A THESIS SUBMITTED TO THE
UNIVERSITY OF BOMBAY
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

BY
RAGHUNATH VITHAL CHAUDHARI

NATIONAL CHEMICAL LABORATORY
POONA (INDIA)
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STUDIES IN GAS - LIQUID REACTIONS

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Statement Required to be Submitted Under Section 0.413 of the Ordinance Relating to the Ph.D. Degree

1. The present thesis is based entirely on the experimental work carried out by me under the guidance of Dr. L. K. Doraiswamy.

2. The literature concerning the problem investigated has been surveyed, and all the necessary references are given in the thesis.

3. Acknowledgement has been made wherever the work presented is based on the results of other workers.

[L. K. Doraiswamy]
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Poona
September 1973

STUDIES IN GAS-LIQUID REACTIONS

Thesis submitted by Raghunath V. Chaudhari for the
degree of Doctor of Philosophy

The following papers based on the material presented in the thesis have either been published or accepted for publication:

1. Physicochemical properties in the reaction of ethylene and hydrogen chloride in liquid media:
   R. V. Chaudhari and L. K. Doraiswamy, J. Chem. and Eng. Data, 1972 17 [4] 428
2. Absorption of PH_3 in an aqueous solution of formaldehyde and hydrochloric acid;
   R. V. Chaudhari and L. K. Doraiswamy, Chem. Eng. Sci., accepted for publication [in press]
3. Simultaneous absorption of ethylene and hydrogen chloride in nitrobenzene medium containing dissolved catalyst: formation of ethyl chloride:
   R. V. Chaudhari and L. K. Doraiswamy, Chem. Eng. Sci., accepted for publication [in press]
4. Simultaneous absorption of two gases which react between themselves in a liquid: an approximate solution:
   R. V. Chaudhari and L. K. Doraiswamy, Chem. Eng. Sci., accepted for publication [in press]

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September 1973

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1. INTRODUCTION

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SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

There are several gas-liquid reactions of industrial importance for which no published information is available which can provide a rational basis for the design of commercial reactors. While this is true of systems in which absorption of a single gas in a liquid followed by a chemical reaction is involved, it is even more true for systems not falling in this simple category. Some typical examples are: two gases dissolving in a liquid and reacting between themselves; two gases dissolving in a liquid and reacting with an active component in the liquid phase; reaction between a gas and two liquid phase components; and absorption of one or more gases followed by a complex chemical reaction.

The present investigation was undertaken with the objective of studying three such special systems, two of them involving experimental studies for specific reactions and the third a theoretical analysis of a complex scheme. The work may therefore be divided into three parts:

I. Studies in the simultaneous absorption of ethylene and hydrogen chloride in a medium of nitrobenzene [containing dissolved aluminium chloride] to produce ethyl chloride: this reaction between two gases in a liquid medium is of great industrial value.

II. Studies on the absorption of phosphine in an aqueous solution of hydrochloric acid and formaldehyde to produce tetrakis-4-hydroxymethyl phosphonium chloride [THPC]: THPC is used in the fire proofing of textiles and is therefore of commercial significance, and the system itself provides an example of an interesting case in which a single gas dissolves and reacts with two liquid phase components.

III. Theoretical analysis of a complex reaction of the type:

$$A + B \rightarrow X \qquad [1]$$

$$B + C \rightleftharpoons E + F \qquad [2]$$

$$A + E \rightarrow Y \qquad [3]$$

In this scheme two gases A and B dissolve in a liquid C and react to give product X. Simultaneously dissolved B reacts with C to give products E and F, one of which [E] reacts with the second dissolved gas A to give product Y. The chlorohydrination of olefins in which chlorine and olefin are dissolved in water to produce chlorohydrin [Y] with the corresponding dichloride [X] as the byproduct provides a striking example of industrial importance conforming to this scheme. The theoretical analysis of this system was taken up in two parts:

[a] Two gases dissolving in a liquid and reacting between themselves: the first reaction of the complex scheme corresponds to this case, the theoretical analysis of which was undertaken with the objective of improving upon the existing methods of analysing such a reaction.

[b] Analysis of the complex scheme: using the analysis

of reaction [1] of the complex scheme mentioned under [a], a complete theoretical analysis was attempted of the complex reaction, with the object of developing expressions for enhancement during absorption.

I. SIMULTANEOUS ABSORPTION OF ETHYLENE AND HYDROGEN CHLORIDE IN NITROBENZENE MEDIUM: FORMATION OF ETHYL CHLORIDE

The reaction between ethylene and hydrogen chloride to ethyl chloride is carried out industrially either in a medium of ethyl chloride itself [in which case the reaction would be under a pressure of several atmospheres as ethyl chloride has a boiling point of 12°C], nitrobenzene, or ethylene dichloride. In the present study investigations were restricted to two liquid media, nitrobenzene and ethylene dichloride.

As a first step in the experimental study of this reaction, the diffusivities and solubilities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were determined at different temperatures at atmospheric pressure. The solubilities of ethyl chloride in nitrobenzene and of hydrogen chloride in nitrobenzene [containing aluminium chloride] were also determined. Three different empirical equations were used to correlate the data. The recommended equation is of the form:

$$\ln X = a + b \ln T \qquad [4]$$

where X represents either diffusivity or solubility, T is the absolute temperature, and a, b are arbitrary constants.

The simultaneous absorption and reaction of ethylene and hydrogen chloride in a medium of nitrobenzene containing dissolved aluminium chloride [catalyst] was then studied. The experimental results indicated that the absorption occurs in the kinetic regime. The reaction was found to be first-order with respect to both the reactants [ethylene and hydrogen chloride] as well as the catalyst. The rate constants calculated were 1.16×10^5, 2.80×10^5, 6.11×10^5 and 1.44×10^6 $[cm^3/g\ mole]^2/sec$ at 30, 40, 50 and 60°C respectively, and the activation energy 16600 cal/g mole. The final rate equation obtained is:

$$R_A = 1.246 \times 10^{17}\ e^{-\frac{16600}{RT}}\ A^* B^* C_o \qquad [5]$$

where R_A is the rate of reaction $[g\ mole/cm^3\ sec]$; A^*, B^* the concentrations of ethylene and hydrogen chloride in nitrobenzene $[g\ mole/cm^3]$; C_o the concentration of the catalyst $[g\ mole/cm^3]$; R the universal gas constant $[cal/g\ mole\ ^oK]$; and T the absolute temperature.

II. ABSORPTION OF PHOSPHINE IN AN AQUEOUS SOLUTION OF FORMALDEHYDE AND HYDROCHLORIC ACID

The absorption of phosphine in an aqueous solution of formaldehyde and hydrochloric acid takes place according to the following reaction to give tetrakis-4-hydroxymethyl phosphonium chloride [THPC]:

$$PH_3 + HCl + 4\ HCHO \rightarrow [CH_2OH]_4\ PCl \qquad [6]$$

This reaction was found to be kinetically controlled in the range of variables studied, being first-order with respect to phosphine and formaldehyde and approximately half-order with respect to hydrochloric acid. The reaction rate constants calculated were 2.34×10^2, 5.88×10^2, 1.84×10^3 and 4.98×10^3 $[\mathrm{cm}^3/\mathrm{g\ mole}]^{1.5}/\mathrm{sec}$ at 4, 13, 27 and 40°C, respectively, and the activation energy 14740 cal/g mole. The final rate equation is:

$$R_A = 8.57 \times 10^{13} \; e^{-\frac{14740}{RT}} \; A^* B_o^{0.5} \; C_o \qquad [7]$$

where R_A is the reaction rate [g mole/cm^3 sec]; and A^*, B_o, C_o the concentrations of phosphine, HCl and HCHO, respectively, in the bulk [g mole/cm^3].

III. THEORETICAL STUDIES IN GAS-LIQUID REACTIONS

[a] An approximate solution to the absorption and reaction of two gases in a liquid:

The problem of simultaneous absorption of two gases which react between themselves has been analysed by previous workers using both the penetration and film theories. In obtaining an analytical solution, a linear profile for the gaseous species in the film has been assumed which is unrealistic. In the present investigation an analytical solution is presented on the basis of a nonlinear profile which conforms very closely to the numerical solution. The approximations suggested are:

$$A = A^* \; e^{-\phi_A \, x/\delta - x} \qquad [8]$$

$$B = B^{*} e^{-\phi_B x/\delta - x} \qquad [9]$$

The following expressions for the enhancement factors ϕ_A and ϕ_B have been obtained:

$$\phi_A - \phi_B \frac{B^{*}}{A^{*}} \frac{D_B}{D_A} \frac{Z_A}{Z_B} = 1 - \frac{B^{*}}{A^{*}} \frac{D_B}{D_A} \frac{Z_A}{Z_B} \qquad [10]$$

and

$$\phi_A = \frac{M}{\phi_A + \phi_B} \qquad [11]$$

where

$$M = \frac{4}{[m+1][n+1]} \frac{Z_A \, k \, A^{*\,m-1} \, B^{*\,n} \, \delta^2}{D_A} \qquad [12]$$

In these equations A, B represent the concentrations of the two gaseous species [g mole/cm^3]; A^{*}, B^{*} the concentrations of A and B at the gas-liquid interphase [g mole/cm^3]; ϕ_A, ϕ_B the enhancement factors; D_A, D_B the diffusion coefficients [cm^2/sec]; Z_A, Z_B the stoichiometric coefficients of A and B respectively; x the distance from the interphase [cm]; δ the film thickness [cm]; and k the reaction rate constant $[(\text{cm}^3/\text{g mole})^{m+n-1} \text{sec}^{-1}]$.

In order to verify the applicability of the approximate solution, it was compared with the numerical solution and was found to be in good agreement, the maximum error being less than 15% for values of $\sqrt{M} < 3$. In the high enahncement region corresponding to high values of $\sqrt{M}$, in the absence of a numerical solution for direct comparison, the validity of the approximation was indirectly established by applying it to the case of a single gas reacting with the liquid in a pseudo mth order regime. It was found that the expression thus obtained was identical with that derived by Danckwerts starting from the basic mass balance equation. Interestingly, in view of the identity between the two expressions, the conclusion emerges that the approximation is quantitatively valid at high values of $\sqrt{M}$.

The approximation suggested can be used in practical computations not only because of its validity at all values of $\sqrt{M}$, but also because it may be regarded as providing a logical extension of the pseudo mth order case for a single gas to the mnth order for two gases dissolving and reacting among themselves.

[b] Absorption accompanied by a complex chemical reaction:

The problem of simultaneous absorption of two gases accompanied by a complex chemical reaction was considered, the reaction scheme mentioned earlier being used. Several industrially important reaction systems follow this complex reaction scheme, and hence a theoretical analysis of such a scheme would be important for design purposes. As already mentioned, one such system is the simultaneous absorption of an olefin [propylene] and chlorine in water:

$$\underset{[A]}{C_3H_6} + \underset{[B]}{Cl_2} \rightarrow \underset{[X]}{C_3H_6Cl_2} \qquad [13]$$

$$\begin{array}{ccccccc} Cl_2 & + & H_2O & \rightleftharpoons & HOCl & + & HCl \\ [B] & & [C] & & [E] & & [F] \end{array} \qquad [14]$$

$$\begin{array}{ccccc} C_3H_6 & + & HOCl & \rightarrow & C_3H_7OCl \\ [A] & & [E] & & [Y] \end{array} \qquad [15]$$

In this analysis, expressions for the enhancement factors ϕ_A and ϕ_B for the two gaseous species A and B were derived for various cases from the basic mass balance equations. In obtaining these solutions the approximations suggested in section [a] were used for the concentration profiles of A and B in the film. It was also assumed that the reactions of A and B are complete in the film. Expressions for ϕ_A and ϕ_B were obtained in terms of the reaction and diffusion parameters and the results presented in the form of plots of ϕ_A or ϕ_B vs. $\sqrt{M}$ [where M is a dimensionless model parameter]. Some aspects of the simultaneous absorption of propylene and chlorine have also been discussed based on this model.

