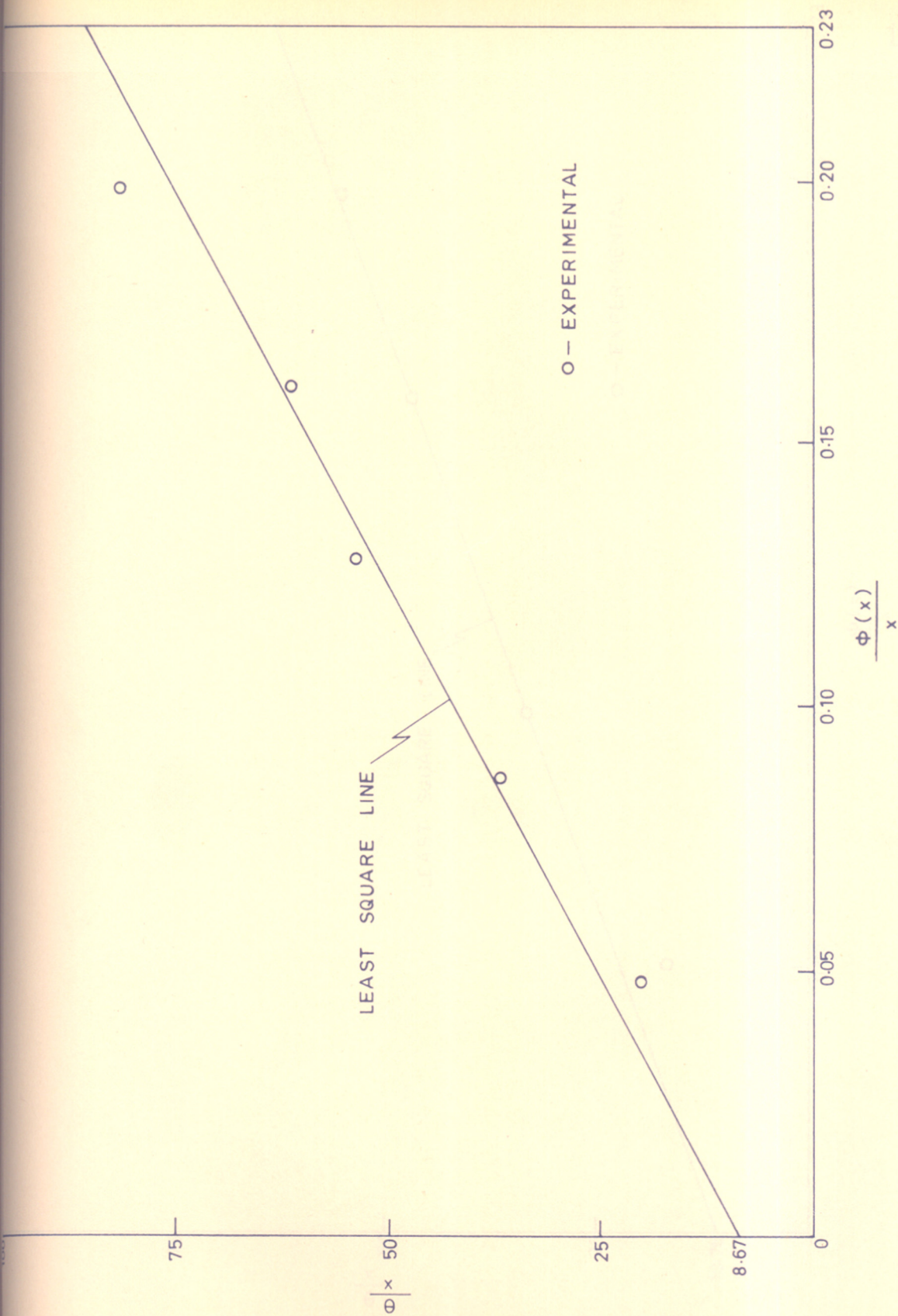


FIG. 4.8. TEST OF MASS TRANSFER MODEL AT 250°C., 100 PSIG.

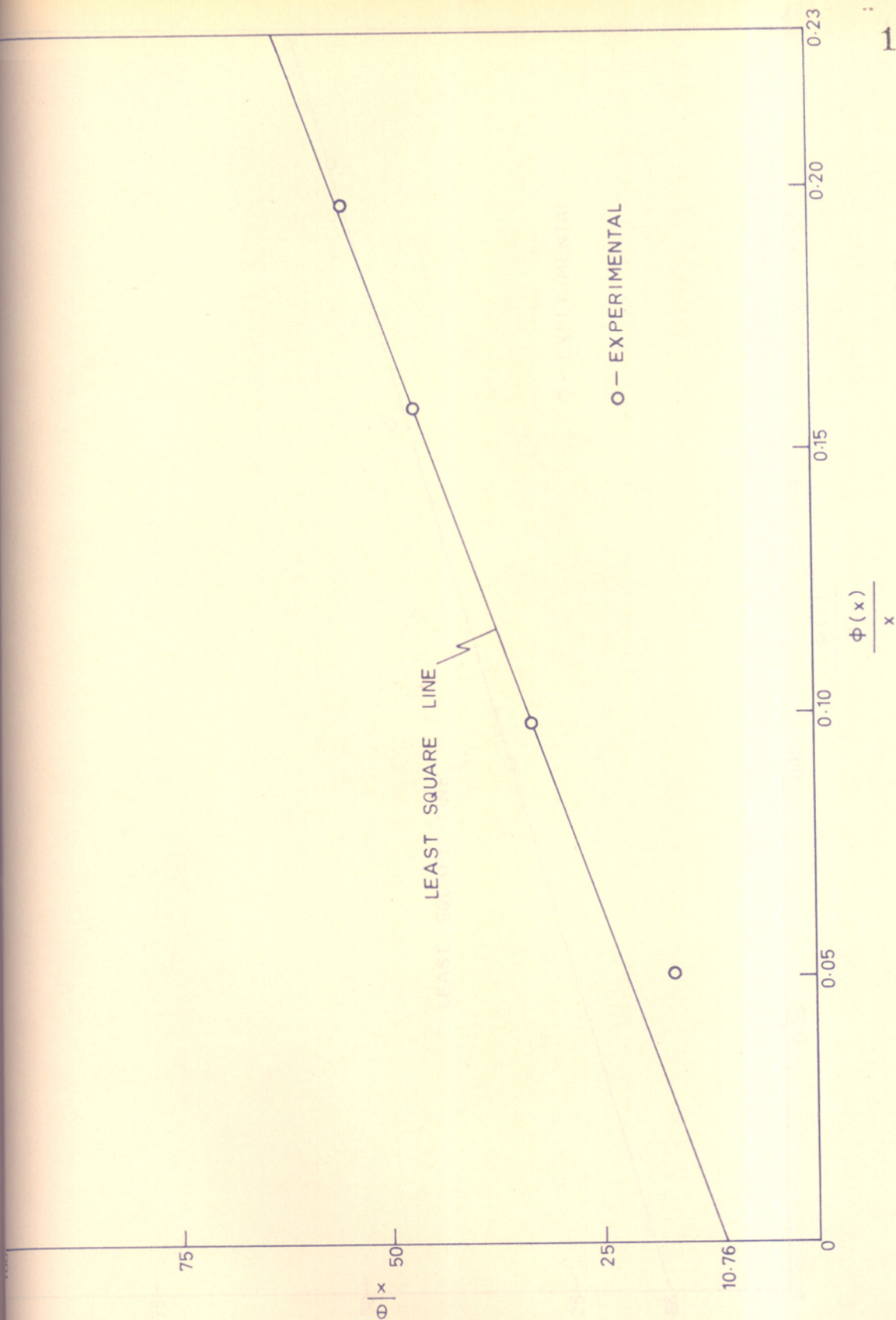


FIG. 4.9. TEST OF MASS TRANSFER MODEL AT 270°C., 30 PSIG.



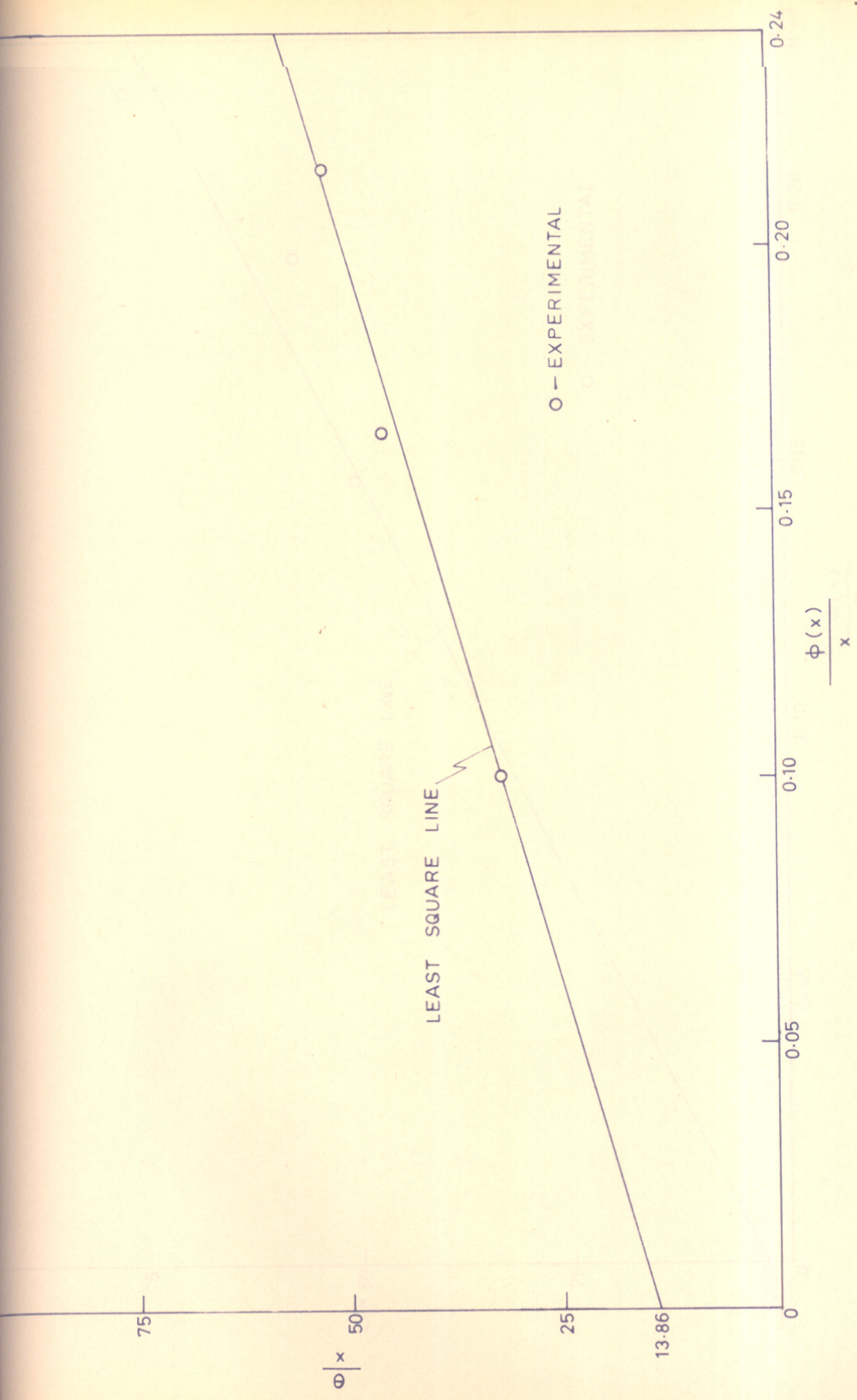


FIG. 4.10. TEST OF MASS TRANSFER MODEL AT 270°C., 70 PSIG.



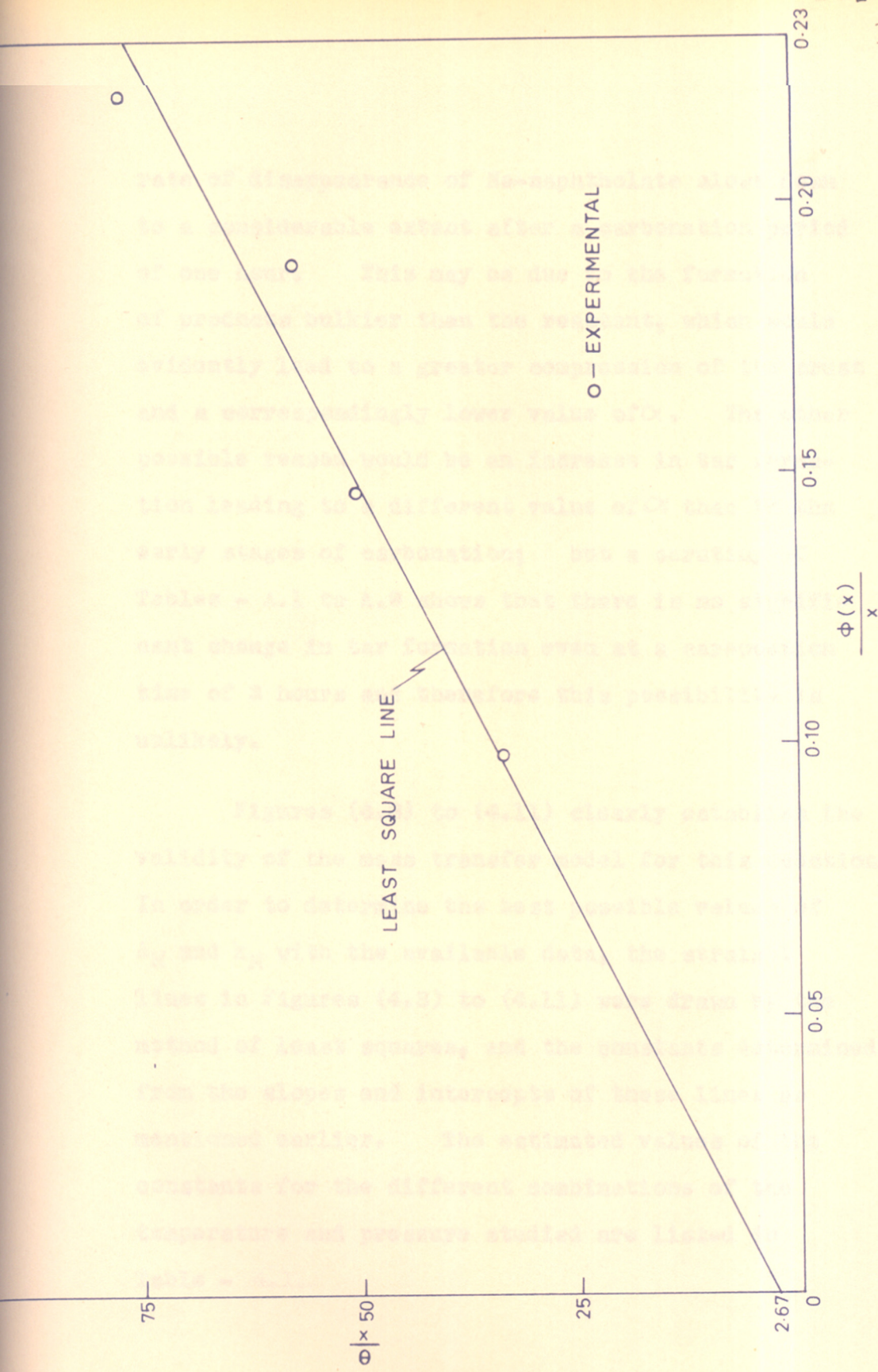


FIG. 4-11. TEST OF MASS TRANSFER MODEL AT 270°C., 100 PSIG.