PART - I

SIMULTANEOUS ABSORPTION OF ETHYLENE AND HYDROGEN CHLORIDE IN NITROBENZENE MEDIUM: FORMATION OF ETHYL CHLORIDE

CHAPTER - 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 MANUFACTURE OF ETHYL CHLORIDE

1.1.1 Historical

Valentine [25] in the fifteenth century announced the production of ethyl chloride by reacting hydrochloric acid and ethyl alcohol. Glauber [25] in 1648 prepared it by digesting rectified spirit of wine with zinc chloride. Reynoso [25] in 1856 produced a mixture of ethyl chloride and diethyl ether by boiling a mixture of alcohol and hydrochloric acid to 100°C in a sealed tube. But ethyl chloride acquired importance as a large tonnage chemical only in 1922 with the beginning of the manufacture of tetraethyl lead in the United States. Its use as a starting material for tetraethyl lead made it an automative chemical and its subsequent expansion has been linked with the growth of the automobile industry. Large scale production of ethyl chloride was first undertaken in the United Kingdom during World War II to meet the demands of tetraethyl lead manufacture. There are three industrial processes for the manufacture of ethyl chloride: catalytic reaction of ethyl alcohol with hydrochloric acid, chlorination of ethane and hydrochlorination of ethylene. It is also produced by the reaction of diethyl sulfate with hydrogen chloride.

1.1.2 Reaction of ethyl alcohol with hydrochloric acid

For many years this was the only established technical process for the manufacture of ethyl chloride, but due to the high cost of ethyl alcohol this route has been replaced by the other two, and by 1955 about 90% of ethyl chloride was being produced by the latter processes. In this process, hydrochloric acid and alcohol are reacted in the presence of a metallic chloride catalyst at 110-140°C, and the ethyl chloride and water are continuously distilled off from the concentrated solution of the catalyst. The reaction may be represented by:

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O \qquad [1.1]$$

1.1.3 Chlorination of ethane

Chlorination may be carried out thermally, catalytically or photochemically. Photochemical chlorination is not used in industry. Thermal chlorination is carried out in a fluid bed of finely divided solid particles at 250-500°C. Reaction may also be carried out under pressure, e.g. 30 psi. Catalytic chlorination is generally carried out in the presence of metal chlorides [18,33] or crystalline carbon [graphite] [23].

1.1.4 Hydrochlorination of ethylene

This reaction is carried out in the presence of a Friedel-Craft catalyst, either in the vapour phase or in the liquid phase:

$$C_2H_4 + HCl \rightarrow C_2H_5Cl - 13.4 \text{ kcal} \qquad [1.2]$$

Ethyl chloride being a low boiling liquid, this reaction is carried out under pressure, or at atmospheric pressure and very low temperatures. In recent years a combination of this and the ethane chlorination process is being used, as the hydrogen chloride from ethane chlorination can be subsequently reacted with ethylene to produce ethyl chloride. This has been found to be more economical than either of the processes operated individually.

1.1.5 Ethyl chloride from diethyl sulfate

Several processes have been proposed for the manufacture of ethyl chloride based on the reaction:

$$[C_2H_5O]_2\ SO_2 + 2\ HCl \rightarrow 2\ C_2H_5Cl + H_2SO_4 \qquad [1.3]$$

According to a British patent [14] ethylene is reacted with sulfuric acid in the presence of an antimony, tin or bismuth catalyst, to give diethyl sulfate, which is subsequently reacted with hydrochloric acid at 40-110°C to give ethyl chloride; but none of the diethyl sulfate processes has so far become industrially established.

1.2 INDUSTRIAL APPLICATIONS OF ETHYL CHLORIDE

The principal use of ethyl chloride is in the manufacture of tetraethyl lead by reacting with lead sodium alloy:

$$4\ Pb\ Na + 4\ C_2H_5Cl \rightarrow Pb[C_2H_5]_4 + 3\ Pb + 4\ NaCl \qquad [1.4]$$

Ethyl cellulose which is used mainly in the plastics and lacquer industries is produced by reacting ethyl chloride with soda cellulose.

Ethyl chloride is used to some extent as an ethylating agent in the synthesis of dyestuffs and fine chemicals.

Limited quantities of ethyl chloride are also used in the production of aerosols, as refrigerent, and for inducing local and general anaesthesia.

For many years ethyl chloride has also been used as the marking substance at an electric power plant on the island of Ischia, in the Bay of Naples.

1.3 GENERAL PROCESSES

The processes for ethyl chloride through hydrochlorination of ethylene in liquid media are briefly discussed below.

In 1934 Tulleners et al [45] produced ethyl chloride by absorbing ethylene and hydrogen chloride gases in a solution of anhydrous aluminium chloride in ethyl chloride at -78°C and atmospheric pressure and claimed a yield of 99.7%. Chamberlain et al [8] produced ethyl chloride by reacting ethylene and hydrogen chloride in a solution of ethyl sulfuric acid containing a bismuth catalyst at atmospheric pressure. Rudkovskii et al [35] studied the reaction in a solution of aluminium chloride in ethyl chloride at -78 to -12°C under atmospheric pressure and obtained 94% conversion of ethylene to ethyl chloride. Later Pierce [32] suggested 1,1,2-trichloroethane as a solvent and studied the reaction at -5 to 55°C at atmospheric pressure using anhydrous aluminium chloride as catalyst. Rudkovskii [36] also claimed an yield of 95% for ethyl chloride and carried out the reaction in ethyl chloride medium at -55 to -12°C under atmospheric pressure using anhydrous aluminium chloride catalyst. In 1946, Bond et al [5] suggested the use of zirconium tetrachloride or zirconium oxychloride as catalyst for this reaction and obtained 35% conversion of ethylene at atmospheric pressure and 130°C; these authors used nitrobenzene as solvent. Fasce et al [13] claimed an yield of 73.7% and carried out the reaction at 12.4°C in a solution of ethyl chloride containing dissolved aluminium chloride as catalyst. Later Axe et al [3] suggested the use of a 85% solution of orthophosphoric acid [H_3PO_4] saturated with BF_3 as catalyst and carried out the reaction in water at 46-55°C and 700 psi obtaining 95% conversion of ethylene to ethyl chloride. Padgitt et al [30] used gallium trihalides [$GaCl_3$, GaI_3, GaF_3, $GaBr_3$] as catalysts for this reaction and obtained yields of 85% at -20°C and atmospheric pressure. In 1950, Bond et al [6] claimed the use of thorium oxychloride as catalyst for this reaction, whereas Hanford et al [16] suggest a peroxygen catalyst. An yield of 100% also has been claimed [Huntress et al, 20] by using anhydrous bismuth trichloride as catalyst in a medium of ethyl chloride at -78°C and atmospheric pressure. Hatch et al [17] have carried out the reaction at 35-38°C and 40 psi by using anhydrous aluminium chloride catalyst in ethyl chloride medium to give an yield of 90%. These authors also suggest the use of high boiling chlorinated solvents instead of ethyl chloride. Kobler et al [26] and O'Connell [29] have claimed a process for ethyl chloride using anhydrous aluminium chloride as catalyst in ethyl chloride medium. Hurt [21] claimed a process for ethyl chloride using anhydrous ferric chloride as catalyst in ethyl chloride medium with 99.6% yield of ethyl chloride at 65°C and 185 psig. Later Brown [7] obtained an yield of 98.5% by carrying out the reaction in a solution of ethyl chloride containing dissolved aluminium chloride as catalyst at 10°C and atmospheric pressure. All these processes have been presented in a tabular form in Table 1.1.

It can be concluded from the summary of the processes discussed above that the Friedel-Craft catalyst, anhydrous aluminium chloride, is the most suitable catalyst for the reaction of ethylene and hydrogen chloride. Ethyl chloride itself is a good solvent, but in order to avoid high pressure or low temperature operations, higher boiling solvents such as nitrobenzene or chlorohydrocarbons [1,1,2-trichloroethane] may be used.

1.4 KINETICS AND MECHANISM

In the literature to date, there is no information available on the kinetics and mechanism of this reaction, except that Terakawa [43] studied the radiation induced addition of hydrogen chloride to ethylene and an apparent activation energy of 6.94 kcal/g mole of ethyl chloride has been reported.

TABLE 1.1

SUMMARY OF THE LITERATURE ON THE CATALYTIC ETHYLATION OF HYDROGEN CHLORIDE TO ETHYL CHLORIDE IN A LIQUID MEDIUM

S.No.	Year	Catalyst used	Solvent	Temperature °C	Pressure	Yield	Conversion	Reference
1	2	3	4	5	6	7	8	9
1	1934	Anhydrous $AlCl_3$	Ethyl chloride	-78	atm.	99.7%	-	45
2	1935	Bismuth catalyst	Ethyl sulfuric acid	-	atm.	-	-	8
3	1936	Anhydrous $AlCl_3$	Ethyl chloride	-78 to -12	atm.	-	$[C_2H_4]$ 94%	35
4	1936	Anhydrous $AlCl_3$	1-1-2 trichloroethane	-5 to 55	atm.	-	-	32
5	1937	Anhydrous $AlCl_3$	Ethyl chloride	-55 to -12	atm.	95%	-	36
6	1946	Zirconium tetrachloride or zirconium oxychloride	Nitrobenzene	130	atm.	-	$[C_2H_4]$ 35%	5
7	1948	Anhydrous $AlCl_3$	Ethyl chloride	12.4	-	73.7%	-	13
8	1948	85% H_3PO_4 Satd. with BF_3	Water	46-55	700 ob	-	$[C_2H_4]$ 95%	3

TABLE 1.1 CONTINUED

1	2	3	4	5	6	7	8	9
9	1950	Gallium trihalides	Ethyl chloride	-20	atm.	85%	-	30
10	1950	Thorium oxychloride	-	-	-	-	-	6
11	1950	Peroxygen catalyst	-	-	High pressure	-	-	16
12		$AlCl_3$ or $BiCl_3$	Ethyl chloride	-78	atm.	100%	-	20
13	1955	Anhydrous $AlCl_3$	Ethyl chloride or high boiling chlorinated solvent	35 to 38	40 psi	90%	-	17
14	1957	Anhydrous $AlCl_3$	Ethyl chloride	51	125 lb/sq.in	-	-	26
15	1958	Anhydrous $AlCl_3$	Ethyl chloride	-	-	-	-	29
16	1966	$FeCl_3$	Ethyl chloride	65	185 psig	99.6%	-	21
17	1967	Anhydrous $AlCl_3$	Ethyl chloride	10	atm.	98.5%	-	7

1.5 SCOPE OF THE PRESENT WORK

From the available literature on the catalytic ethylation of hydrogen chloride to ethyl chloride in a liquid medium as presented in the foregoing sections it can be seen that much of the information is patented and no data are reported on the absorption and reaction of ethylene and hydrogen chloride in a liquid medium. No attempt has been made to determine the controlling mechanism in this reaction which could be used as the basis in the design of plants for ethyl chloride.