rate of disappearance of Na-naphtholate slows down to a considerable extent after a carbonation period of one hour. This may be due to the formation of products bulkier than the reactant, which would evidently lead to a greater compression of the crust and a correspondingly lower value of  $\alpha$ . The other possible reason would be an increase in tar formation leading to a different value of  $\alpha$  than in the early stages of carbonation; but a scrutiny of Tables - A.1 to A.9 shows that there is no significant change in tar formation even at a carbonation time of 3 hours and therefore this possibility is unlikely.

Figures (4.3) to (4.11) clearly establish the validity of the mass transfer model for this reaction. In order to determine the best possible values of  $A_M$  and  $k_M$  with the available data, the straight lines in Figures (4.3) to (4.11) were drawn by the method of least squares, and the constants determined from the slopes and intercepts of these lines as mentioned earlier. The estimated values of the constants for the different combinations of the temperature and pressure studied are listed in Table - 4.1.

TABLE - 4.1

ESTIMATED VALUES OF THE CONSTANTS  $A_M$  AND  $k_M$ 

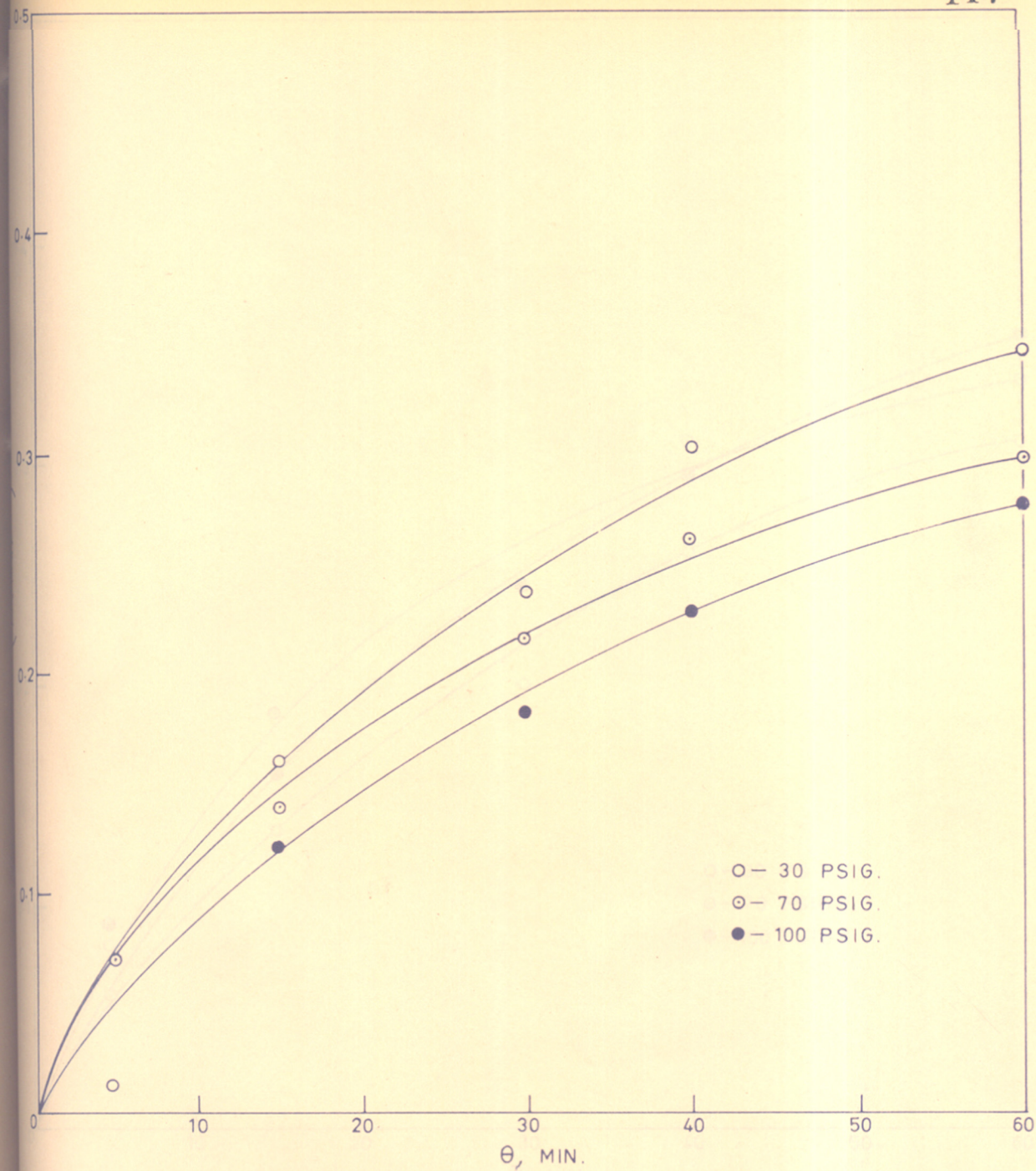
Temperature °C.	Pressure psig.	$A_M$ (from mass trans- fer experiments)	$A_M$ (from kinetic data)	$k_M$ (from kinetic data)
230	70	35	36.3	32.7
230	100	13	36.0	45.6
250	70	39	57.8	11.9
250	100	20	26.0	38.5
270	70	74	41.6	13.2
270	100	26	8.1	116.2

It may be noted that  $A_M$  decreases with increase in pressure at each of the three temperatures studied. An inspection of the defining equation for  $A_M$  shows that this would be the expected trend, since an increase in pressure at a given temperature would lead to a higher value of  $C_0$  and thus a lower value of  $A_M$ .  $k_M$  should also evidently increase with pressure since  $\alpha$  would tend to have a lower value at higher pressures. This is also borne out by the estimated values of  $k_M$  at each of the three temperatures recorded in Table - 4.1.

#### 4.2.4 Chemical reaction model

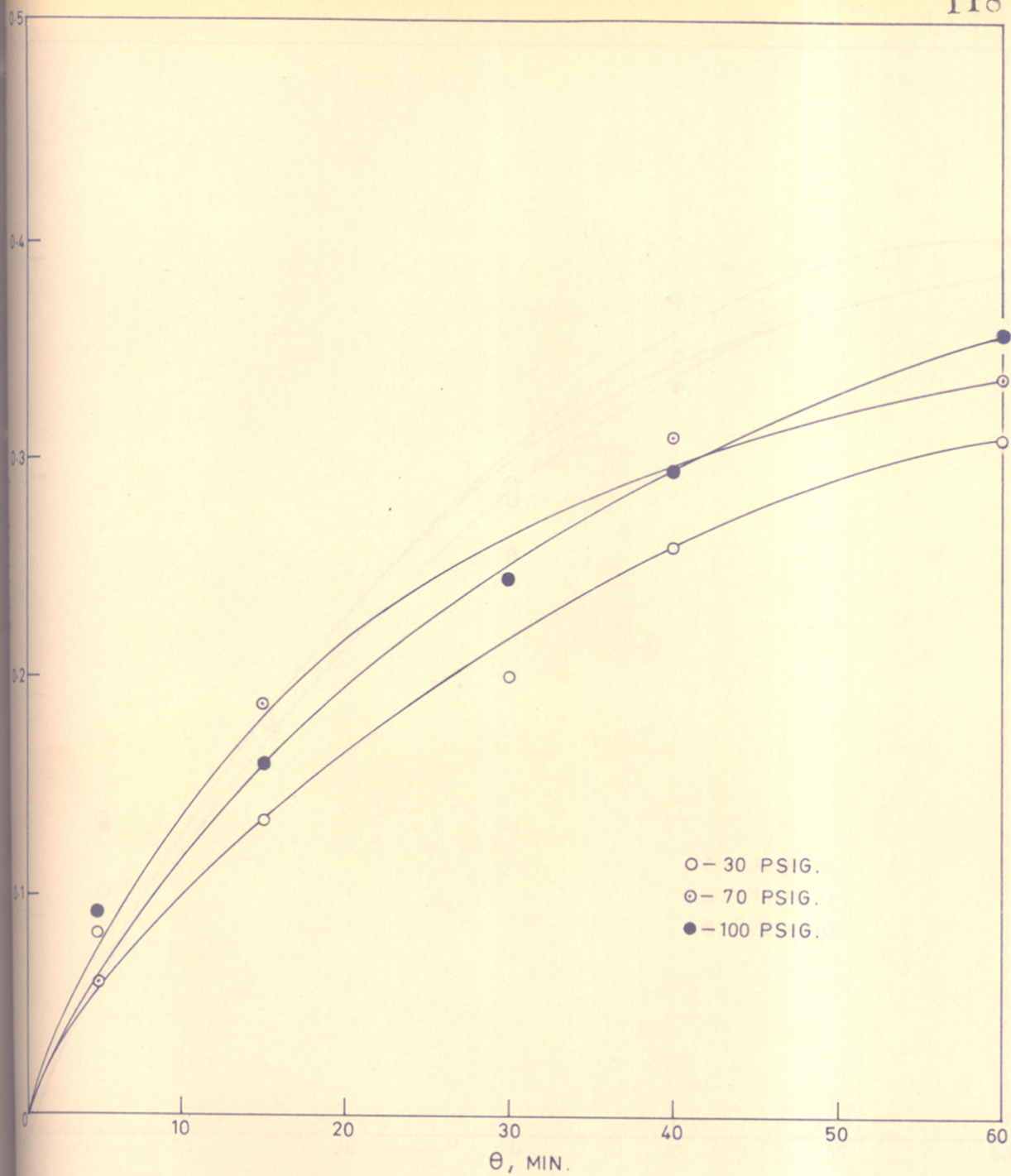
A reference to Equation (4.22) shows that a plot of carbonation time  $\theta$  as a function of  $\left[1 - (1 - x)^{\frac{1}{3}}\right]$  should give a straight line passing through the origin. The estimated values of  $\left[1 - (1 - x)^{\frac{1}{3}}\right]$  are shown in Tables - A.10 to A.12, and the corresponding plots at different temperatures and pressures appear in Figures (4.12) to (4.14). Clearly the chemical reaction model is not acceptable as was anticipated in Section 4.1.3.





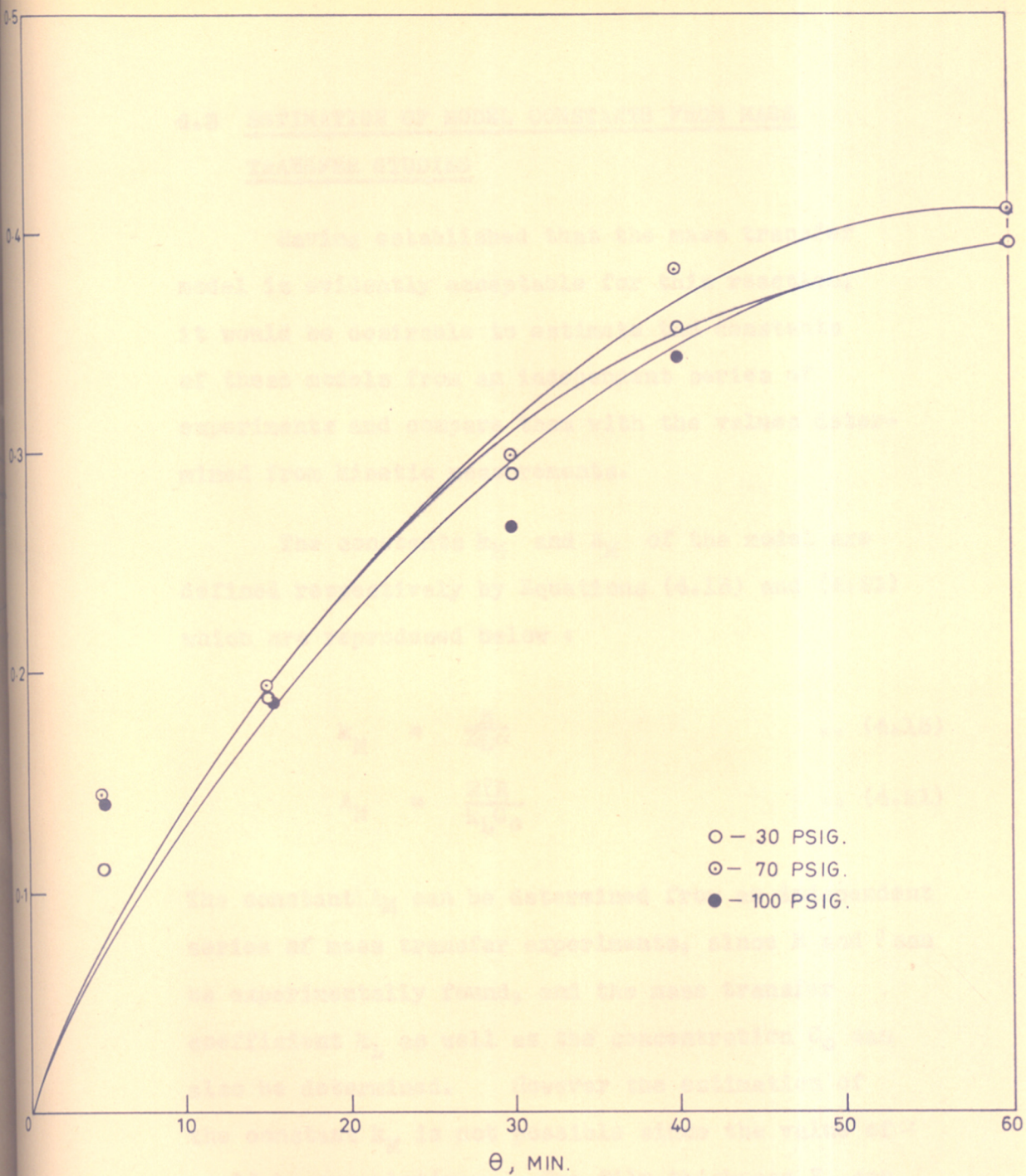
4.12. TEST OF CHEMICAL REACTION MODEL AT 230°C.





4.13. TEST OF CHEMICAL REACTION MODEL AT 250°C.





4.14. TEST OF CHEMICAL REACTION MODEL AT 270° C.

### 4.3 ESTIMATION OF MODEL CONSTANTS FROM MASS TRANSFER STUDIES

Having established that the mass transfer model is evidently acceptable for this reaction, it would be desirable to estimate the constants of these models from an independent series of experiments and compare them with the values determined from kinetic measurements.

The constants  $k_M$  and  $A_M$  of the model are defined respectively by Equations (4.15) and (4.21) which are reproduced below :

$$k_M = \frac{R}{Z_L \alpha} \quad \dots (4.15)$$

$$A_M = \frac{2 \rho R}{k_L C_0} \quad \dots (4.21)$$

The constant  $A_M$  can be determined from an independent series of mass transfer experiments, since  $R$  and  $\rho$  can be experimentally found, and the mass transfer coefficient  $k_L$  as well as the concentration  $C_0$  can also be determined. However the estimation of the constant  $k_M$  is not possible since the value of  $\alpha$  would be speculative. The film thickness  $Z_L$  can be determined from a knowledge of the mass transfer and diffusion coefficients (61, 67). In the following

treatment an attempt is made to estimate  $A_M$ ; also the magnitude of the empirical constant  $\alpha$  is estimated from a knowledge of  $k_M$ .

#### 4.3.1 Determination of the density and average radius of the naphtholate particles

Na-naphtholate is extremely sensitive to atmospheric oxidation and as such the determination of its properties has to be carefully carried out. A series of dehydration runs was made and the naphtholate particles discharged and stored under kerosene oil in the absence of air. The density of Na-naphtholate particles was then determined under kerosene oil as described in Appendix - B.1 which also includes a sample calculation.

The determination of the radius of the particle also posed considerable difficulties since no two dehydration batches gave identical particle sizes; also there was a considerable spread of sizes. In each batch dehydration was carried out under the very carefully controlled conditions established earlier in Chapter - 3. In these runs the reaction was stopped at the end of dehydration, and the product discharged under kerosene as in the case of density determination. For each such batch

the average value of the particle radius was determined by observation through a microscope. This was repeated for several batches carried out under identical condition of dehydration, and the overall average radius was then estimated.

It may be pointed out that the particle shape also varied from batch to batch, being cylindrical to near spherical. The average radius for each batch was therefore determined by measuring the sizes of a particle population of about 50 and determining the equivalent radius of each particle from a knowledge of its shape and dimensions. ~~The~~ Based on several observations the average value of the radius of the naphtholate particle was estimated to be 0.168 cm.

#### 4.3.2 Determination of $C_0$ and the mass transfer coefficient $k_L$

$C_0$  represents the saturation solubility of  $\text{CO}_2$  in kerosene oil. A solubility apparatus for determining this has been described in Chapter - 2. As will be pointed out later, the solubility as a function of time up to the saturation solubility is necessary in estimating the mass transfer coefficient. Hence the experimental programme with the solubility

apparatus was organized in such a way as to enable the determination of the  $\text{CO}_2$  content of kerosene oil as a function of time. The experimental procedure has been described in detail in Chapter - 2.

Solubility as a function of time was obtained for the following conditions :

Temperature, °C.		Pressure, psig.
230	..	70
230	..	100
250	..	70
250	..	100
270	..	70
270	..	100

The results obtained, together with a sample calculation, are given in Appendix B.2.

The determination of the mass transfer coefficient  $k_L$  is not straightforward. It can be seen that this coefficient has units of length/time (cm./min. in this case). The mass transfer coefficient that is usually determined in an experimental programme is the volume coefficient and has the units l/time (in this case l/min.). In order, therefore, to obtain the specific mass transfer coefficient  $k_L$ , the following relationship should be used :

$$k_L = \frac{k_L^v}{a} \quad \dots (4.27)$$



in which  $a$  represents the interfacial area per unit volume.

The data presented in Appendix - B.2 enable the calculation of the volume coefficient  $k_L^n$ , as shown in the sample calculation in Appendix - B.3. This involves a knowledge of the variation of the solubility with time, which is determined from the equation,

$$\frac{dC}{d\theta} = k_L^n (C_0 - C) \quad \dots (4.28)$$

The values of  $k_L^n$  calculated for the different conditions are listed in Table - B.2 of Appendix - B.3, which also contains plots of concentration vs. time for these conditions to enable the determination of  $\frac{dC}{d\theta}$  at different concentrations.

The interfacial area  $a$  can be calculated by the method of Danckwerts and Sharma (53) and Kothari and Sharma (56). These investigators employed a vessel in which the specific mass transfer coefficient was measured under conditions where the surface area of the liquid could be directly estimated by assuming it to be equal to the cross-sectional area of the containing vessel, provided the conditions were so

adjusted that the liquid surface remained undisturbed.  $a$  would then be simply

$$a = \frac{\text{cross sectional area of the vessel}}{\text{volume of the liquid}} \quad \dots (4.29)$$

This method was successfully adopted in the present case, after ensuring that the stirring conditions were such that there was a minimum disturbance of the liquid surface. Since a paddle type stirrer was used, this condition was not probably completely achieved. Nevertheless, as a first approximation, it has been assumed that the surface remained undisturbed. Based on this, the following value of the interfacial area has been used in estimating  $k_L$  from Equation (4.27):

$$a = 0.07848 \text{ cm.}^2/\text{cm.}^3$$

The values of the specific mass transfer coefficient  $k_L$  calculated from this value of  $a$  are also listed in Table - B.2 of Appendix - B.3.

Using the values of the particle density, radius, mass transfer coefficient and the saturation solubility, the values of  $A_M$  were calculated from Equation (4.21). These are included in Table - 4.1

which also contains the constants determined from kinetic measurements. It will be seen that there is a remarkably good agreement between the constants at all conditions, thus vindicating the proposed mass transfer model for Kolbe-Schmitt carbonation.

As stated earlier the estimation of  $k_M$  depends on a knowledge of the film thickness and the empirical constant  $\alpha$ . The film thickness can be obtained from the equation,

$$Z_L = \frac{D}{k_L} \text{ (cm.)} \quad \dots (4.2)$$

Using these values of  $Z_L$ , and a value of 0.1 for  $\alpha$  (which is the normal value used for a solid catalyst), it was found that the values of  $k_M$  were usually about 1/10th the values determined from kinetic analysis. This is probably because of the fact that  $\alpha$  in the present case would be considerably lower in view of the high compaction that would be expected with reaction products being bulkier than the reactant. Because of the highly speculative nature of this constant, it is not possible at this stage to compare the values of  $k_M$  determined from mass transfer experiments with those obtained from

kinetic measurements, but the values of  $\alpha$  calculated from Equations (4.2) and (4.15) using the experimental values of  $k_M$  are found to be of the order of 0.01. This accounts for the discrepancy between the values of  $k_M$  calculated from Equation (4.15) using  $\alpha = 0.1$  and those calculated from kinetic studies. It may be pointed however that  $\alpha$  can be considerably lower than 0.1 for certain industrial catalysts (69).

The excellent agreement between the values of the constant  $A_M$  calculated from kinetic measurements and from mass transfer experiments should be viewed in the light of the fact that in the mass transfer experiments the agitation was not as vigorous as in the kinetic experiments. The r.p.m. in the mass transfer runs was lower, since in these runs it was desired to keep the liquid surface as undisturbed as possible. A reference to Fig.(4.2) shows that r.p.m. has very little effect beyond a value of 40, although this effect apparently disappears altogether only after about 150 r.p.m. Since in all the experiments, including those organized for mass transfer studies, the r.p.m. was above 40, the error introduced in maintaining different r.p.m.'s in the kinetic and mass transfer experiments can be assumed to be negligible.

## CHAPTER - 5

### STATISTICAL OPTIMIZATION

Problems like the present one can be investigated by two main methods of approach - (i) by studying the fundamental relationships affecting the particular process, and (ii) by studying empirically the effect of various changes in operating conditions without necessarily being concerned with the exact mechanism involved.

Thus, for the problem at hand, the mechanism of the principal reaction was first studied so as to formulate a rational engineering basis for the interpretation of the results. Several runs had to be carried out, initially for a preliminary understanding of the process, and subsequently for verifying a suggested reaction model. The data and the resultant conclusions have already been presented in Chapters - 3 and 4. The final objective of the full scale process is its optimum conditions, however,

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## CHAPTER - 5

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statistical (empirical) approach, and in this connection the following facts may be noted. The ranges of temperature and pressure for the reaction were first established in Chapter - 3 both from a knowledge of the reported literature and the preliminary runs carried out. A reaction model was then proposed in Chapter - 4 (within the ranges of these temperatures and pressures) by carrying out the carbonation under conditions far removed from the probable optimum by operating at low reaction times. However enough data was collected (under conditions where high yields were obtained) to enable a statistical optimization of the process, which is described in the present chapter.

The maximum conversion and yield of BON acid obtained during the kinetic study were 35% and 80% respectively. The highest yields reported in the literature are : 79% using a ball mill type reactor (25), and 83% in a continuous process using an excessive amount of 2-naphthol as solvent (29). This shows that some of the conditions employed during the studies reported in Chapters- 2 and 3 are probably quite close to the optimum. Thus, before planning an independent series of experiments with the object of locating the optimum conditions,

it was decided first to analyse the data already collected for finding out the significance of each independent variable, i.e. temperature, pressure and time. The response function in the present case can conveniently be taken as the yield of BON acid, since it is based on the recovery of 2-naphthol (on which the economy of the process depends).

### 5.1 THREE LEVEL FACTORIAL DESIGN

#### 5.1.1 Main effects and interactions

The kinetic data at three levels of temperature ( $230^{\circ}$ ,  $250^{\circ}$  and  $270^{\circ}$  C.), pressure (30, 70 and 100 psig.) and time (1, 2 and 3 hr.) are reproduced in the three level factorial design format in Table - 5.1. They are further resolved into two-way Tables - 5.2A, 5.2B and 5.2C for the 3 pairs of factors by summing over the levels of the third factor. The coded notations used in the tables are as follows : factors are represented by capital letters, C for temperature, P for pressure and T for time; and the three levels by the corresponding small letters with suffixed numerals, i.e.  $c_0$ ,  $c_1$ ,  $c_2$  for the three levels of temperature ( $230^{\circ}$ ,  $250^{\circ}$  and  $270^{\circ}$  C.),  $p_0$ ,  $p_1$ ,  $p_2$  for the three levels of pressure (30, 70, and 100 psig.), and  $t_0$ ,  $t_1$ ,  $t_2$

TABLE - 5.1

## DATA FOR 3 x 3 x 3 FACTORIAL EXPERIMENTS

Levels of factor T	Levels of factor C			Levels of factor P			Levels of factor P		
	$c_1$			$c_2$					
	$c_0$	$p_0$	$p_1$	$p_0$	$p_1$	$p_2$	$p_0$	$p_1$	$p_2$
$t_0$	68.5	73.0	72.8	68.66	72.8	80.1	72.0	72.5	73.1
$t_1$	74.5	75.0	72.0	74.55	72.0	81.5	76.0	75.5	76.0
$t_2$	70.5	72.5	69.5	74.69	69.5	84.5	76.0	65.0	70.5

TABLE - 5.2A

T x P

	P <sub>0</sub>	P <sub>1</sub>	P <sub>2</sub>	Sum
t <sub>0</sub>	213.80	225.60	213.76	653.16
t <sub>1</sub>	222.00	226.50	226.55	675.05
t <sub>2</sub>	205.00	223.50	221.19	649.69
Sum	640.80	675.60	661.50	1977.90

TABLE - 5.2B

T x C

	$c_0$	$c_1$	$c_2$	Sum
$t_0$	210.16	224.90	218.10	653.16
$t_1$	224.05	229.50	221.50	675.05
$t_2$	217.69	230.00	202.00	649.69
Sum	651.90	684.40	641.60	1977.90

TABLE - 5.2C

P x C

	$c_0$	$c_1$	$c_2$	Sum
$p_0$	213.5	214.3	213.0	640.8
$p_1$	220.5	246.1	209.0	675.6
$p_2$	217.9	224.0	219.6	661.5
Sum	651.9	684.4	641.6	1977.9



for the three levels of time (1, 2, 3 hr.).

The data runs represented in Table - 5.1 were carried out in random order so as to avoid any possible bias caused by the influence of systematic disturbances such as time trends. Care was taken to use the same quality of raw materials, so that there would not be any batch-to-batch variation in the raw materials.