The present work was therefore undertaken with the following objectives:

[a] to experimentally determine the physicochemical properties such as solubilities and diffusivities of the systems involved in order to provide accurate data for the kinetic analysis as under [b]; and

[b] to study the mechanism of simultaneous absorption of ethylene and hydrogen chloride in a medium of nitrobenzene and ethylene dichloride [containing dissolved aluminium chloride] to produce ethyl chloride and establish the kinetics of this industrially important system.

CHAPTER - 2

PHYSICOCHEMICAL DATA FOR THE SYSTEM

CHAPTER 2

PHYSICOCHEMICAL DATA FOR THE SYSTEM

2.1 INTRODUCTION

Physicochemical properties such as diffusivities and solubilities are very necessary in any study of gas-liquid reactions, and are also important in the theoretical understanding of the liquid state and solutions. Thus the diffusion coefficients and solubilities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride should be known in order to carry out a detailed analysis of the kinetics of the ethylation of hydrogen chloride to ethyl chloride in the two liquid media [nitrobenzene and ethylene dichloride].

Many empirical correlations [1,42,46] have been proposed for estimating the diffusion coefficients of gases in liquids, but all these are of uncertain accuracy and the estimated values cannot be relied upon fully. The experimental determination of the diffusion coefficients of sparingly soluble gases into liquids is a problem of considerable technical difficulty and so far there is no method which is of general applicability. Most of the theories too lack the generality required for their application to a wide variety of systems.

Gas-liquid mass transfer can only be by diffusion into the liquid from the interface, so that the phenomenon of diffusion is central to the discussion of gas-liquid reactions. Hence it was decided to experimentally determine these data for the system of simultaneous absorption of ethylene and hydrogen chloride in liquid media to produce ethyl chloride.

Solubilities are also equally important in studying gas-liquid reactions. Considerable work has been reported on the solubilities of gases in liquids which include theories, empirical correlations, data on different systems, and a variety of apparatus, and these have been reviewed by Battino et al [4]. The solubility studies were carried out in the same reactor which was subsequently used for studying the kinetics of ethylation of hydrogen chloride to ethyl chloride in a liquid medium. With nitrobenzene as solvent, solubilities of hydrogen chloride were also determined at various concentrations of aluminium chloride [which is used as catalyst in the ethylation reaction]. The solubility of ethyl chloride in nitrobenzene was also determined.

2.2 DIFFUSIVITIES

2.2.1 Choice of method

The diffusion of sparingly soluble gases into liquids can be studied in two ways: [a] by measuring the transfer of the gas in the liquid phase, and [b] by measuring the concentration gradients in the diffusing system. The important features in any method are the accurate measurement of the transport of very small quantities of the gas and prevention of convection currents set up by the density changes accompanying that movement. Several methods and apparatus have been used, such as: diaphragm cells, gas absorption in steady state laminar flow systems [jets, spheres, etc.], gas absorption in unsteady state quiescent systems, dropping mercury electrode, Ringbom apparatus, and interferometric techniques. All these methods have been reviewed by Himmelblau [19]. The most commonly used methods are: unsteady state methods, and those based on the diaphragm cell [steady state methods].

In the diaphragm cell method, the dissolved gas is allowed to diffuse through the pores of a sintered disc into a solution of lower concentration. The concentration on both sides of the disc are maintained constant, and the rate of transfer under steady conditions is found by measuring the changes in the concentrations on each side of the disc. A good evaluation of this method is given by Gordon [15]. This method has been used most successfuly for electrolytes where very small concentrations can be determined accurately by chemical means, but is not suitable for sparingly soluble gases due to the difficulty in determining very small quantities accurately which can also be lost during sampling.

In the unsteady state methods there is the major problem of eliminating convection currents. Convection is usually prevented by putting the denser liquid underneath the lighter one or by adding an electrolyte to one solution to increase its density, on the assumption that the electrolyte has little effect on the diffusion of the gas. The more general way of eliminating convection is to enclose the liquid in a capillary, as in the Ringbom apparatus [34] which provides a simple and convenient method of determining diffusion coefficients of sparingly soluble gases into liquids.

This method has been selected in the present work for determining the diffusion coefficients of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride.

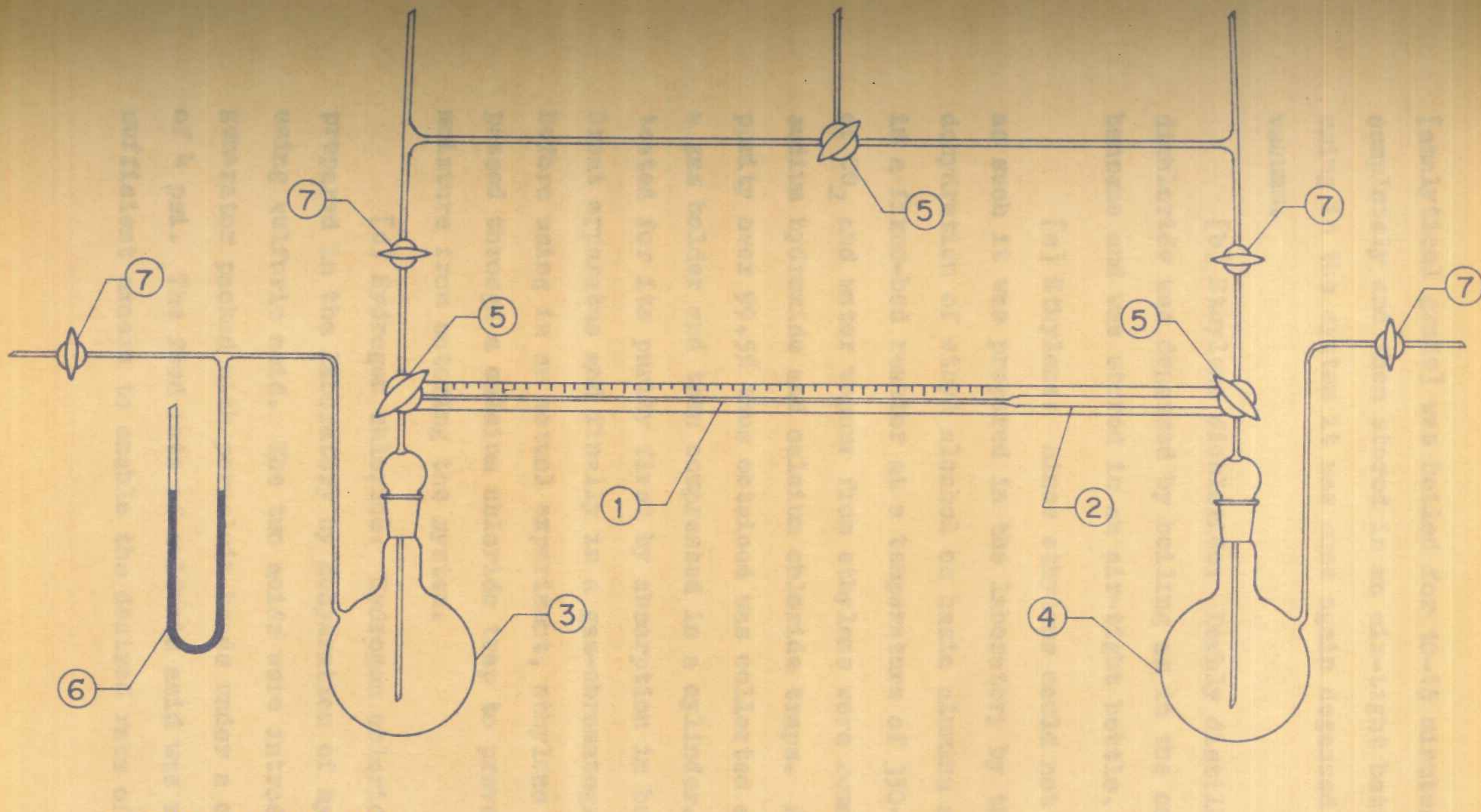
2.2.2 Apparatus

A modified version of Ringbom's apparatus [39] was used [Figure 2.1]. It consists of two capillaries fused together and connected to two different reservoirs through three-way capillary stopcocks. The fine capillary was 40 cm and the other 10 cm in length. The area of cross section of the fine capillary was 1.42×10^{-2} cm^2 and that of the other 3.41×10^{-2} cm^2. The reservoir flasks were of 250 ml capacity each. The side arm of the left reservoir was connected to a Hg manometer, the other end of which was closed. The fine capillary was graduated in mm and was calibrated before fusing. One more capillary cell with fine and coarse capillary cross sections of 1.25×10^{-2} and 6.87×10^{-2} cm^2, respectively, was fabricated.

This apparatus was tested by studying known systems, such as CO_2-water, H_2S-water, O_2-water, and Cl_2-water before using for the unknown systems.

2.2.3 Materials

[a] Nitrobenzene: Pure vacuum distilled nitrobenzene



1 FINE CAPILLARY
2 COARSE CAPILLARY
3 RESERVOIR FOR GAS-SATURATED LIQUID
4 RESERVOIR FOR PURE LIQUID (GAS FREE)
5 THREE-WAY STOPCOCK
6 Hg MANOMETER
7 ONE-WAY STOPCOCK

FIG. 2·1: APPARATUS FOR DETERMINING THE DIFFUSION COEFFICIENTS OF GASES IN LIQUIDS [analytical grade] was boiled for 10-15 minutes to degas it completely and then stored in an air-tight bottle. Before using in the system it was once again degassed by applying vacuum.

[b] Ethylene dichloride: Doubly distilled ethylene dichloride was degassed by boiling as in the case of nitrobenzene and was stored in an air-tight bottle.

[c] Ethylene: Since ethylene could not be obtained as such it was prepared in the laboratory by the catalytic dehydration of ethyl alcohol on basic alumina as catalyst in a fixed-bed reactor at a temperature of 350-390°C. Traces of CO_2 and water vapour from ethylene were removed by using sodium hydroxide and calcium chloride traps. Ethylene of purity over 99.5% thus obtained was collected over water in a gas holder and then compressed in a cylinder. The gas was tested for its purity first by absorption in bromine in an Orsat apparatus and finally in a gas-chromatographic apparatus. Before using in an actual experiment, ethylene was again passed through a calcium chloride trap to prevent traces of moisture from entering the system.

[d] Hydrogen chloride: Hydrogen chloride gas was also prepared in the laboratory by dehydration of hydrochloric acid using sulfuric acid. The two acids were introduced into a generator packed with porcelein beads under a constant pressure of 4 psi. The feed rate of sulfuric acid was maintained in sufficient excess to enable the desired rate of hydrogen chloride

gas to be obtained by adjusting the hydrochloric acid rate. Hydrogen chloride thus generated was passed through sulfuric acid and calcium chloride traps to remove moisture completely.

[e] Water: Doubly distilled [in glass] water was degassed by boiling for 10-15 minutes in a closed system under a slightly reduced pressure. This was introduced into the reservoir flasks while hot.

[f] Oxygen, chlorine, carbon dioxide, of purity more than 99.8% were used. Hydrogen sulfide gas of purity 99.5% was prepared by the well known Kipp's apparatus by reaction of ferrous sulfide and hydrochloric acid.

2.2.4 Experimental procedure

The procedure adopted was similar to that of Smith et al [39]. In between gas-saturated and gas-free solvent columns, a pure gas phase was maintained. The gas free solvent column was a dead-end column, whereas the gas-saturated solvent column was left confluent with the reservoir. As the gas diffused into the pure solvent, the gas saturated column moved [replacing the gas diffused] towards the pure solvent column. This displacement was measured as a function of time. The system was fully closed to prevent any effect of atmospheric fluctuations. During a run the thermostat maintained constant temperature to ± 0.05°C.