The three selected levels in the case of temperature and time are at equal intervals, while in the case of pressure they are not exactly at equal intervals. Considering this inequality of intervals as not being very significant, as a first approximation the three levels of pressure may, for the purpose of analysis, be treated as though they are at equal intervals.

The main effects and interactions of the three factors were resolved into their linear and quadratic effects. The details of the calculations are not given as they are readily available (41). The final results obtained are tabulated with their variance ratios in Table - 5.3.

TABLE - 5.3

COMPLETE ANALYSIS OF VARIANCE OF TABLE - 5.1

Source of variation	Sum of squares	Degrees of freedom	Mean square	Variance ratio
<b>Main effects</b>				
T	(Linear	0.6689	1	0.276
	(Quadratic	41.3437	1	17.049 +
P	(Linear	23.8050	1	9.816 *
	(Quadratic	44.2817	1	18.261 +
C	(Linear	5.8939	1	2.431
	(Quadratic	105.0020	1	43.299 +
<b>Two factor interactions</b>				
$L_T L_P$	21.9510	1	9.052 *	
$Q_T L_P$	0.2225	1	0.0917	
$L_T Q_P$	1.3806	1	0.569	
$Q_T Q_P$	12.0734	1	4.978	
$L_T L_C$	46.5310	1	19.188 +	
$Q_T L_C$	9.7865	1	4.035	
$L_T Q_C$	0.1951	1	0.080	
$Q_T Q_C$	11.3102	1	4.664	
$L_P L_C$	0.4034	1	0.166	
$Q_P L_C$	1.9600	1	0.808	
$L_P Q_C$	16.2000	1	6.680 *	
$Q_P Q_C$	117.8133	1	48.583 +	

TABLE - 5.3 (contd.)

Source of variation	Sum of squares	Degrees of freedom	Mean square	Variance ratio
Three factor interactions :				
T x P x C	19.4	8	2.425	
Total	480.0	26		

\* Significant, &lt; 5%

+ Highly significant, &lt; 1%

### 5.1.2 Interpretation

Since each treatment was tested only once, there is no direct estimate of the experimental error variance by which the significance of the effects may be judged. It is commonly found in non-replicated experiments that the higher term interaction mean squares are used to give an estimate of the error variance. Thus, in this case, a three factor interactions mean square may be used to give an estimate of error variance. For 1 and 8 degrees of freedom, the 5% and 1% values of F obtained from the standard table (66) are 5.32 and 11.3 respectively. This shows that the most highly significant effect of interaction is that of the quadratic P x quadratic C. The reason for this marked effect can be examined from the data of Table - 5.2C. A sharp peak is observed at level  $p_1$  and  $c_1$ . The yield shows very sensitive changes in the levels of P and C factors on either side of the  $p_1$  and  $c_1$  levels, indicating thereby that  $p_1$  and  $c_1$  are the best conditions for the factors P and C. All the quadratic terms of the main effects of T, P and C factors are highly significant. When the quadratic effects and the interactions become highly

significant, the response value can be assumed as near to the optimum value. The technique of local exploration is then used so that the optimum can be specified more precisely, and the conditions most suitable for practical use determined. The three factor interaction mean square, which is taken to give an estimate of the error variance, corresponds to a standard error of  $\sqrt{2.425} = 1.557$ . The 95% confidence limits to be attached to the observations of Table 5.1 are therefore  $\pm 2.31 \times 1.557 = \pm 3.596$ , where 2.31 is the 5% value of "t" for 8 degrees of freedom.

## 5.2 POLYNOMIAL REPRESENTATION OF THE RESPONSE SURFACE

Having reached a near stationary region, it remains to be ascertained whether a true maximum, a ridge, or possibly a saddle point, has been reached. If the true maximum has not been reached, then what further experiments are needed? For an elucidation of this, a polynomial of a degree higher than the first may be fitted to the response surface in the region and analysed by the method of Box and Wilson (66) which involves the following calculations in the present case :

(i) Determination of the 3 co-ordinates of the new center,  $x_{1S}$ ,  $x_{2S}$ ,  $x_{3S}$ , and the value  $Y_S$  of the response at this point.

(ii) Transformation of the equation to the canonical form,

$$Y - Y_S = B_{11} X_1^2 + B_{22} X_2^2 + B_{33} X_3^2$$

(iii) Determination of the equations for the new axes ( $X$ 's) in terms of the old co-ordinates ( $x$ 's).

A polynomial second degree equation for the three factors,  $x_1$ ,  $x_2$  and  $x_3$ , may be represented as

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{13}x_1x_3 \quad \dots (5.1)$$

where  $x_1$ ,  $x_2$  and  $x_3$  in the present case represent temperature, pressure and time;  $y$  is the observed yield or response; the coefficients  $b_1$ ,  $b_2$ ,  $b_3$  are the linear effects;  $b_{11}$ ,  $b_{22}$  and  $b_{33}$  are the quadratic effects; and  $b_{12}$ ,  $b_{23}$  and  $b_{13}$  are the interaction effects.

With the help of the data presented in Table - 5.1, the 3-dimensional second degree equation



for the response surface was fitted by evaluating the coefficients in the equation by programming the data in a computer.\* The following equation for the response surface results :

$$\begin{aligned}
 Y = & -599.65 + 0.32764 x_1 + 5.0635 x_2 + \\
 & 36.214 x_3 - 0.001869 x_1^2 - 0.00955 x_2^2 \\
 & -2.2556 x_3^2 - 0.00068131 x_1 x_2 - \\
 & 0.1254 x_2 x_3 + 0.054099 x_1 x_3 \quad \dots (5.2)
 \end{aligned}$$

### 5.3 ANALYSIS OF THE FITTED EQUATION

#### 5.3.1 Determination of the center of the system

The center, S, of the contour of Equation (5.2) was found by differentiating the right hand side with respect to each of the variables,  $x_1$ ,  $x_2$  and  $x_3$ , in turn and equating the results to zero. The following three equations are obtained :

$$\begin{aligned}
 0.003738 x_1 + 0.0006813 x_2 - 0.054099 x_3 \\
 & = 0.32764 \\
 0.0006813 x_1 + 0.0191 x_2 + 0.1254 x_3 & \dots (5.3) \\
 & = 5.0635 \\
 -0.054099 x_1 + 0.1254 x_2 + 4.5112 x_3 \\
 & = 36.214
 \end{aligned}$$

---

\* CDC-3600 computer of the Tata Institute of Fundamental Research was used.

TABLE - 5

## SOLUTION OF EQUATION (5.3)

		s		
0.003738	0.000681	-0.054099	0.32764	0.277960
0.000681	0.019100	0.125400	5.063500	5.208700
-0.054099	0.125400	4.571200	36.21400	40.796500
0.061140	0.011144	-0.884843	5.35838	4.546314
	0.137750	0.961925	36.32494	37.444800
		1.662600	3.184363	4.842609
				0.601470

Equations (5.3) may be solved for  $x_1$ ,  $x_2$  and  $x_3$  by the straight forward method of elimination, or by a more convenient and rapid method (41). The solution is presented in Table - 5. From this the co-ordinates of the center, S, are found to be :

$$x_{1S} = 250.048 \text{ (temperature, } ^\circ\text{C.)}$$

$$x_{2S} = 69.792 \text{ (pressure, psig.)}$$

$$x_{3S} = 1.915 \text{ (time, hr.)}$$

By substituting these values in Equation (5.2), the yield  $Y_S$  predicted at the center, S, is obtained as

$$Y_S = 79.5 \text{ (yield, \%)}.$$

### 5.3.2 Determination of the coefficients of the canonical form

The canonical form of Equation (5.2) is given by

$$Y - Y_S = B_{11} X_1^2 + B_{22} X_2^2 + B_{33} X_3^2 \quad \dots (5.4)$$

where  $B_{11}$ ,  $B_{22}$  and  $B_{33}$  are the transformed coefficients while  $X_1$ ,  $X_2$  and  $X_3$  are the transformed variables. The coefficients,  $B_{11}$ ,  $B_{22}$  and  $B_{33}$ , were calculated by solving the following characteristic determinant (of Equation (5.2) ).

$$f(B) = \begin{vmatrix} -0.001869-B & - 0.0003406 & + 0.027049 \\ -0.0003406 & - 0.00955-B & - 0.0627 \\ +0.027049 & - 0.0627 & - 2.2556-B \end{vmatrix} = 0 \quad \dots (5.5)$$

There will be three values of B which when subtracted from the diagonal terms in the manner shown above will cause the determinant to vanish. On solving the determinant (5.5), the following cubic equation in B is obtained :

$$B^3 + 2.267019 B^2 + 0.0211219 B + 0.000024515 \quad \dots (5.6) \\ = 0$$

The last term of the cubic equation is so small that it may not be significantly different from zero. Thus,

$$B (B^2 + 2.267 B + 0.0211) = 0 \quad \dots (5.7)$$

The roots of B obtained are as follows :

$$\begin{aligned} B_{11} &= -2.2576, \\ B_{22} &= -0.0688, \\ B_{33} &= 0 \end{aligned}$$

The canonical form of the fitted second degree Equation (5.2) is therefore

$$Y - 79.5 = -2.2576 X_1^2 - 0.0088 X_2^2 - 0 X_3^2 \quad \dots (5.8)$$

Since the signs of both the remaining canonical coefficients are the same, the contours of the fitted surface are ellipses. Since they are negative the point (yield)  $Y_3$  is a maximum of the fitted surface. Hence the levels of the co-ordinates  $x_{13}$ ,  $x_{23}$  and  $x_{33}$  of the point  $Y_3$  are at maximum.

In this case it has turned out that the optimum could be estimated without recourse to further analysis. Quite often this may not be the case and it would be necessary to organise further exploration. The essential feature of this exploration is the establishment of the relationship between the two axes. This is shown in the next section.

### 5.3.3 Determination of the axes of the fitted second degree surface

The equations of the new transformed axes, say  $X$ , will take up the following general form in terms of old axes :

$$X_1 = m_{11} (x_1 - x_{13}) + m_{12} (x_2 - x_{23}) + m_{13} (x_3 - x_{33}) \quad \dots (5.9)$$

The coefficients,  $m_{11}$ ,  $m_{12}$  and  $m_{13}$ , of Equation (5.9) can then be determined from the characteristic determinant (5.5) by substituting the value of  $B_{11} = -2.2576$  for  $B$  in it. On solving the determinant, the three equations in  $m_{11}$ ,  $m_{12}$  and  $m_{13}$  obtained are :

$$\begin{aligned} 2.25593 m_{11} - 0.00034 m_{12} + 0.02705 m_{13} &= 0 \\ -0.00034 m_{11} + 2.24835 m_{12} - 0.06270 m_{13} &= 0 \quad \dots (5.10) \\ 0.02705 m_{11} - 0.06270 m_{12} + 0.0020 m_{13} &= 0 \end{aligned}$$

These equations form a consistent set, and values of  $m$ 's may be obtained by substituting an arbitrary value for any one of them, say  $m_{13} = 1$ ; then on solving the first two equations,  $m_{11}$ ,  $m_{12}$  and  $m_{13}$  are found to be proportional to  $-0.01134$ ,  $0.02789$  and  $1.0$ . Dividing these values by the square root of their sum of squares, the required values may be obtained.

$$\begin{aligned} m_{11} &= -0.01134, \\ m_{12} &= 0.02789, \\ m_{13} &= 1.0 \end{aligned}$$

The values of the coefficients of the equations for  $X_2$  and  $X_3$  can be found by substituting the values of  $B_{22}$  and  $B_{33}$  respectively for  $B$  in the



determinant of (5.5) and proceeding as in the case of  $X_1$ . The following equations for the transformed axes are thus obtained.

$$\begin{aligned} X_1 &= 0.0113 (x_1 - x_{1S}) + 0.0289 (x_2 - x_{2S}) \\ &\quad + (x_3 - x_{3S}) \\ X_2 &= -0.0974 (x_1 - x_{1S}) - 0.9953 (x_2 - x_{2S}) \dots (5.11) \\ &\quad + 0.0124 (x_3 - x_{3S}) \\ X_3 &= 0.9095 (x_1 - x_{1S}) - 0.4111 (x_2 - x_{2S}) \\ &\quad + 0.0577 (x_3 - x_{3S}) \end{aligned}$$

Taking advantage of the orthogonal property, reciprocal transformation of the equations to the old axes in terms of the new axes can be made.

$$\begin{aligned} (x_1 - x_{1S}) &= -0.0113 X_1 - 0.0974 X_2 + 0.9095 X_3 \\ (x_2 - x_{2S}) &= 0.0289 X_1 - 0.9953 X_2 - 0.4111 X_3 \\ (x_3 - x_{3S}) &= X_1 + 0.0124 X_2 + 0.057 X_3 \dots (5.12) \end{aligned}$$

#### 5.4 CONFIRMATION OF THE OPTIMUM CONDITIONS

Four repeat runs were carried out at the estimated optimum conditions of temperature, pressure and time, and the following data were obtained :

Estimated optimum temperature : 250°C.  
Estimated optimum pressure : 69.8 psig.  
Estimated optimum time : 1.9 hr.

Conversion to BON acid, %	Yield of BON acid, %
34.2	78.0
35.0	79.8
34.5	80.8
35.5	80.0

The average yield works out to 79.65%, with a standard deviation of 0.682.

APPENDICES

RESULTS OF KINETIC RUNS



Temperature

Pressure

Reaction Time

min

Conversion (%)

Run	Time (min)	Conversion (%)	Total Conversion (%)
1	10	10	10
2	20	20	20
3	30	30	30
4	40	40	40
5	50	50	50
6	60	60	60
7	70	70	70
8	80	80	80
9	90	90	90
10	100	100	100

**APPENDIX-A**  
**RESULTS OF KINETIC RUNS**

TABLE - A.1

Charge :	(	Carbonation :	(
2-naphthol	)	Temperature	)
.. 5 moles	)	.. 230°C.	)
Dehydration :	)	Pressure	)
.. 8 hr.	)	.. 30 psig.	)
Time	)	2-naphthol:kerosene	)
.. 1 : 2.5	)	ratio	)
2-naphthol:kerosene	)	.. 1 : 1	)
ratio	)		)
Additive, CaCl <sub>2</sub>	)		)
.. 2%	)		)

EXPERIMENTAL KINETIC

DATA

No.	Carbonation time	min.	2-naphthol recovered	moles	2-naphthol consumed	moles	BON acid formed	moles	2-naphthol lost as tar	%	Conversion (x"),	%	Yield (y),	%	Total conversion (x),	%
1	5	4.25	0.75	0.149	12.02	2.98	19.7	17.98								
2	15	3.70	1.30	0.719	11.60	14.38	55.5	40.36								
3	30	3.37	1.63	1.142	9.76	22.84	70.0	55.44								
4	40	3.15	1.85	1.440	8.20	28.80	77.8	65.80								
5	60	2.87	2.13	1.460	13.40	29.20	68.5	71.80								
6	120	3.11	1.89	1.410	9.60	28.20	74.5	66.00								
7	180	2.84	2.16	1.520	12.80	30.40	70.5	73.60								

TABLE - A.2

Charge :		Carbonation :						
2-naphthol	.. 5 moles	Temperature	.. 230°C.					
Dehydration :		Pressure	.. 70 psig.					
Time	.. 8 hr.	2-naphthol:kerosene	.. 1 : 1					
2-naphthol:kerosene	.. 1 : 2.5	ratio						
Additive, CaCl <sub>2</sub>	.. 2%							
EXPERIMENTAL KINETIC DATA								
No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x <sup>n</sup> ), %	Yield (y), %	Total conversion (x), %
1	5	4.29	0.71	0.260	8.90	5.20	36.9	19.30
2	15	3.86	1.14	0.665	9.50	13.30	58.4	36.10
3	30	3.48	1.52	1.072	8.96	21.44	70.5	51.84
4	40	3.28	1.72	1.240	9.60	24.80	72.0	59.20
5	60	3.12	1.88	1.380	10.42	27.60	73.0	65.62
6	120	3.03	1.97	1.475	9.90	29.50	75.0	68.90
7	180	2.83	2.17	1.575	11.90	31.50	72.5	74.90



TABLE - A.3

Charge :	(	Carbonation :	(
2-naphthol .. 5 moles	)	Temperature .. 230°C.	)
Dehydration :	)	Pressure .. 100 psig.	)
Time .. 8 hr.	)	2-naphthol:kerosene .. 1 : 1	)
2-naphthol:kerosene .. 1 : 2.5	)	ratio	)
ratio	)		)
Additive, CaCl <sub>2</sub> .. 2%	)		)

EXPERIMENTAL KINETIC DATA

No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x"), %	Yield (y), %	Total conversion (x), %
1	5	3.511	1.489	0.878	12.23	17.56	58.90	47.33
2	15	3.900	1.100	0.510	11.80	10.20	46.30	32.20
3	30	3.538	1.462	0.787	13.70	15.74	53.84	45.00
4	40	3.340	1.660	1.020	12.80	20.40	61.40	53.60
5	60	3.156	1.844	1.266	11.70	25.32	68.66	62.20
6	120	3.065	1.935	1.440	9.90	28.80	74.50	67.50
7	180	2.885	2.115	1.580	10.70	31.60	74.69	73.90



TABLE - A.5

Charge :	)	Carbonation :	(
2-naphthol .. 5 moles	)	Temperature .. 250°C.	(
Dehydration :	)	Pressure .. 70 psig.	(
Time .. 8 hr.	)	2-naphthol:kerosene .. 1 : 1	(
2-naphthol:kerosene .. 1 : 2.5	)	ratio	(
ratio	)		(
Additive, CaCl <sub>2</sub> .. 2%	)		(

EXPERIMENTAL KINETIC DATA

No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x''), %	Yield (y), %	Total conversion, (x), %
1	5	4.35	0.646	0.239	8.13	4.8	36.6	17.71
2	15	3.77	1.230	0.370	7.20	17.4	70.6	42.00
3	30	3.39	1.610	1.260	7.00	25.2	78.0	57.40
4	40	3.08	1.910	1.460	8.80	29.6	77.0	68.00
5	60	3.05	1.950	1.560	7.80	31.2	80.1	70.20
6	120	2.86	2.120	1.725	7.90	34.5	81.5	76.90
7	180	2.82	2.180	1.842	6.76	36.8	84.5	80.44

TABLE - A.6

Charge :	)	Carbonation :	(
2-naphthol .. 5 moles	)	Temperature .. 250°C.	(
Dehydration :	)	Pressure .. 100 psig.	(
Time .. 8 hr.	)	2-naphthol:kerosene .. 1 : 1	(
2-naphthol:kerosene .. 1 : 2.5	)	ratio	(
ratio	)		(
Additive, CaCl <sub>2</sub> .. 2%	)		(

EXPERIMENTAL KINETIC DATA

No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x <sup>n</sup> ), %	Yield (y), %	Total conversion (x), %
1	5	4.110	0.890	0.360	10.6	7.2	40.5	25.00
2	15	3.695	1.305	0.745	11.2	14.9	57.0	41.02
3	30	3.266	1.734	1.074	13.2	21.5	61.9	56.16
4	40	3.060	1.940	1.300	12.8	26.0	67.0	64.80
5	60	2.860	2.140	1.540	12.0	30.8	72.0	73.60
6	120	2.860	2.140	1.625	10.3	32.5	76.0	75.30
7	180	2.690	2.310	1.760	11.0	35.2	76.0	81.40



TABLE - A.8

Charge :	(	Carbonation :	(
2-naphthol	)	Temperature	(
.. 5 moles	)	.. 270°C.	(
Dehydration :	)	Pressure	(
Time	)	.. 70 psig.	(
.. 8 hr.	)	2-naphthol:kerosene	(
2-naphthol:kerosene.. 1 : 2.5	)	.. 1 : 1	(
ratio	)	ratio	(
Additive, CaCl <sub>2</sub>	)		(
.. 2%	)		(

## EXPERIMENTAL KINETIC DATA

No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x <sup>u</sup> ), %	Yield (y), %	Total conversion (x), %
1	5	3.743	1.257	0.637	12.4	12.7	50.7	37.30
2	15	3.560	1.440	0.92	10.4	18.4	63.7	47.20
3	30	3.125	1.875	1.411	9.3	23.2	75.0	65.72
4	40	2.798	2.202	1.622	11.6	32.4	73.7	76.50
5	60	2.681	2.319	1.675	13.0	33.5	72.5	79.90
6	120	2.690	2.310	1.620	13.8	32.4	70.0	76.60
7	180	2.520	2.480	1.650	16.6	33.0	66.5	82.60



TABLE - A.9

Charge :	(	Carbonation :	(
2-naphthol	)	Temperature	) .. 270°C.
.. 5 moles	)	Pressure	) .. 100 psig.
Dehydration :	)	2-naphthol:kerosene..	) 1 : 1
Time	)	ratio	)
.. 8 hr.	)		)
2-naphthol:kerosene..	)		)
ratio	)		)
1 : 2.5	)		)
Additive, CaCl <sub>2</sub>	)		)
.. 2%	)		)

EXPERIMENTAL KINETIC DATA

No.	Carbonation time min.	2-naphthol recovered moles	2-naphthol consumed moles	BON acid formed moles	2-naphthol lost as tar %	Conversion (x''), %	Yield (y), %	Total conversion (x), %
1	5	3.80	1.20	0.61	11.8	12.2	50.8	36.2
2	15	3.66	1.34	0.95	7.8	19.0	70.8	45.8
3	30	3.25	1.75	1.30	9.0	26.0	75.0	61.0
4	40	2.99	2.01	1.56	9.0	31.2	77.5	71.4
5	60	2.76	2.24	1.64	12.0	32.8	73.1	77.6
6	120	2.77	2.23	1.69	10.8	33.8	76.0	78.4
7	180	2.48	2.52	1.77	14.9	35.5	70.5	85.9

TABLE - A.10

## CALCULATIONS FOR TESTING THE PROPOSED MODELS

230° C., 30 psig.		230° C., 70 psig.		230° C., 100 psig.							
$\theta$	$\frac{\Phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$	$\theta$	$\frac{\Phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$	$\theta$	$\frac{\Phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$			
5	27.8	0.0328	0.0127	5	10.6	0.0995	0.1921	5	26.0	0.03626	0.0691
15	37.2	0.08326	0.1576	15	46.58	0.06305	0.1216	15	41.6	0.07202	0.1386
30	54.1	0.1272	0.2362	30	66.6	0.09568	0.1806	30	58.0	0.1160	0.2162
40	61.0	0.1649	0.3007	40	74.63	0.1211	0.2259	40	67.5	0.1398	0.2584
60	83.5	0.1908	0.3449	60	96.5	0.1508	0.2769	60	91.5	0.1644	0.2996

TABLE - A.11

## CALCULATIONS FOR TESTING THE PROPOSED MODELS

$\theta$	250°C., 30 psig.			250°C., 70 psig.			250°C., 100 psig.			
	$\frac{\theta}{x}$	$\frac{\phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$	$\frac{\theta}{x}$	$\frac{\phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$	$\theta$	$\frac{\theta}{x}$	$\frac{\phi(x)}{x}$	$1-(1-x)^{\frac{1}{\theta}}$
5	21.6	0.0442	0.0838	5	28.2	0.0316	5	20	0.0480	0.0914
15	43.6	0.0699	0.1306	15	35.6	0.0881	15	36.6	0.0873	0.1613
30	60.0	0.1103	0.2062	30	52.25	0.1339	30	53.5	0.1281	0.2403
40	67.0	0.1413	0.2608	40	59.0	0.1739	40	61.5	0.1611	0.2940
60	89.0	0.1712	0.3124	60	85.5	0.1841	60	81.5	0.1994	0.3585

TABLE - A.12

## CALCULATIONS FOR TESTING THE PROPOSED MODELS

270°C., 30 psig.		270°C., 70 psig.		270°C., 100 psig.							
$\theta$	$\frac{\phi(x)}{x}$	$1-(1-x)$	$\theta$	$\frac{\theta}{x}$	$\frac{\phi(x)}{x}$	$1-(1-x)$	$\theta$	$\frac{\theta}{x}$	$\frac{\phi(x)}{x}$	$1-(1-x)$	
5	16.5	0.05626	0.1128	5	13.4	0.0751	0.1441	5	13.6	0.0746	0.1392
15	32.7	0.09824	0.1847	15	31.8	0.1017	0.1919	15	32.7	0.0982	0.1847
30	47.0	0.1576	0.2886	30	45.5	0.1644	0.3002	30	49.1	0.1464	0.2693
40	54.5	0.1978	0.3563	40	52.3	0.2141	0.3828	40	56.0	0.1888	0.3411
60	77.5	0.2183	0.3898	60	75.0	0.2332	0.4143	60	76.1	0.2199	0.3927

APPENDIX - B.1

DENSITY OF SOLID NAPHTHOLENE

A sample of solid naphthalene (containing kerosene oil) was taken in a stoppered bottle under inert dry atmosphere from the reactor at the end of the dehydration step (see Chapter - 3). Inert dry kerosene oil (50<sup>o</sup>-55<sup>o</sup>C, range) was added to the bottle, which was allowed to cool down to room temperature (25<sup>o</sup>C.). The sample (20-25 gm) + kerosene oil was then transferred into a specific gravity bottle (50 ml.) under dry inert atmosphere and weighed accurately.

The sample from the specific gravity bottle was transferred into a beaker, the bottle was washed with water, and more water added to the beaker containing the sample. Complete dissolution of solid naphthalene was then ensured. After separating the oil, the naphthalene content was estimated by flame titration (Chapter - 4).

**APPENDIX-B**

DATA FOR ESTIMATING THE CONSTANTS OF THE MASS TRANSFER MODEL

APPENDIX - B.1DENSITY OF SODIUM NAPHTHOLATE

A sample of sodium naphtholate (containing kerosene oil) was taken in a stoppered bottle under inert dry atmosphere from the reactor at the end of the dehydration step (see Chapter - 2). More dry kerosene oil (240<sup>o</sup>-260<sup>o</sup>C. range) was added to the bottle, which was allowed to cool down to room temperature (28<sup>o</sup>C.). The sample (Na-naphtholate + kerosene oil) was then transferred into a specific gravity bottle (50 ml.) under dry inert atmosphere and weighed accurately.

The sample from the specific gravity bottle was transferred into a beaker, the bottle was washed with water, and wash water added to the beaker containing the sample. Complete dissolution of sodium naphtholate was then ensured. After separating the oil, the naphtholate content was estimated by diazo titration (Chapter - 2).



Sample calculation

Weight of specific gravity bottle (50 ml.)	..	23.364 gm.
Weight of specific gravity bottle + sample	..	67.711 gm.
Weight of the sample	..	43.847 gm.
Volume occupied by the sample	..	50 ml.
Sodium 2-naphtholate content (as determined by diazo titration)	..	6.82704 gm.
Density of kerosene oil	..	0.7847 gm./ml.
Weight of kerosene oil in the sample	..	$43.847 - 6.827$ $= 37.02$ gm.
Volume occupied by kerosene oil	..	$\frac{37.02}{0.7847} = 47.18$ ml.
Volume occupied by Na 2-naphtholate in the sample	..	$50 - 47.18 = 2.82$ ml.
Density of Na 2-naphtholate	..	$\frac{6.827}{2.83} = 2.421$ gm./ml.  $= 0.0146$ gm-mole/ml.

APPENDIX - B.2SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL(240° - 265°C. RANGE)

The detailed procedure is given in Chapter - 2 and the solubility apparatus is shown in Fig. (2.6).

The content of CO<sub>2</sub> in kerosene oil at intervals of 2-3 minutes was determined by drawing samples from the reactor and analysing, till the saturation solubility of CO<sub>2</sub> in kerosene oil at the particular temperature and pressure was reached. This is illustrated below.