For analysis, the displacement of the free meniscus in cm was plotted as a function of $\sqrt{t}$, and by taking points beyond the initial equilibrium, we were able to determine the slope by the method of least squares. A plot of d vs $\sqrt{t}$ for a few systems is presented in Figure 2.2, while the experimental data are given in Appendix 1. In the initial part of the experiment, when the absorption rate is high, the interface conditions are uncertain and so the observations had to be made for a longer period.

The values of diffusion coefficients were calculated from the following equation of Stefan [40]:

$$D = \frac{\pi}{4\,\beta^2\,Q^2}\left(\frac{V}{\sqrt{t}}\right)^2 \qquad [2.1]$$

where

$$\beta = \alpha_T\left(\frac{T}{273}\right)\left(\frac{P}{760}\right) \qquad [2.2]$$

Values of α, the Bunsen absorption coefficient, required for calculating the diffusion coefficient of known systems were obtained from the International Critical Tables [22]; and those of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were calculated from the solubility data, discussed in the next section, as follows:

The Bunsen absorption coefficient α is defined as the volume of the gas, reduced to $0^{\circ}C$ and one atm, dissolved by unit volume of the solvent at the temperature of the experiment under a partial pressure of the gas at one atm. If V_o is the volume of the gas dissolved, reduced to STP, V_1 the volume of the solvent, and p the partial pressure of the gas in atm, then the Bunsen coefficient α is given by:

$$\alpha = \frac{V_o}{V_1 p} \qquad [2.3]$$

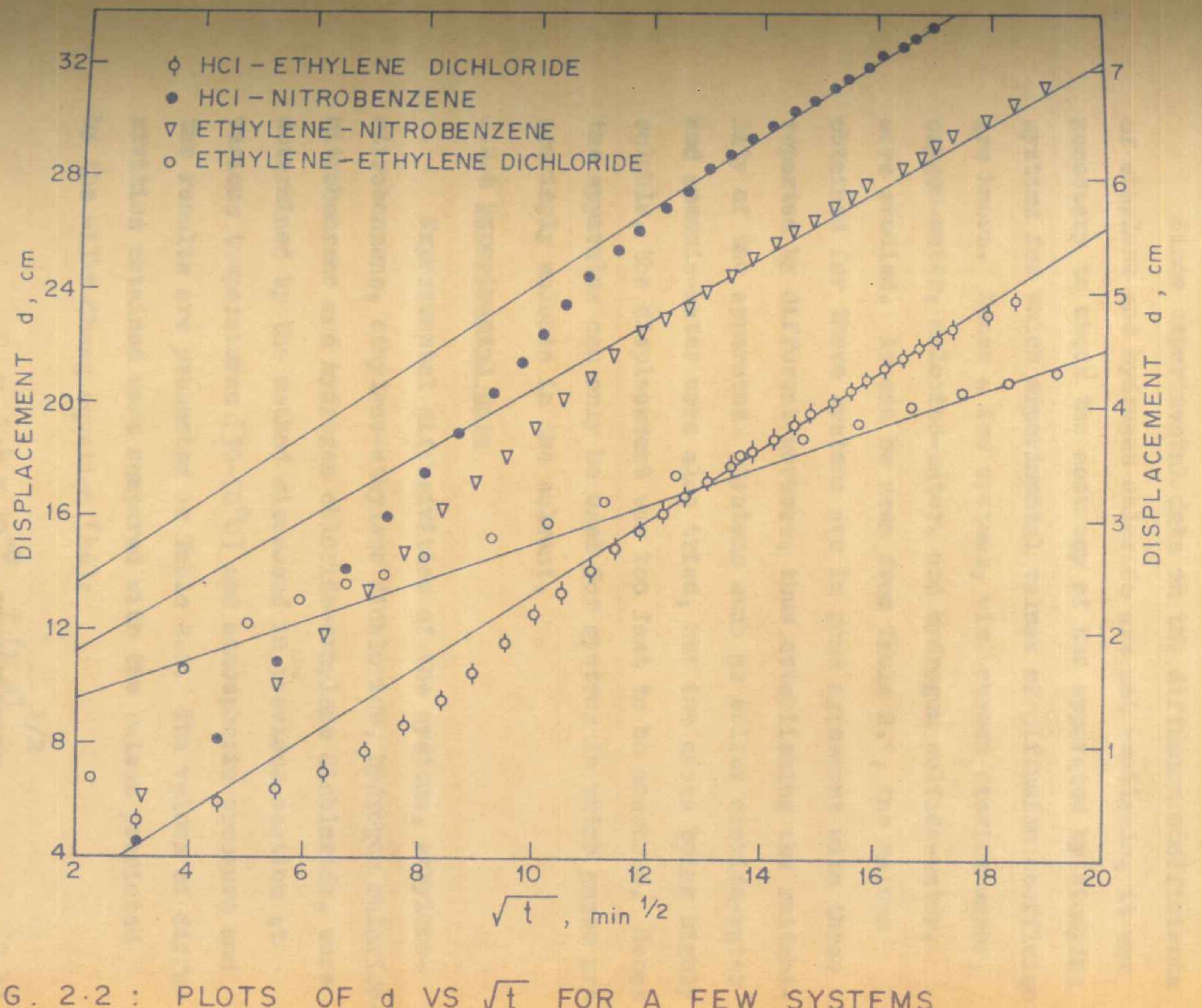


FIG. 2.2 : PLOTS OF d VS $\sqrt{t}$ FOR A FEW SYSTEMS

2.2.5 Test of apparatus

Since experimental data on the diffusion coefficients of ethylene and hydrogen chloride are not available, it was necessary to check the accuracy of the apparatus by studying systems for which experimental values of diffusion coefficients are known. Hence a few systems, viz. carbon dioxide-water, oxygen-water, chlorine-water, and hydrogen sulfide-water, were studied. As can be seen from Table 2.1, the values obtained for these systems are in good agreement with those reported by different workers, thus establishing the suitability of the apparatus. Systems such as sulfur dioxide-water and ammonia-water were also tried, but the gases being highly soluble, the displacement was too fast to be measured. Hence the apparatus can only be used for systems in which gases are sparingly soluble in the solvent.

2.2.6 Experimental data

Experimental diffusivities of the systems, ethylene-nitrobenzene, ethylene-ethylene dichloride, hydrogen chloride-nitrobenzene and hydrogen chloride-ethylene dichloride, were determined by the method discussed in the previous section at various temperatures [30-70°C] and atmospheric pressure and the results are presented in Table 2.2. The values of diffusivities obtained were compared with the values predicted by the Wilke-Chang equation [46]:

$$D = 7.4 \times 10^{-8} \frac{T\,[x\,M]^{1/2}}{\mu\,\nu^{0.6}} \qquad [2.4]$$

TABLE 2.1

EXPERIMENTAL VALUES OF THE DIFFUSION COEFFICIENT FOR KNOWN SYSTEMS [TEST OF THE APPARATUS]

System	Temperature ^oK	Experimental values obtained $D \times 10^5$	Experimental values reported $D \times 10^5$	Reference
CO_2-water	300.0	2.145	-	-
	298.0	-	1.90	47
	298.0	-	1.87	37
	303.0	-	2.29	31
	303.0	-	2.25	10
	303.0	-	2.15	42
Cl_2-water	303.0	1.593	1.62	28
	303.0	-	1.74	31
	298.0	-	1.89	10
O_2-water	303.0	2.903	-	-
	298.0	-	2.60	27
	298.0	-	2.42	10
H_2S-water	303.0	1.922	-	-
	289.0	-	1.77	12
	298.0	-	1.36	24

TABLE 2.2

EXPERIMENTAL VALUES OF DIFFUSION COEFFICIENTS

System	Temperature ^oK	Experimental value $D \times 10^5$, cm^2/sec	Values obtained by Wilke-Chang equation $D \times 10^5$, cm^2/sec
Ethylene-nitrobenzene	303.0	2.370	1.518
	313.0	2.715	1.834
	323.0	3.058	2.176
	333.0	3.290	2.564
Ethylene-1,2 ethylene dichloride	288.0	2.750	2.427
	292.0	3.350	2.565
	298.0	3.840	2.845
	303.0	4.110	3.090
Hydrogen chloride-nitrobenzene	299.0	1.750	1.963
	303.0	2.157	2.127
	313.0	2.380	2.571
	323.0	2.680	3.050
	331.5	2.920	3.594
Hydrogen chloride-1,2 ethylene dichloride	288.0	3.180	3.390
	298.5	3.890	3.970
	303.0	4.310	4.330

This is the most commonly used equation for predicting diffusivities of systems for which experimental data are not available. It can be seen from Table 2.2 that the values obtained for hydrogen chloride-nitrobenzene and hydrogen chloride-ethylene dichloride systems are in good agreement [to within 10 and 5%, respectively] with the values predicted by Wilke-Chang equation, but for the ethylene-nitrobenzene and ethylene-ethylene dichloride systems the Wilke-Chang equation gives errors of 30 and 26%, respectively. Hence the Wilke-Chang equation is not recommended for predicting the diffusion coefficients for the latter systems.

To ascertain the reproducibility of the results, one particular run was repeated five times [for the hydrogen chloride-nitrobenzene system at 30°C], and the values obtained were: 2.3×10^{-5}, 2.0×10^{-5}, 2.32×10^{-5}, 2.27×10^{-5}, 1.9×10^{-5}, the average deviation from the mean value of 2.16×10^{-5} being 7.6%.

It may be mentioned here that the effect of the concentration of the dissolved gas on the diffusivity is insignificant in this case, since the concentration is low enough to maintain the viscosity of the solution the same as that of the pure solvent.

2.2.7 Correlation of data

The theoretical and semitheoretical equations proposed for diffusivities of dissolved gases in liquids, as reviewed by Himmelblau [19], do not clearly indicate the temperature dependence of the diffusivity because either they involve temperature dependent parameters or temperature dependent variables such as viscosity. Since the experimental data are so scattered, even for the CO_2-water system, it is difficult to draw conclusions concerning the temperature dependence of diffusion coefficients from empirical evidence. Hence to establish a relationship between diffusivity and temperature for each of the systems studied, the following empirical equations should be effective over moderate temperature ranges and were used to fit the data:

$$\ln D = a + \frac{b}{T} + c \ln T \qquad [2.5]$$

$$\ln D = a + \frac{b}{T} + \frac{c}{T^2} \qquad [2.6]$$

$$\ln D = a + b \ln T \qquad [2.7]$$

The values of the constants and the error estimate in ln D for all the three equations are presented in Table 2.3. Since the values of the error estimate in ln D for all the three equations are within the experimental error of 7.6%, it is evident that all the three equations fit the data well, and Equation 2.7 which is the simplest is recommended for predicting the effect of temperature on the diffusion coefficients of the systems studied.