Sample calculation

Reactor pressure	..	70 psig.
Reactor temperature	..	250°C.
Time interval, $\theta$	..	15 min.
Barometric pressure	..	71.5 cm. Hg
Room temperature	..	27°C.
Initial volume of kerosene in oil burette	..	2 ml.
Final volume of kerosene in burette	..	14.25 ml.
Initial volume of kerosene in CO <sub>2</sub> burette	..	36.0 ml.

Final volume of kerosene in CO <sub>2</sub> burette	..	10.5 ml.
Volume of kerosene oil sample	..	12.25 ml.
Volume of CO <sub>2</sub> released	..	13.25 ml.
Volume of CO <sub>2</sub> released per ml. of kerosene oil.	..	1.08 ml.

$$s = \frac{71.5}{76.0} \cdot \frac{273}{300} \cdot \frac{44}{22400} \cdot 1.08$$

$$= 0.001817 \text{ gm./ml.}$$

$$\text{or} \quad = 0.00004129 \text{ gm.mole/ml. CO}_2 \text{ at 15 min.}$$

The solubilities of CO<sub>2</sub> from time  $\theta = 2$  min. to  $\theta =$  till saturation were determined at three temperatures (230°, 250° and 270°C.) and at two pressures (70 and 100 psig.), and the data are summarized in Table-B.1.

TABLE - B.1

SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL

Temperature °C.	Pressure psig.	Time $\theta$ min.	Solubility at time $\theta$		Saturation solubility	
			C x 10 <sup>2</sup> gm./ml.	C x 10 <sup>4</sup> moles/ml.	C* x 10 <sup>2</sup> gm./ml.	C* x 10 <sup>4</sup> moles/ml.
1	2	3	4	5	6	7
230	70	4	0.076	0.173		
		8	0.142	0.322		
		12	0.200	0.455	0.2368	0.537
		16	0.232	0.527		
		17	0.237	0.537		
230	100	2	0.140	0.318		
		4	0.244	0.555		
		6	0.330	0.750	0.4346	0.99
		10	0.418	0.950		
		13	0.435	0.990		
250	70	3	0.039	0.039		
		6	0.078	0.177		
		9	0.118	0.268	0.1817	0.412
		12	0.154	0.350		
		15	0.182	0.412		

TABLE - B.1 (contd.)

1	2	3	4	5	6	7
250	100	2 6 10 13 15	0.092 0.156 0.254 0.300 0.316	0.118 0.354 0.578 0.680 0.719	0.3159	0.719
270	70	2 5 8 10 12	0.017 0.043 0.068 0.084 0.091	0.038 0.097 0.155 0.191 0.207	0.0913	0.207
270	100	2 5 7 9 12	0.059 0.148 0.198 0.222 0.246	0.134 0.336 0.450 0.505 0.560	0.2461	0.56

APPENDIX - B.3MASS TRANSFER COEFFICIENT

The mass transfer coefficient of CO<sub>2</sub> in kerosene oil at any time  $\theta$  can be computed from

$$\frac{dC}{d\theta} = k_L'' (C^* - C) \quad \dots (4.28)$$

$$\text{or } k_L'' = \frac{\frac{dC}{d\theta}}{(C^* - C)}$$

Plots of  $C$  vs.  $\theta$  at three temperatures (230°, 250° and 270°C.) and at two pressures (70 and 100 psig.) are shown in Figs. (B.1) to (B.6). For a given set of operating conditions,  $\frac{dC}{d\theta}$  was then calculated by graphical differentiation of the corresponding curve of  $C$  vs.  $\theta$  at different values of  $C$ , and an average value of  $k_L''$  obtained over the entire concentration range.

Sample calculation

From Fig. (B.1), at 230°C. 70 psig. and  $\theta = 10$  min.,

$$\frac{dC}{d\theta} = 0.000003095$$



$$C^* - C = 0.0000147$$

$$\therefore k_L'' = \frac{0.000003095}{0.0000147} = 0.2105 \frac{1}{\text{min.}}$$

Similar calculations were performed for different values of  $\theta$  (i.e. concentration) thus giving an average value of  $k_L''$  equals 0.2043 at 230°C. and 70 psig.

The specific mass transfer coefficient  $k_L$  of Equation (4.1) has the following relationship with the volume coefficient  $k_L''$  determined experimentally.

$$k_L = \frac{k_L''}{a} \frac{\text{cm.}}{\text{min.}}$$

where  $a = \frac{\text{cross sectional area of the vessel}}{\text{volume of the liquid}}$

In the present case

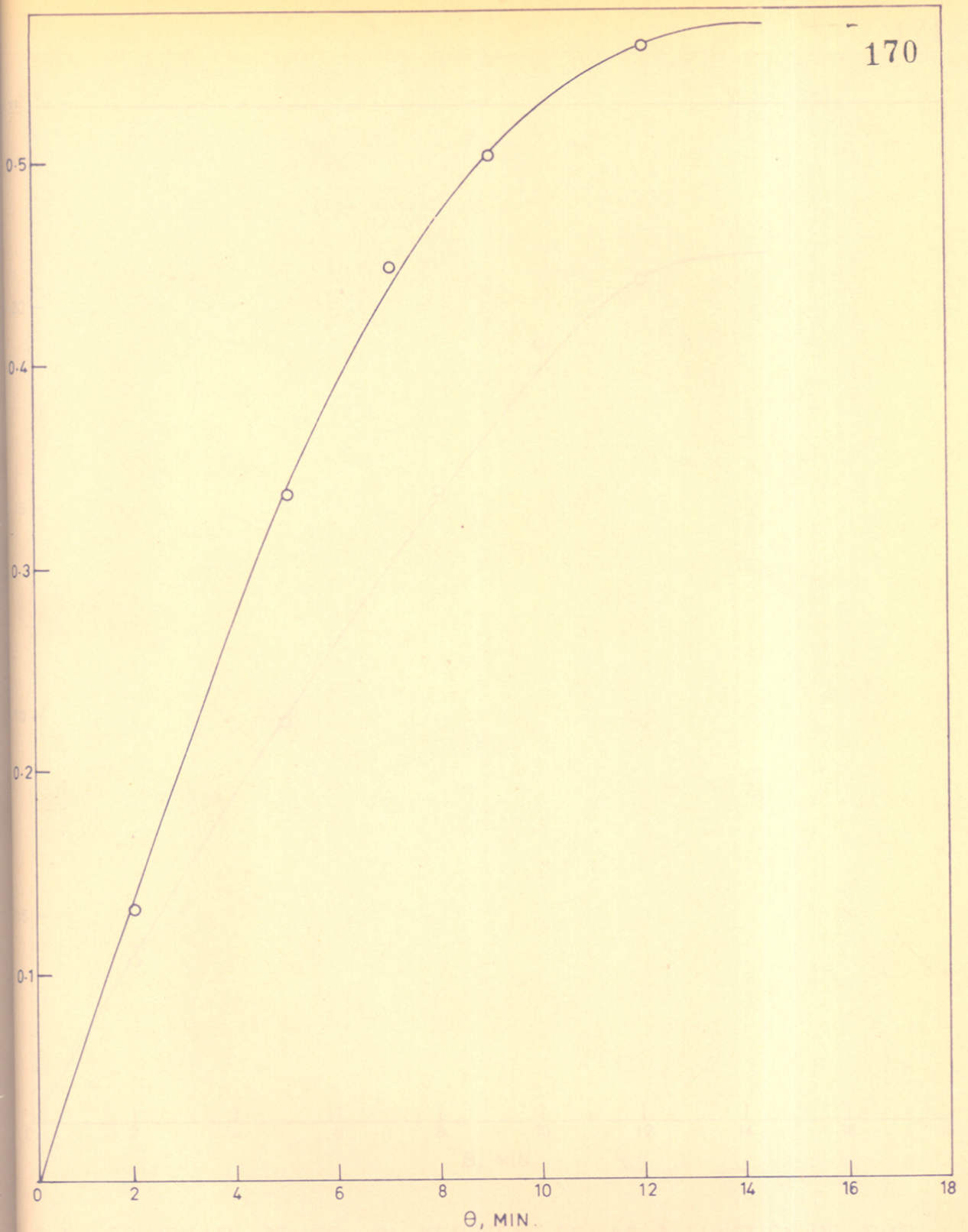
$$a = \frac{3.14 \times 100}{4000} = .07848 \frac{\text{cm.}^2}{\text{cm.}^3}$$

$$\therefore k_L = \frac{0.2105}{0.07848} = 2.6839 \frac{\text{cm.}}{\text{min.}}$$

The values of  $k_L$  and  $k_L''$  obtained at different temperatures and pressures are summarized in Table - B.2.

TABLE - B.2

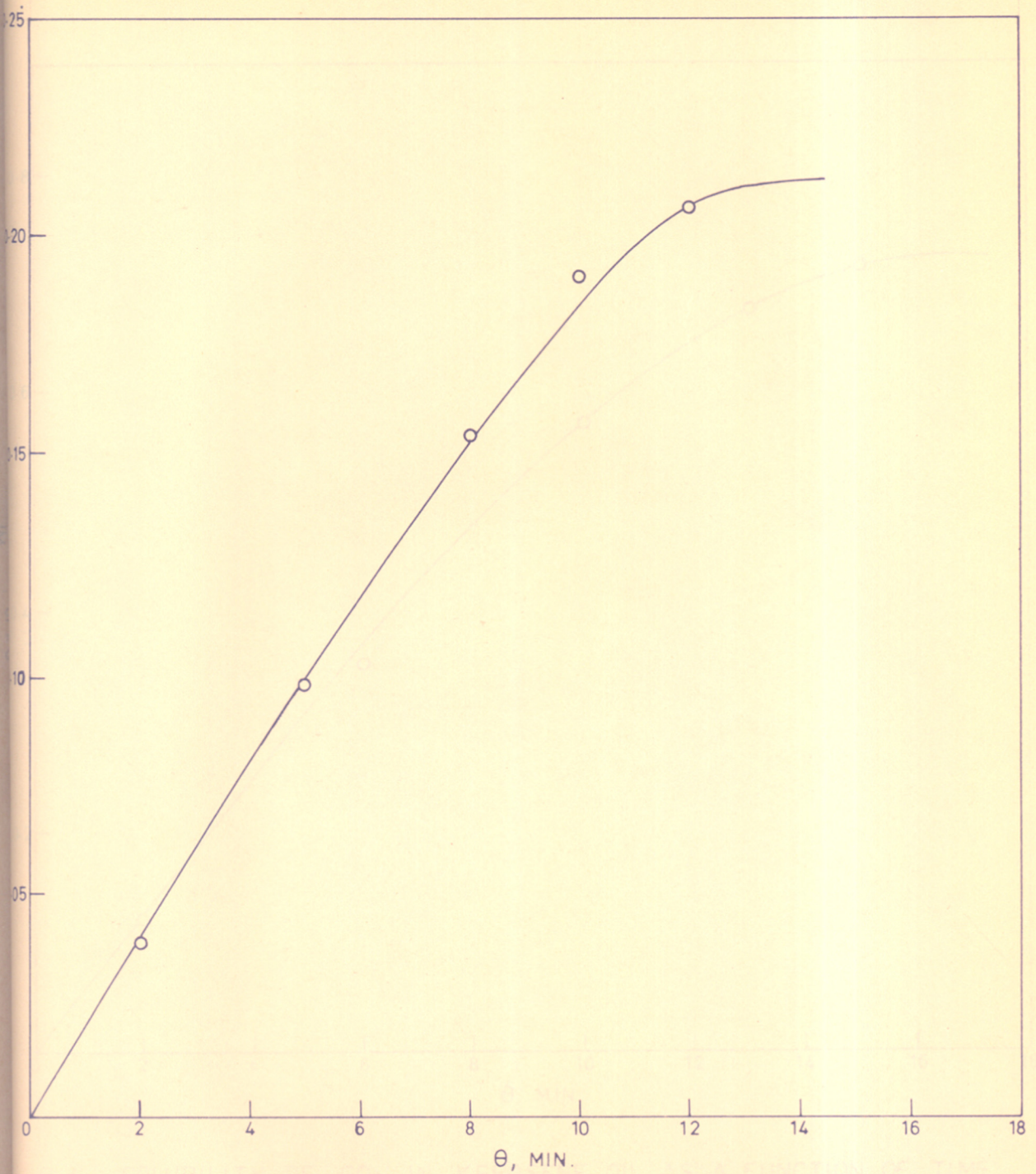
Temperature	Pressure	Specific mass transfer coefficient, $k_L$	Volume mass transfer coefficient (ave.), $k_L$
$^{\circ}\text{C.}$	psig.	cm./min.	l./min.
230	70	2.6042	0.2043
230	100	3.9429	0.3093
250	70	3.0855	0.2420
250	100	3.3915	0.2660
270	70	3.2194	0.2525
270	100	3.3405	0.2620



B-6. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME

AT 270°C., 100 PSIG.