The results have also been presented graphically as ln D vs 1/T in Figure 2.3. It may be noted that, although good straight lines can be drawn for all the systems based on the Arrhenius form of temperature dependence, the existence

TABLE 2.3

VALUES OF THE CONSTANTS IN EQUATIONS 2.5, 2.6 AND 2.7

Equation	System	Value of the constants for diffusivity			Estimate of error [in ln D]	Values of the constants for solubility			Estimate of error [in ln S]
		a	b	c		a	b	c	
1	2	3	4	5	6	7	8	9	10
$\ln X = a + \frac{b}{T} + c\ln T$	Ethylene-nitrobenzene	1.35×10^{2}	-7.78×10^{3}	-2.10×10	6.52×10^{-5}	-2.12×10^{2}	1.14×10^{4}	3.06×10	3.91×10^{-4}
	Ethylene-ethylene dichloride	5.44×10^{2}	-2.64×10^{4}	-8.17×10	2.97×10^{-3}	-5.06×10^{2}	2.40×10^{4}	7.48×10	3.52×10^{-3}
	Hydrogen chloride-nitrobenzene	3.14×10^{2}	-1.63×10^{4}	-4.75×10	3.87×10^{-3}	1.49×10	1.21×10^{3}	$-2.79\times$	1.11×10^{-4}
	Hydrogen chloride-ethylene dichloride	-1.07×10^{2}	2.77×10^{3}	1.53×10	6.85×10^{-5}	1.78×10^{2}	-5.85×10^{3}	-2.73×10	7.58×10^{-5}
	Ethyl chloride-nitrobenzene	-	-	-	-	-4.28×10^{2}	2.51×10^{4}	6.15×10	4.50×10^{-3}
	Ethyl chloride-ethylene dichloride	-	-	-	-	-1.86×10^{3}	8.22×10^{4}	2.80×10^{2}	3.45×10^{-3}
$\ln X = a + \frac{b}{T} + \frac{c}{T^2}$	Ethylene-nitrobenzene	-1.91×10	6.62×10^{3}	-1.23×10^{6}	5.83×10^{-5}	9.34	-7.64×10^{3}	1.48×10^{6}	4.43×10^{-4}
	Ethylene-ethylene dichloride	-1.35×10^{2}	7.62×10^{4}	-1.16×10^{7}	4.15×10^{-4}	6.27×10	-3.81×10^{4}	5.86×10^{6}	2.09×10^{-3}
	Hydrogen chloride-nitrobenzene	-3.44×10	1.63×10^{4}	-2.79×10^{6}	3.75×10^{-3}	$-5.64\times$	3.14×10^{3}	-1.67×10^{5}	1.10×10^{-4}
	Hydrogen chloride-ethylene dichloride	2.08×10	-1.65×10^{4}	2.18×10^{-7}	9.96×10^{-7}	-1.96×10	1.10×10^{4}	-1.29×10^{6}	5.89×10^{-5}
	Ethyl chloride-nitrobenzene	-	-	-	-	3.14×10	-2.20×10^{4}	4.35×10^{6}	4.22×10^{-3}
	Ethyl chloride-ethylene dichloride	-	-	-	-	1.57×10^{2}	-8.74×10^{4}	1.27×10^{7}	6.89×10^{-7}

1	2	3	4	5	6	7	8	9	10
$\ln X = a + b\ln T$	Ethylene-nitrobenzene	-3.07×10	3.51	-	4.11×10^{-4}	3.67×10	-6.38	-	3.92×10^{-3}
	Ethylene-ethylene dichloride	-5.39×10	7.68	-	2.99×10^{-3}	4.61×10	-7.96	-	4.67×10^{-3}
	Hydrogen chloride-nitrobenzene	-3.62×10	4.44	-	4.19×10^{-3}	4.06×10	-6.60	-	7.76×10^{-5}
	Hydrogen chloride-ethylene dichloride	-4.39×10	5.92	-	1.05×10^{-4}	4.54×10	-7.50	-	5.97×10^{-4}
	Ethyl chloride-nitrobenzene	-	-	-	-	1.16×10^{2}	-1.92×10	-	5.03×10^{-3}
	Ethyl chloride-ethylene dichloride	-	-	-	-	9.45×10	-1.54×10	-	1.40×10^{-1}

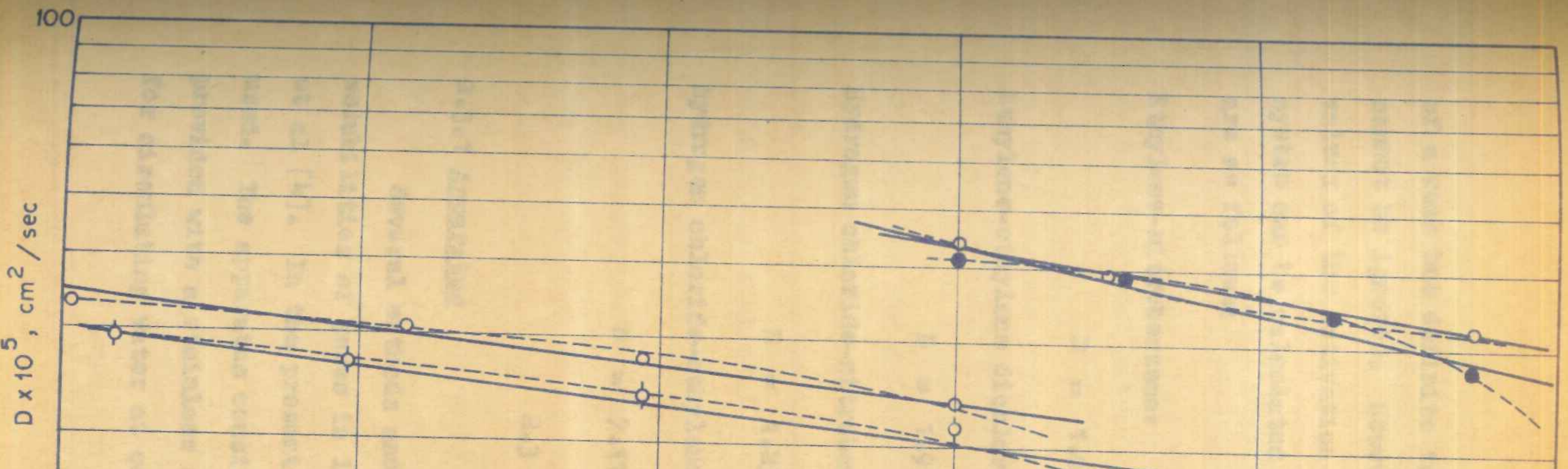


FIG. 2.3 : TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT FOR THE SYSTEMS STUDIED

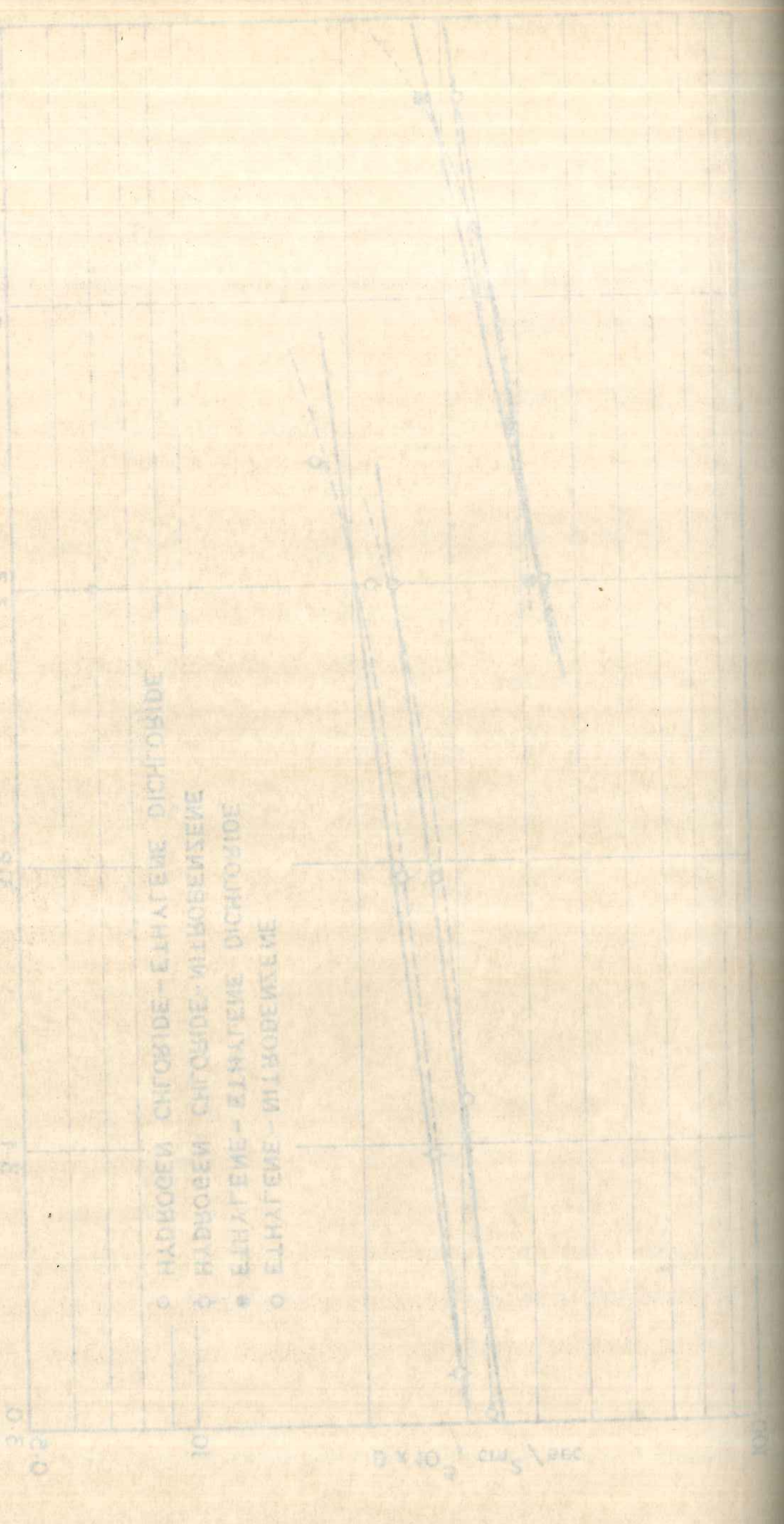


FIG 2.3 TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENTS FOR THE SYSTEMS

of a weak but definite trend [as shown by the dotted curves] cannot be ignored. However, from Figure 2.3, approximate values of the activation energy [in cal/g mole] for each system can be calculated and the corresponding equations are as follows:

Ethylene-nitrobenzene:

$$D = 1.073 \times 10^2 \ e^{-1744/T} \qquad [2.8]$$

Ethylene-ethylene dichloride:

$$D = 1.932 \times 10^4 \ e^{-2536/T} \qquad [2.9]$$

Hydrogen chloride-nitrobenzene:

$$D = 1.231 \times 10^2 \ e^{-1230/T} \qquad [2.10]$$

Hydrogen chloride-ethylene dichloride:

$$D = 7.112 \times 10^3 \ e^{-2229/T} \qquad [2.11]$$

2.3 SOLUBILITIES

2.3.1 Apparatus

Several methods and apparatus for determining the solubilities of gases in liquids have been reviewed by Battino et al [4]. In the present work the saturation method was used. The apparatus consisted of a stirred glass vessel provided with a stainless steel stirrer and an outer jacket for circulating water at constant temperature. This has been discussed in detail in Chapter 3. An outlet for sampling was also provided to the vessel. Constant temperature with a variation of ± 0.05°C was maintained by using a thermostat. This kind of an apparatus was chosen to obtain the solubility data under the experimental conditions employed for the ethylation of hydrogen chloride to ethyl chloride [in nitrobenzene or ethylene dichloride as solvent].

2.3.2 Materials

Ethylene, hydrogen chloride, nitrobenzene, ethylene dichloride, as described in Section 2.2.3, 99.9% pure ethyl chloride and analytical grade aluminium chloride [from the stock which was used for the ethylation reaction] were used. The purity of ethyl chloride was tested by vapour phase chromatographic analysis.

2.3.3 Procedure

Solvent, 400-500 ml, was introduced into the reactor, and the circulation of water at the required temperature was started through the outer jacket. After about 1 hr [when thermal equilibrium was reached], the gas was allowed to bubble through the liquid under constant stirring. Samples were withdrawn at intervals of 10-15 min for analysis, and this was continued until saturation was reached as indicated by the constancy of at least 2-3 consecutive readings. Care was taken to ensure that no moisture entered the reactor, as this can greatly alter the solubility.

The same procedure was adopted for all the systems other than ethyl chloride in nitrobenzene. All the runs were carried out at a pressure of 0.93 atm [which is the atmospheric pressure at Poona]. The barometric pressure was recorded for every run.

2.3.4 Chemical analysis

[a] Hydrogen chloride: A sample containing hydrogen chloride was introduced in a flask containing a known quantity of NaOH solution, the blank reading of which was already taken against standard HCl. Some NaOH was consumed by reacting with hydrogen chloride from the sample, and the excess NaOH was back-titrated against standard HCl. The difference between the blank and back readings gave the amount of hyrogen chloride in the sample. The solubility of HCl was then calculated from the relationship:

$$S = \frac{[x_1 - x_2]\, N_1\, [36.5]}{X}\, 10^3 \qquad [2.12]$$

where S represents the solubility, gm/litre; x_1, x_2 the blank and the back readings, X the volume of the sample, and N_1 the normality of HCl solution.

[b] Hydrogen chloride in presence of aluminium chloride: Since aluminium chloride reacts with NaOH, the "blank" reading was taken by titrating with standard HCl a sample of nitrobenzene containing aluminium chloride [but no HCl] which had been added to an aliquot of standardized NaOH, and then the same procedure described above was followed.

[c] Ethylene: Ethylene was analyzed by a method described

by Thomas et al [44] for the determination of olefins. In this method a sample was introduced in a flask containing carbon tetrachloride and 10 per cent sulfuric acid solution, and was chilled thoroughly in ice. To this a known quantity of bromate-bromide solution was added. Some of the bromine liberated from this solution was consumed in reacting with ethylene in the sample. The excess bromine was converted to iodine by adding 10-15 ml of 15 per cent potassium iodide solution and was titrated against standard sodium thiosulfate solution [back reading]. A blank reading of the bromate-bromide solution was also taken against sodium thiosulfate solution. Then the difference between the blank and the back readings gave the sodium thiosulfate equivalent to the ethylene in the sample. The solubility was calculated from the following relationship:

$$S = \frac{[x_1 - x_2]\, N_2\, 28}{2\, X}\, 10^3 \qquad [2.13]$$

2.3.5 <u>Solubility of ethyl chloride in nitrobenzene</u>

The solubility of ethyl chloride in nitrobenzene was determined by a volumetric method. 2 ml of nitrobenzene was taken in a 20 ml bulb provided with a capillary outlet, which was then cooled to 0°C and an excess [about 5 ml] of liquid ethyl chloride was introduced in this bulb. This mixture was stirred well and kept at 0°C for 10-15 minutes. Ethyl chloride being miscible with nitrobenzene in the liquid state was uniformly mixed. Then the mixture was shifted to a bath maintained at a constant [desired] temperature, when the quantity of ethyl chloride in excess of the solubility at that temperature escaped out. After some time the outflow of ethyl chloride ceased, and at this stage 2 ml of nitrobenzene was considered to be saturated with ethyl chloride at that temperature. The sample was then heated further to desorb out [at 100°C] the ethyl chloride completely, and this was collected in an eudiometer. The amount of ethyl chloride collected in the eudiometer corresponded to the quantity required to saturate 2 ml nitrobenzene at the temperature of the experiment. The solubility was plotted against 1/T and the line was extrapolated to obtain the solubility at 100°C. This was added to the observed value of the solubility at a particular temperature to give the corrected value of the solubility at that temperature. The experiments were carried out over the temperature range of 25-50°C.

2.3.6 Experimental data

The solubilities of the systems, ethylene-nitrobenzene, ethylene-ethylene dichloride, hydrogen chloride-nitrobenzene, hydrogen chloride-ethylene dichloride and ethyl chloride-nitrobenzene were determined by the procedure outlined above at different temperatures and at atmospheric pressure at Poona. The results are presented in Table 2.4. For the system ethyl chloride-ethylene dichloride the data reported by Stephen et al [41] were used in working out the correlations.

The solubility of hydrogen chloride in nitrobenzene

TABLE 2.4

EXPERIMENTAL VALUES OF SOLUBILITIES

[AT 0.93 atm PRRESURE]

System	Temperature ^{o}K	Solubility in gm/lit
Ethylene-nitrobenzene	286.0	1.9685
	303.0	1.2600
	313.0	0.9975
	323.0	0.8400
	333.0	0.7610
Ethylene-1,2 ethylene dichloride	280.0	3.6690
	287.0	2.6590
	292.5	2.4280
	300.5	2.0510
Hydrogen chloride-nitrobenzene	302.0	18.9800
	307.0	17.0200
	323.0	15.1100
	323.0	12.0400
	332.0	10.2200
Hydrogen chloride-1,2 ethylene dichloride	278.0	23.1500
	293.0	16.3600
	298.0	14.2800
	305.0	11.7800
	314.0	9.3000
Ethyl chloride-nitrobenzene	298.5	620.0
	303.0	401.0
	308.0	296.3
	313.5	227.3
	323.0	128.6

at various aluminium chloride concentrations was also studied and the effect of aluminium chloride concentration is shown in Figure 2.4. It can be seen that the solubility is a very mild function of aluminium chloride concentration [in nitrobenzene] at lower temperatures, and the greatest increase observed is of the order of 9.6% at 29°C in the concentration range studied. At higher temperatures the effect of aluminium chloride on the solubility of hydrogen chloride is negligibly small.

An attempt was also made to determine the solubility of ethylene in nitrobenzene in the presence of aluminium chloride, but due to analytical problems and formation of a complex between ethylene and the chloride, no precise values of the solubility could be obtained. From the data on hydrogen chloride solubility in nitrobenzene containing aluminium chloride, it may be concluded that aluminium chloride has negligible effect on the solubility of ethylene. This is also supported by the theory that salts have an effect on the solubility only when they are ionised, and in the present situation aluminium chloride is not in the ionic form, nitrobenzene being a nonpolar solvent.

2.3.7 Correlation of data

The theoretical equations for estimating solubilities do not clearly indicate the temperature dependence and it is very difficult to arrive at generalised conclusions based on the empirical equations. Hence it was decided to fit an empirical correlation for each system separately. As reviewed

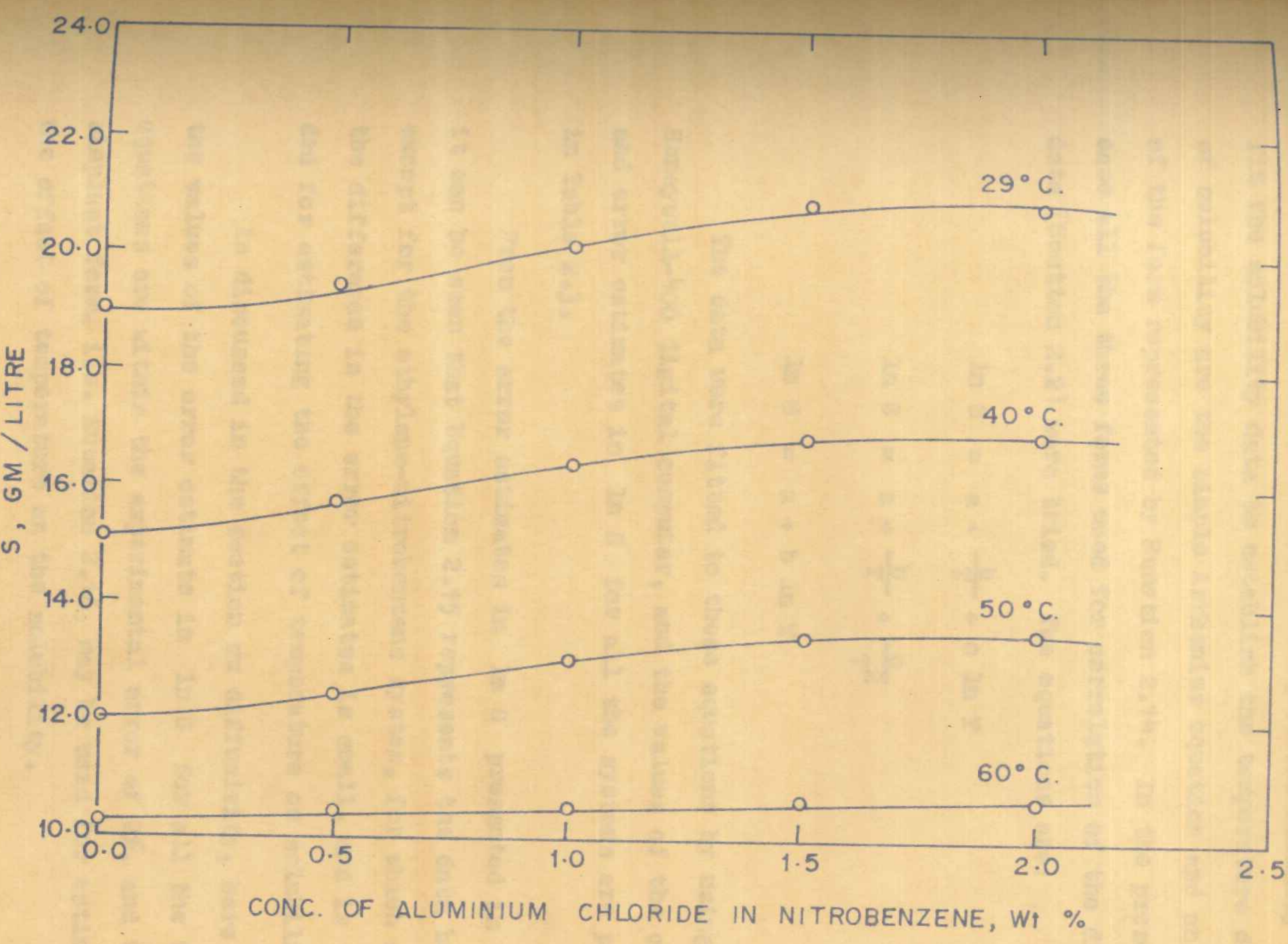


FIG. 2·4 : SOLUBILITY OF HYDROGEN CHLORIDE IN NITROBENZENE IN THE PRESENCE OF ALUMINIUM CHLORIDE by Battino et al [4], the types of equations normally used to fit the solubility data to establish the temperature dependence of solubility are the simple Arrhenius equation and an equation of the form represented by Equation 2.14. In the present case all the three forms used for correlation of the diffusivity data [Section 2.2] were tried. The equations are:

$$\ln S = a + \frac{b}{T} + c \ln T \qquad [2.14]$$

$$\ln S = a + \frac{b}{T} + \frac{c}{T^2} \qquad [2.15]$$

$$\ln S = a + b \ln T \qquad [2.16]$$

The data were fitted to these equations by using a Honeywell-400 digital computer, and the values of the constants and error estimates in $\ln S$ for all the systems are presented in Table 2.3.

From the error estimates in $\ln S$ presented in Table 2.3, it can be seen that Equation 2.15 represents the data best, except for the ethylene-nitrobenzene system, for which also the difference in the error estimates is small, and is recommended for estimating the effect of temperature on solubility.