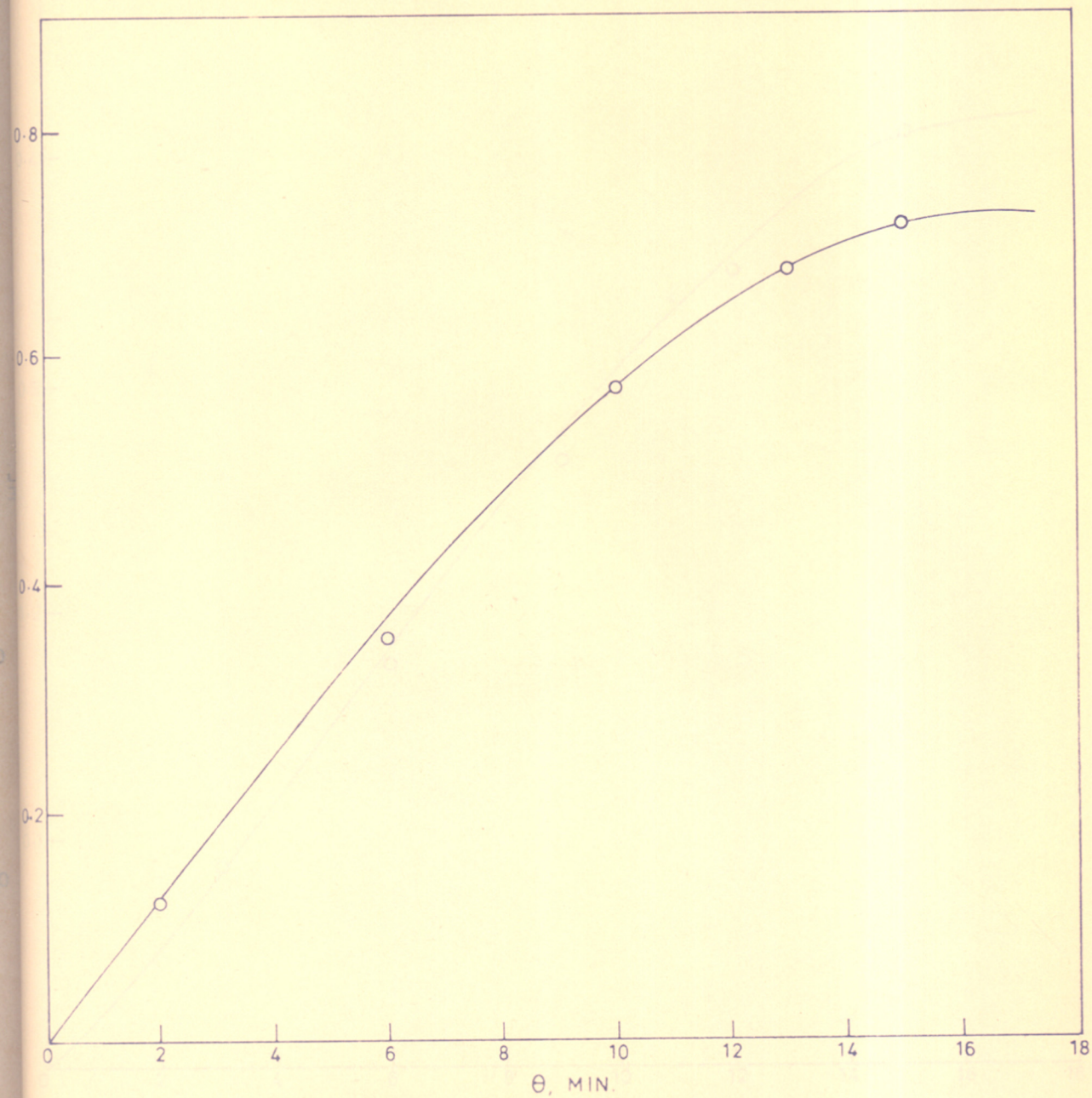




B. 5. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME

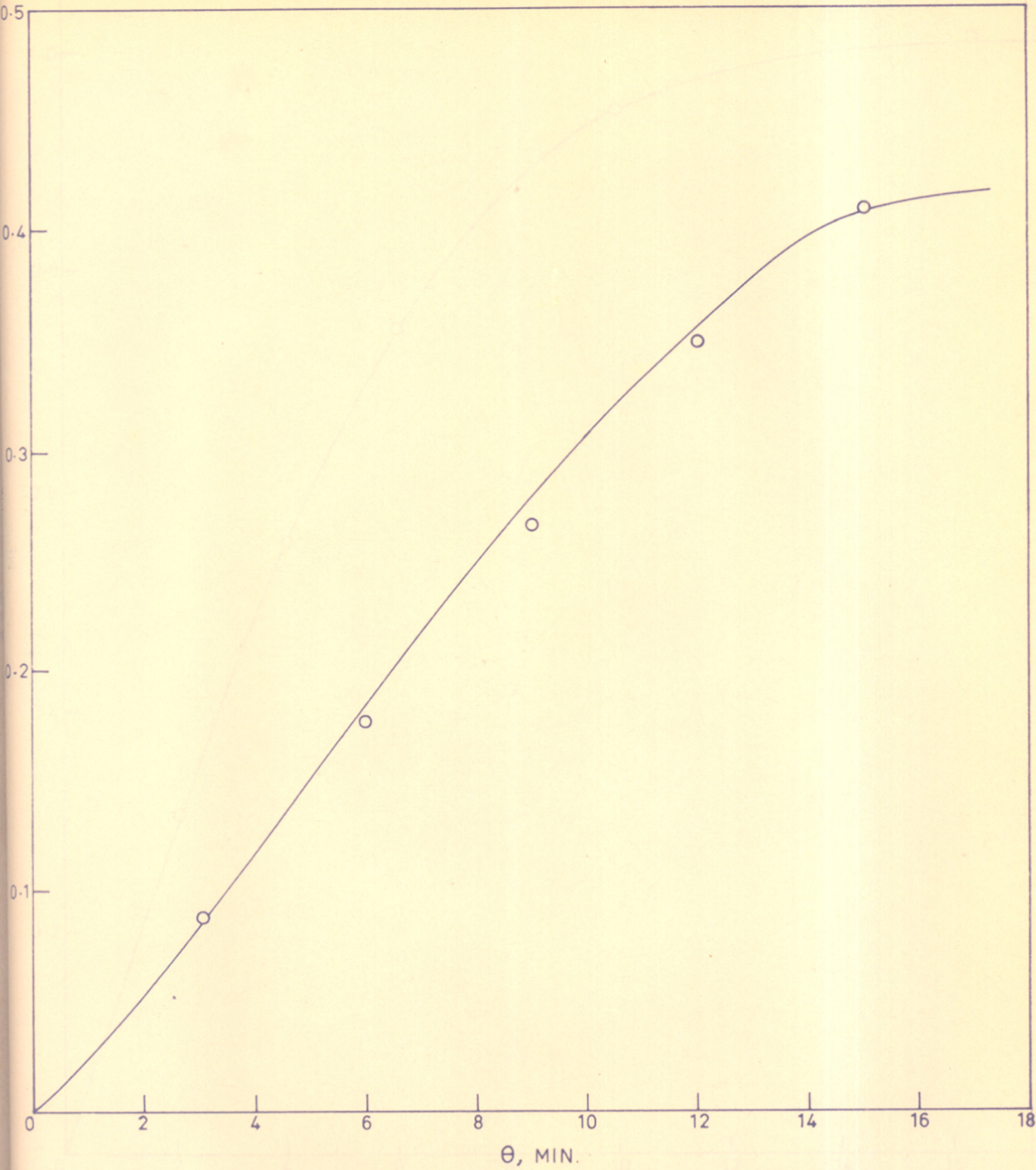
AT 270°C., 70 PSIG.





6. B.4. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME  
AT 250°C., 100 PSIG





B.3. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME  
AT 250°C., 70 PSIG.



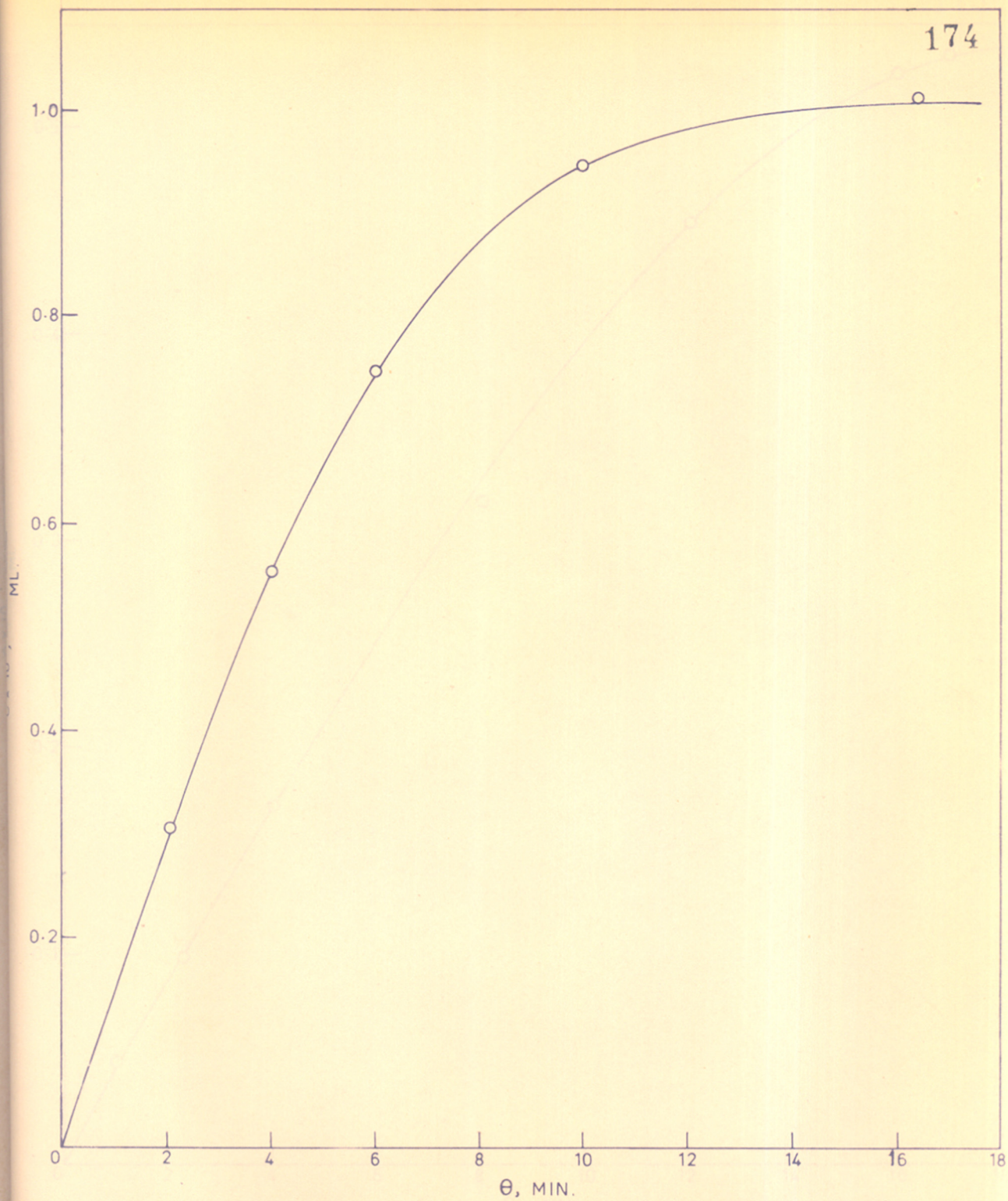


FIG. B-2. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME  
AT 230°C., 100 PSIG.



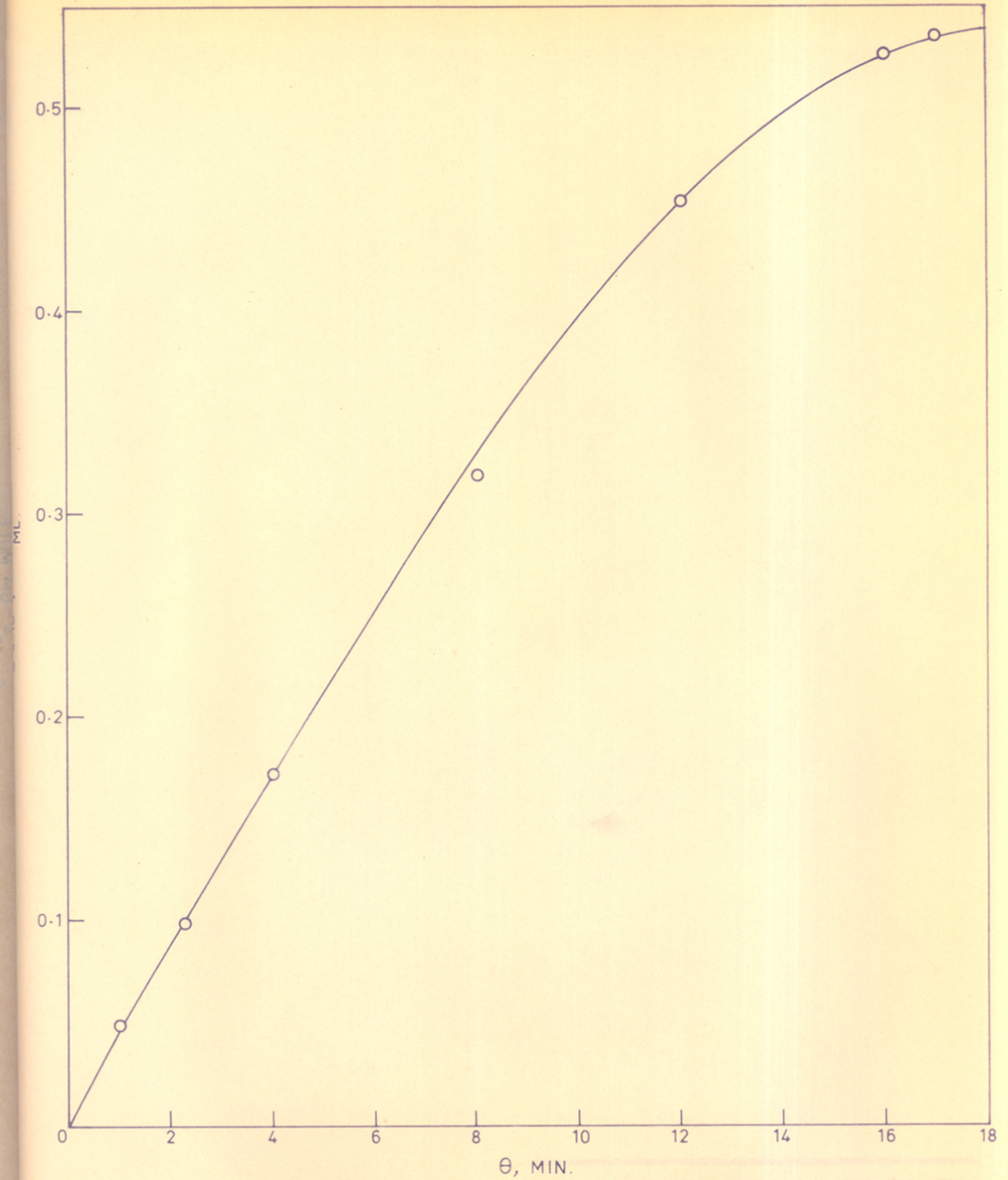


FIG. B-1. SOLUBILITY OF CO<sub>2</sub> IN KEROSENE OIL AS A FUNCTION OF TIME  
AT 230°C., 70 PSIG.