As discussed in the section on diffusivity, here also the values of the error estimate in $\ln S$ for all the three equations are within the experimental error of 2%, and the simplest form, i.e. Equation 2.16, may be used for estimating the effect of temperature on the solubility.

From the Arrhenius plots [Figure 2.5], the approximate

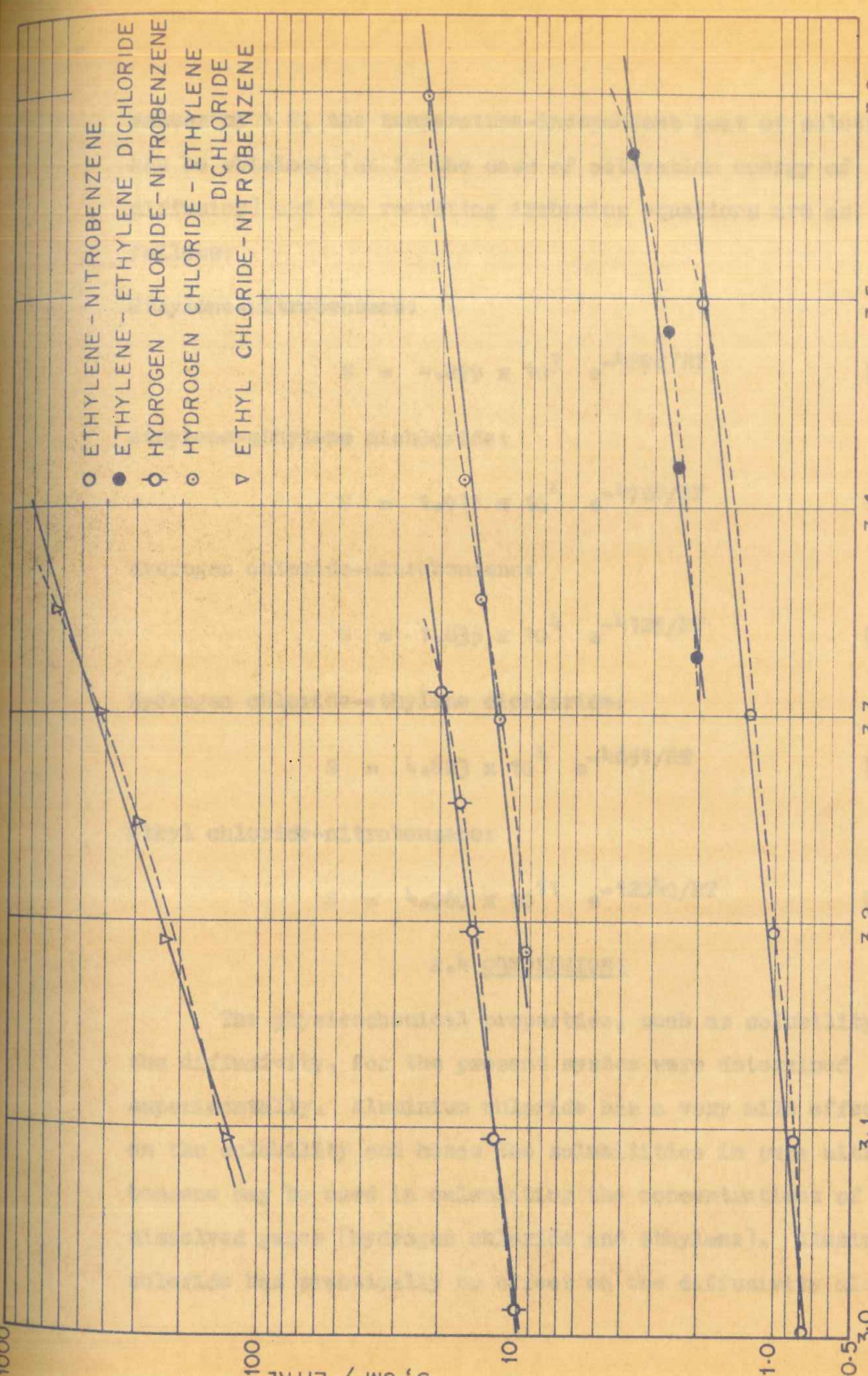


FIG. 2·5: TEMPERATURE DEPENDENCE OF SOLUBILITY FOR THE SYSTEMS STUDIED values of △ H, the temperature-independent heat of solution, can be obtained [as in the case of activation energy of diffusion] and the resulting Arrhenius equations are as follows:

Ethylene-nitrobenzene:

$$S = 4.299 \times 10^{3} \; e^{-4898/RT} \qquad [2.17]$$

Ethylene-ethylene dichloride:

$$S = 1.931 \times 10^{4} \; e^{-4767/RT} \qquad [2.18]$$

Hydrogen chloride-nitrobenzene:

$$S = 1.835 \times 10^{4} \; e^{-4125/RT} \qquad [2.19]$$

Hydrogen chloride-ethylene dichloride:

$$S = 4.823 \times 10^{4} \; e^{-4651/RT} \qquad [2.20]$$

Ethyl chloride-nitrobenzene:

$$S = 4.060 \times 10^{11} \; e^{-12040/RT} \qquad [2.21]$$

2.4 CONCLUSIONS

The physicochemical properties, such as solubility and the diffusivity, for the present system were determined experimentally. Aluminium chloride has a very mild effect on the solubility and hence the solubilities in pure nitrobenzene may be used in calculating the concentrations of the dissolved gases [hydrogen chloride and ethylene]. Aluminium chloride has practically no effect on the diffusivity also, since the concentrations of aluminium chloride used in the present work are too low to change the viscosity of nitrobenzene. Finally it is concluded that these data can be used in analysing the mechanism of absorption and reaction of ethylene and hydrogen chloride in nitrobenzene medium containing dissolved aluminium chloride catalyst.

CHAPTER - 3

KINETICS AND MECHANISM OF ABSORPTION

CHAPTER 3

KINETICS AND MECHANISM OF ABSORPTION

3.1 INTRODUCTION

The simultaneous absorption and reaction of ethylene and hydrogen chloride in a medium of nitrobenzene containing dissolved aluminium chloride [as catalyst] produces mainly ethyl chloride [under certain conditions traces of a polymer are formed]. The addition of hydrogen chloride takes place by the well known Friedel-Craft reaction:

$$C_2H_4 + \text{HCl [anhydrous]} \xrightarrow{\text{Anhydrous } AlCl_3} C_2H_5Cl + 13.4 \text{ kcal}$$

Ethyl chloride is mainly produced by this route and as discussed in Chapter 1, the most commonly used solvent is ethyl chloride itself. But in order to avoid high pressure equipment, it was decided to use nitrobenzene as solvent in the kinetic study; also being very high boiling, the effect of temperature can be conveniently studied to establish the kinetics. Surprisingly there is no information available in the literature on the kinetics of this reaction, which could be used in the rational design of reactors for ethyl chloride. The purpose of the present investigation was to provide the kinetic data for this important reaction and establish the regime of control. Also, since very few reactions involving simultaneous absorption of two gases have been studied, it was considered desirable to attempt a complete analysis of this reaction.

3.2 EXPERIMENTAL

3.2.1 Reactor assembly

The selection of a suitable reactor is one of the important considerations in any experimental programme associated with gas-liquid reactions. Initially this reaction was carried out in a stirred cell similar to that described by Danckwerts [11], in which it was observed that the reaction was diffusion controlled and it was not possible to determine the kinetics of the reaction. In order to ascertain whether the reaction occurs in the kinetic regime [very slow reaction] an agitated contactor was used since the mass transfer coefficients are much larger in such a reactor than in a stirred cell. This was confirmed from the preliminary rate data in the agitated contactor, which is recommended for studying the gas-liquid reactions falling in the kinetic regime. Thus a standard all-glass agitated contactor provided with baffles and a jacket for temperature control was used in the present work. A diagrammatic sketch of the reactor and the complete assembly are shown in Figure 3.1. A stainless steel stirrer was used with a six bladed propeller type impeller. The ratio of the diameter of the blade to the diameter of the tank was about 0.52, which is an optimum one for getting high mass transfer coefficient values [38]. Temperature control was attained by using a thermostatic bath, with a variation of ± $0.05^{\circ}C$. The other important parts of the assembly are the capillary flowmeters to measure gas inlet flowrates and a

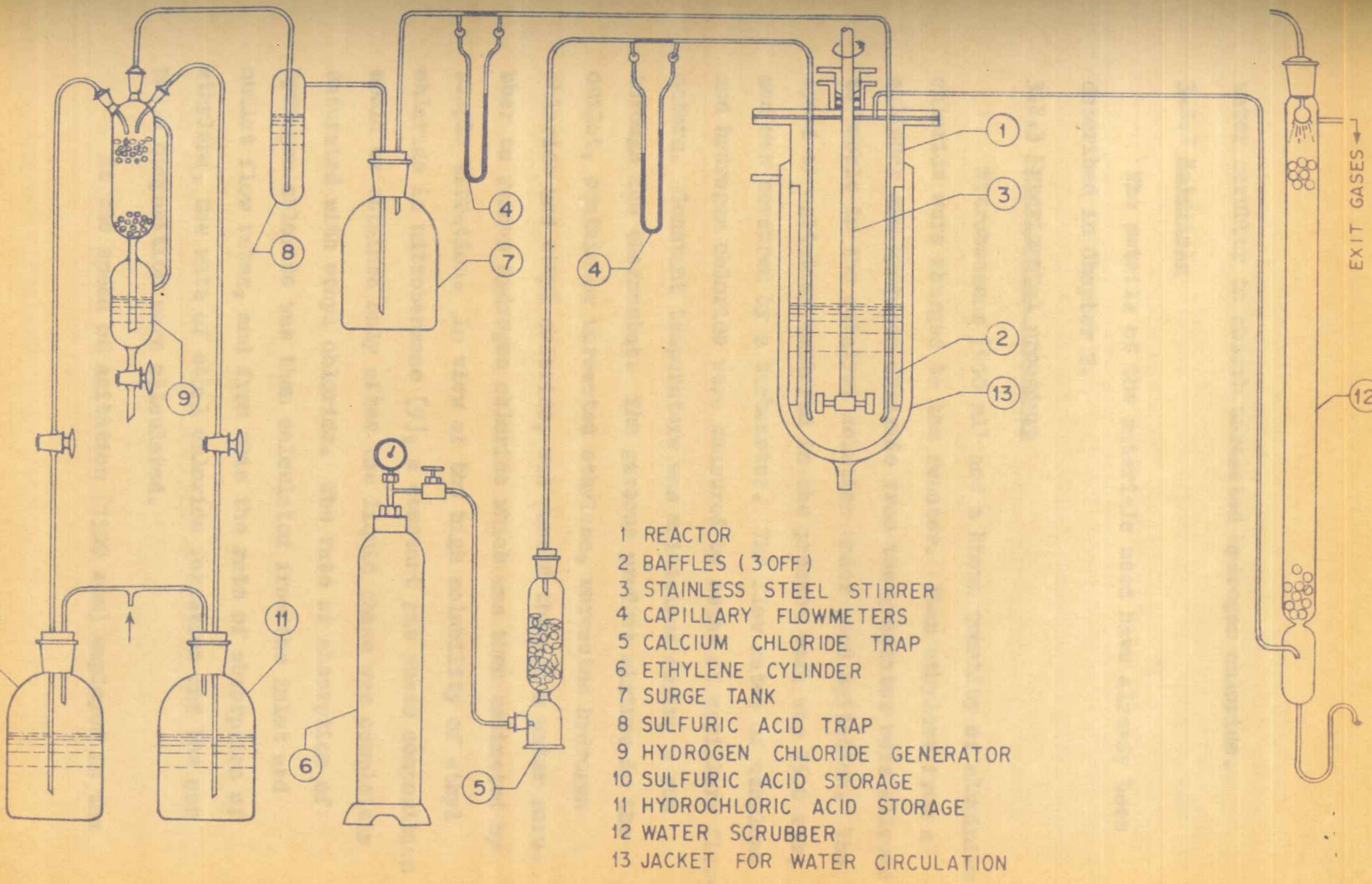


FIG. 3·1 : A SKETCH OF THE REACTOR ASSEMBLY FOR THE ABSORPTION EXPERIMENTS water scrubber to absorb unreacted hydrogen chloride.