NOMENCLATURE

- $k_p$  = constant defined by Equation (1.11)
- $A$  = surface area per unit volume,  $\frac{a_s}{V}$
- $k_{p1}, k_{p2}, k_{p3}$  = coefficients of polynomial (1.11) defined by Equation (1.1)
- $k_{p1}, k_{p2}$  = transformed coefficients, Equation (1.4)
- $C_{p0}$  = concentration of  $O_2$  in bulk phase
- $C_{p1}$  = concentration of  $O_2$  in surface phase,  $\frac{C_{p0} k_{p1}}{k_{p1} + k_{p2}}$
- $C_{p2}$  = concentration of  $O_2$  in surface phase,  $\frac{C_{p0} k_{p2}}{k_{p1} + k_{p2}}$
- $C_{p3}$  = concentration of  $O_2$  in surface phase,  $\frac{C_{p0} k_{p3}}{k_{p1} + k_{p2} + k_{p3}}$
- $C_{p4}$  = concentration of  $O_2$  at reaction surface,  $\frac{C_{p0} k_{p1} k_{p2}}{k_{p1} k_{p2} + k_{p1} k_{p3} + k_{p2} k_{p3}}$
- $k_1, k_2, k_3$  = factors (independent variables) under investigation. These are also denoted as  $k_1, k_2, k_3$  in the polynomial (1.11) and in the transformed equation (1.4)
- $k_1, k_2, k_3$  = quantitative levels of the factors 1, 2, 3

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**NOMENCLATURE**

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$D_e$	=	effective diffusion coefficient, $\frac{\text{cm.}^2}{\text{min.}}$
$D$	=	diffusion coefficient, $\frac{\text{cm.}^2}{\text{min.}}$
$H$	=	Henry's law constant
$K$	=	chemical rate constant, $\frac{1}{\text{min.}}$
$k_L, k_L'$	=	mass transfer coefficient, $\frac{\text{cm.}}{\text{min.}}$
$k_L''$	=	volume mass transfer coefficient, $\frac{1}{\text{min.}}$
$k_M$	=	constant defined by Equation (4.15)
$N_A$	=	moles of $\text{CO}_2$ diffusing per unit time, $\frac{\text{gm.mole}}{\text{min.}}$
$n_A$	=	moles of $\text{CO}_2$ diffusing per unit time per unit surface, $\frac{\text{gm.mole}}{\text{min.cm.}^2}$
$m_{11}, m_{12},$ $m_{13}$	=	coefficients of Equation (5.9)
$p$	=	partial pressure of $\text{CO}_2$ , atm.
$R$	=	initial radius of naphtholate sphere, cm.
$r$	=	radius of unreacted naphtholate at any time $\theta$ , cm.
$r'$	=	reduced radial co-ordinate, $\frac{r}{R}$
$S$	=	center of the contour
$x$	=	fraction naphtholate reacting
$x'$	=	moles of 2-naphthol converted to BON acid per mole charged
$x''$	=	moles of BON acid formed per mole 2-naphthol charged

- $x_1, x_2, x_3$  = factors (independent variables) used in the polynomial equation of the response surface. These are also denoted by C, P, T in the three level factorial analysis  
 $X_1, X_2, X_3$  = transformed axes, Equation (5.4)  
 $x_{1S}, x_{2S}, x_{3S}$  = co-ordinates of the center, S  
 $y$  = response or the numerical result of an experiment; the dependent variable  
 $Y$  = response calculated from an equation assumed to fit the experimental conditions  
 $Y_S$  = response calculated from the experimental conditions at the 'center' of the contour  
 $Z_L$  = thickness of equivalent kerosene film, cm.

#### Greek letters

- $\alpha$  = constant of Equation (4.8)  
 $\rho$  = density of naphtholate particle,  $\frac{\text{gm. mole}}{\text{ml.}}$   
 $\theta$  = time, min.  
 $\tau$  = tortuosity factor  
 $\epsilon$  = volume void fraction



BIBLIOGRAPHY

Patents

1. Schmitt, G., U.S.P. 81,549 (1904); *Patent* 105.
2. Schmitt, G. and Folke, G., U.S.P. 84,447 (1905), *J. Pract. Chem.* 2, 53 (1906).
3. Schmitt, G., U.S.P. 110,595 (1907), *J. Pract. Chem.* 22 (1907).
4. Harlow, G., U. S. P. 75,754 (1904); *Patent* 100.
5. Murray, G. W., U.S.P. 1,450,000 (1923), *Ch. 11*, 1924 (1923).
6. Bellack, G. L., U.S.P. 1,470,000 (1923), *Ch. 11*, 2075 (1923).
7. Goss, W. W., U.S.P. 1,505,000 (1923), *Ch. 11*, 2120 (1923).
8. *Paracetin* form, *Wright, Bayer and Co.*, U.S.P. 125,000 (1901), *Patent* 15, 298.
9. *Paracetin* form, *J. S.*, U.S.P. 490,000 (1901), *Patent* 12, 298.
10. *Calcium, G. W.*, *Alison, A. S.*, and *Wright, G. W.*, U.S.P. 1,545,000 (1923).
11. *Wright, G. W.*, U.S.P. 1,570,000 (1923), *Ch. 11*, 2121 (1923).
12. *Wright, G. W.*, U.S.P. 1,700,000 (1927), *Ch. 11*, 2482 (1927).
13. *Wright, G. W.*, U.S.P. 1,725,000 (1927), *Ch. 11*, 2712 (1927).
14. *Wright, G. W.*, U.S.P. 1,750,000 (1927), *Ch. 11*, 2713 (1927).

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**BIBLIOGRAPHY**

---

BIBLIOGRAPHYPatents

- 1 Schmitt, R., G.P. 31,240 (1884); Frdl.1, 236.
- 2 Schmitt, R. and Kolbe, C., U.S.P. 350,468 (1886), J. Prakt. Chem. 2, 53 (1955).
- 3 Schmitt, R., U.S.P. 410,295 (1889), J. Prakt. Chem. 53 (1955).
- 4 Marasse, S., G. P. 78,708 (1894); Frdl.4, 152.
- 5 Shorey, E. C., U.S.P. 1,450,990 (1922), C.A. 17, 1968 (1923).
6. Wallach, R. N., U.S.P. 1,470,039 (1922), C.A. 17, 3879<sup>2</sup> (1923).
- 7 Cone, L. H., U.S.P. 1,503,984 (1923); C.A.18, 3193 (1924).
- 8 Farbenfabriken vorm. Friedr. Bayer and Co., G.P. 423,034 (1923). Frdl. 15, 295.
- 9 Farbenindustrie, I. G., G.P. 436,524 (1924); Frdl. 15, 298.
- 10 Calcott, W. S., Hitch, A. R., and Mahr, H. W., U.S.P. 1,648,839 (1924).
- 11 Franz Andre, U.S.P. 1,593,816 (1925), C.A.20, 3131 (1926).
- 12 Schwenk, E., U.S.P. 1,700,546 (1927), C.A.23, 3462 (1929).
- 13 Dieterle, P., U.S.P. 1,725,394 (1927), C.A.23, 4712 (1929).
- 14 Wacker, A., B.P. 384,619 (1932); C.A. 27, 1895, (1932); Fr. P. 738,815 (1932).

Patents

- 15 Brown and Co., B.P. 460,282 (1936).
- 16 Lecher, H. Z. and Sealera, M., U.S.P. 2,132,356, and 2,132,357 (1937).
- 17 Lecher, H. Z. and Sealera, M., B. P. 483,795 (1938); C. A. 32, 7067 (1938).
- 18 Cruikshank and Fairweather and Co., B. P. 511,393 (1939).
- 19 Silin, N. F. and Moschekinzeaya, N. K., U.S.S.R. 53,678 (1940); C. A. 35, 1414 (1941).
- 20 Sievie, G. and Co., Belg. 448,284 (1943), C.A. 42, 223a (1948).
- 21 Gershazen, G. I., U.S.S.R. 64,328 (1943); C.A. 40, 5072 (1946).
- 22 Siegle, G. and Co., G.P. 740,446 (1943); C.A. 39, 2296 (1945).
- 23 Wolthuis, E. and Shafer, H. M., U.S.P. 2,453,105 (1945).
- 24 Higgins, E. B., Wood, T., U.S.P. 2,531,380, and 2,534,022 (1948).
- 25 Hodges, F. J. and Nadler, M. S., U.S.P. 2,544,881 (1949).
- 26 Higgins, E. B., B.P. 647,997 (1950).
- 27 Fry, D. J. and Ilford Ltd., B.P.638,196 (1950); C.A. 44, 9481 (1950).
- 28 Farlwerke Hoechst A. G., B.P. 736,476 (1955); G.P.937, 957 (1956); C.A.50, 8736 (1956).
- 29 Farbenfabriken Bayer A. G., B.P. 774,837 (1957); Span. P. 228,428 (1956); C.A.51, 12145 (1957).
- 30 G.P. 941,429 (1956); U.S.P. 2,808,434 (1957); C.A. 53, 321 (1959).

Journals

- 31 B.I.O.S. 986 Vols. 1 and 2.
- 32 Tijmastra, Sr., Ber. 39, 16 (1906).

Journals

- 33 Wiebe, R., Goddy, V. S. and Heins, C., Ind. Eng. Chem. 24, 823 (1924).
- 34 Schwenk, E., Chem. Ztg. 53, 297 (1929).
- 35 Karpukhin, P. P. and Khusid, I. E., Ukrain Chem. J. 10, 375 (1935); C.A. 30, 2191 (1936).
- 36 Chem. Abst. 33, 72944 (1939).
- 37 Fuson, R. C. and McKeever, C. H., J. Am. Chem. Soc. 62, 999 (1940).
- 38 Gershzon, G. I., J. Gen. Chem. U.S.S.R. 13, 68 (1943); C.A. 38, 1219 (1944).
- 39 Gilman, H., Arntzen, C. E. and Webb, F. J., J. Org. Chem. 10, 374 (1945).
- 40 Cameron, D., Jesken, H. and Baine, O., J. Org. Chem. 15, 233 (1950).
- 41 Box, G. E. P., and Wilson, K. B., J. Royal Statistical Soc. series B, Vol.13 (1951).
- 42 Hales, J. L., Jones, J. I. and Lindsey, A. S., J. Chem. Soc. 3145 (1954).
- 43 Baine, O., Adamson, G. F., Barton, J. W., Fitch, J. L., Swayampati, D. R. and Jeskey, H., J. Org. Chem. 19, 510 (1954).
- 44 Von Seidel, F., Wolf, L. and Krause, H., J. Prakt. Chem. (4), 2, 53 (1955); C.A. 54, 443f (1960).
- 45 Von Lecher, H. Z. and Scalera, M., J. Prakt. Chem. (4), 3, 232 (1956).
- 46 Lindsey, A. S. and Jeskey, H., Chem. Rev. 57, 583 (1957).
- 47 Chem. Abst. 52, 13795 (1958).
- 48 Bijawat, H. C., Kunte, M. V. and Doraiswamy, L. K., Chem. Eng. Prog. Vol. 55, No.10, 80 (1959).

Journals

- 49 Chem. Abst. 54, 1462 (1960).
- 50 Chem. Abst. 55, 27904 (1961); G.P. 1,089,102 (1960).
- 51 Narsimhan, G., Chem. Eng. Sci., 16, 7 (1961).
- 52 Kawasaki, E., Sansranite, J., Walsh, T. J., Am. Inst. Chem. Eng. J., 8, 48 (1962).
- 53 Sharma, M. M. and Dankwerts, P. V., Chem. Eng. Sci. Vol.19, 991 (1964).
- 54 Phadtare, P. G. and Doraiswamy, L. K., Ind. Eng. Chem. Vol.4, 274 (July 1965).
- 55 Massoth, F. E., Ind. Eng. Chem. Vol. 5, 351 (July 1966).
- 56 Kothari, P. J. and Sharma, M. M., Chem. Eng. Sci., Vol. 21, 391 (1966).
- 57 Chem. Abst. 61, 833 (1965).
- 58 Chem. Abst. 62, 1796f (1966).

Books

- 59 Allen's Commercial Organic Analysis, Vol.3, J. and A. Churchill, London (1925).
- 60 Kolthoff, I. M. and Belcher, R., "Volumetric Analysis," Interscience Publishers, Inc., New York (1947).
- 61 Hougen, O. A. and Watson, K. M., "Chemical Process Principles," Part III, John Wiley and Sons, Inc., London (1947).
- 62 Vogel, A. I., "Elementary Practical Organic Chemistry," Longmans Green and Co., New York (1948).
- 63 Mitchell, J. and Smith, D. M., "Aquametry" Chemical Analysis, Vol.V, Interscience Publishers, Inc., New York (1948).

Books

- 64 Fierz-David and Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publishers, Inc., New York (1949).
- 65 Venkataraman, K., "Chemistry of Synthetic Dyes," Vol. I, Academic Press, New York (1952).
- 66 Davies, O. L., "The Design and Analysis of Industrial Experiments," Oliver and Boyd, London (1954).
- 67 Brooks, B. T., Boord, C. E., Kurtz, Jr., S. S. and Schmerling, L., "The Chemistry of Petroleum Hydrocarbon," Vol. I, Reinhold Publishing Corporation, New York (1955).
- 68 Levenspiel, O., "Chemical Reaction Engineering," John Wiley and Sons, Inc., New York (1962).
- 69 Vaidyanathan, K., Ph.D. thesis entitled "A kinetic study of the catalytic oxidation of benzene," submitted to the University of Bombay (1967).

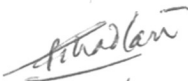


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