3.2.2 Materials

The details of the materials used have already been described in Chapter 2.

3.2.3 Experimental procedure

Nitrobenzene [400 ml] and a known quantity of aluminium chloride were charged to the reactor. Then ethylene from a cylinder and hydrogen chloride from the generator were allowed to bubble in the catalyst solution under good agitation. The speed of agitation employed in the present work was 1500 rpm, and was measured by a tachometer. The flow rates of ethylene and hydrogen chloride were measured by means of capillary flowmeters. Constant temperature was maintained during a run through the thermostat. The gaseous product mixture in the outlet, containing unreacted ethylene, unreacted hydrogen chloride and ethyl chloride, was passed through a water scrubber to remove hydrogen chloride which was then estimated by simple titration. In view of the high solubility of ethyl chloride in nitrobenzene [9], a constant gas phase composition could be obtained only after the liquid phase was completely saturated with ethyl chloride. The rate of absorption of hydrogen chloride was then calculated from the inlet and outlet flow rates, and from this the rate of absorption of ethylene, the rate of ethyl chloride formation and the gas phase composition were calculated.

At the speed of agitation [1500 rpm] employed in the present work, the gas phase is expected to be completely backmixed. Hence the concentrations of ethylene and hydrogen chloride in the liquid phase [nitrobenzene] were calculated from the partial pressures [obtained from the gas phase composition] and the solubilities. The solubility data for these systems have been discussed in the previous section. The solubility of hydrogen chloride in nitrobenzene containing aluminium chloride has been shown to be a very mild function of aluminium chloride concentration. In spite of this marginal difference, solubilities at corresponding values of aluminium chloride concentration were used in calculating the concentrations of hydrogen chloride in nitrobenzene. The effect of aluminium chloride on the solubility of ethylene could not be studied due to analytical problems [9], but from the data on hydrogen chloride solubility in nitrobenzene containing aluminium chloride, it may be concluded that aluminium chloride has negligible effect on the solubility of ethylene, and hence the values obtained in pure nitrobenzene were used in calculating the concentrations.

3.3 RESULTS AND DISCUSSION

3.3.1 Organisation of experiments

Initially this reaction was studied by saturating the liquid phase with hydrogen chloride and then passing ethylene through it, thus observing the rate of absorption of ethylene as a function of time. Samples were withdrawn for analysis of hydrogen chloride in the liquid phase. This method was similar to that normally employed for the absorption of a single gas in a reacting liquid, but was discarded since there was significant stripping of the dissolved hydrogen chloride, which disturbed the gas phase composition of ethylene, based on which ethylene concentration was calculated. A few runs were carried out using this method, correction due to hydrogen chloride stripping being made by estimating the concentrations of the chloride in the liquid bulk as well as the gas phase. Even so it was found that the values of the rate constants obtained by this method were considerably different from those estimated by the procedure described in the experimental section. The latter method [in which two gases are absorbed simultaneously] is considerably more accurate for the present system and was hence followed in the bulk of the experiments carried out.

The type of the contactor to be finally used normally varies with the regime of absorption, and hence it is important to discern the probable regime of control from the preliminary runs. In view of the very slow rates of absorption observed, as a first step, kinetic control was assumed and the experiments were organised to broadly fix the ranges of catalyst concentration and temperature at which the absorption would be unambiguously in the kinetic regime. These experiments were carried out in the agitated contactor described earlier and the approximate values of the enhancement factors ϕ_A and ϕ_B defined below were calculated:

$$\phi_A = \frac{R_A}{k_L \underline{a}\, A^*} \qquad [3.1]$$

$$\phi_B = \frac{R_B}{k_L \underline{a}\, B^*} \qquad [3.2]$$

where R_A, R_B represent the specific rates of absorption of ethylene and hydrogen chloride respectively, [g mole/cm^3 sec]; k_L the liquid film mass transfer coefficient [cm/sec]; $\underline{a}$ the effective interfacial area [cm^2/cm^3]; and A^*, B^* the solubilities of ethylene and hydrogen chloride in nitrobenzene [g mole/cm^3] respectively.

The reaction is said to be kinetically controlled when the reaction rate is very much less than the transport rate. The conditions to be satisfied for the kinetic control are:

$$\phi_A \ll 1 \qquad [3.3]$$

$$\phi_B \ll 1 \qquad [3.4]$$

These conditions do not need a prior knowledge of either the rate constant or the reaction orders, and thus provide a powerful basis for evaluating raw data and ensuring kinetic control.

For estimating the enhancement factors and thus verifying the applicability of conditions 3.3 and 3.4, a knowledge of $k_L\underline{a}$ is necessary. Using a value of $k_L\underline{a} \simeq 0.15$ sec^{-1}, normally obtained for agitated contactors [38], at the speed of agitation of 1500 rpm, the experimentally determined rates of absorption R_A and R_B [which in this case are equal], and the solubilities A^* and B^* reported in an earlier chapter [2.3], the applicability of the conditions was verified. It may be mentioned here that the value of $k_L\underline{a}$ used is reasonably accurate for this type of equipment at 1500 rpm. The same value of $k_L\underline{a}$ has been assumed for ethylene and hydrogen chloride in the present work, since the difference in their diffusivity values is small [2.2].

As a supporting test for the complete elimination of mass transfer effects, the effect of stirrer speed was also studied and it was found that [Figure 3.2] beyond a speed of 1300 rpm there was no effect of stirrer speed on the rate of absorption. Hence a speed of agitation above 1300 rpm was used in all the experiments.

In order to attempt a detailed kinetic analysis of the reaction, over 80 experiments were then carried out covering the following ranges of variables:

Temperature: 30-70°C
Catalyst concentration: $9 \times 10^{-5} - 2.8 \times 10^{-4}$ g mole/cm^3
Ethylene concentration: $4 \times 10^{-6} - 3.5 \times 10^{-5}$ g mole/cm^3
Hydrogen chloride concentration: $4 \times 10^{-5} - 4.2 \times 10^{-4}$ g mole/cm^3

Concentration changes were achieved by varying the flow rates of the two gases and their molar ratios.

3.3.2 Regimes of control

If the reaction is sufficiently slow, the whole liquid

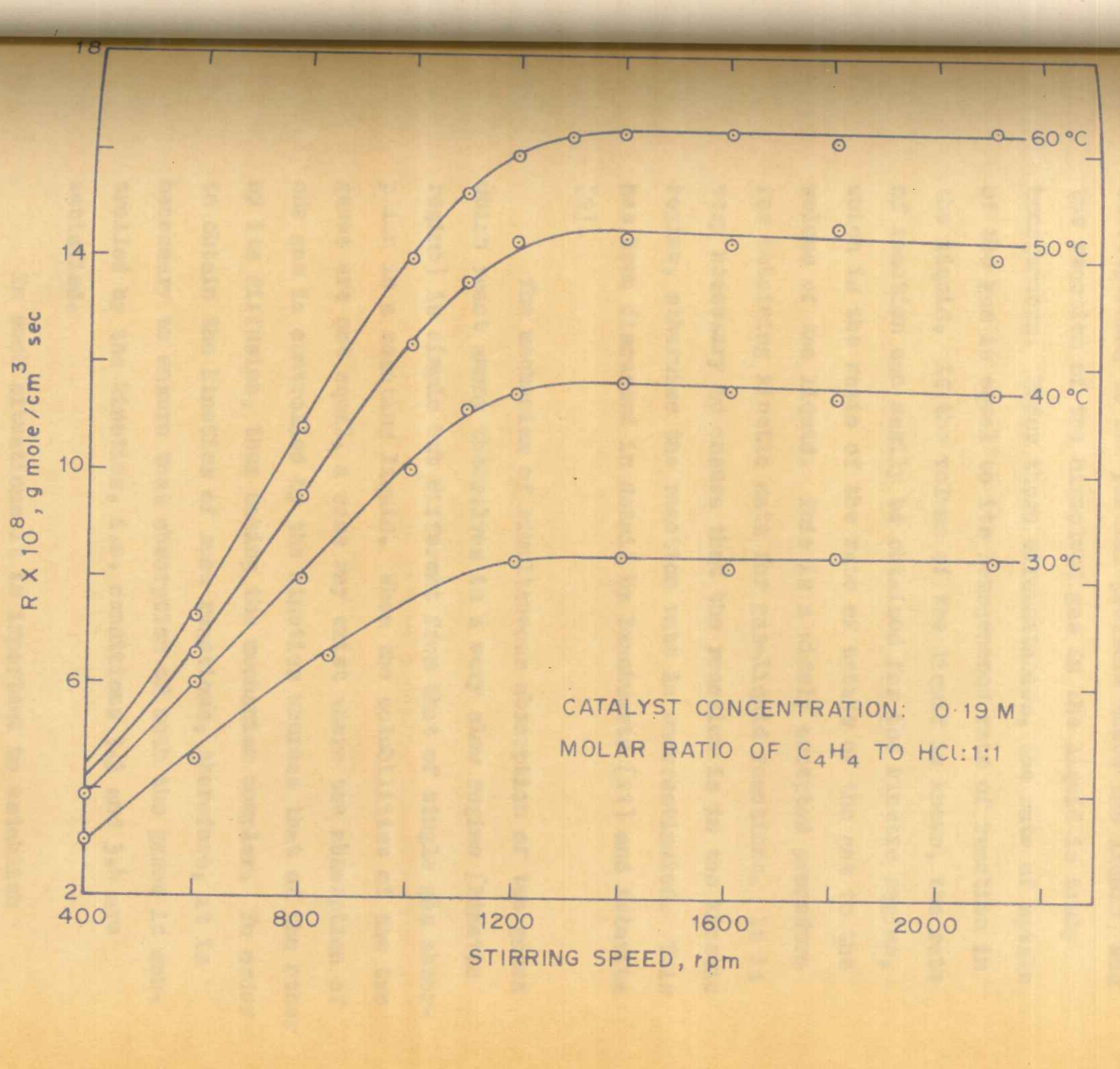


FIG. 3·2: EFFECT OF SPEED OF AGITATION ON THE RATE OF ABSORPTION remains saturated with unreacted gas [at a concentration corresponding to its partial pressure above the liquid] and the reaction of the dissolved gas in the liquid is truly homogeneous. Under these circumstances, the rate of uptake of the gas is equal to its homogeneous rate of reaction in the liquid. If the volume of the liquid is known, the rate of reaction can easily be obtained for the kinetic regime, which is the ratio of the rate of uptake of the gas to the volume of the liquid. This is a widely accepted procedure for obtaining kinetic data for gas-liquid reactions. It is very necessary to ensure that the reaction is in the kinetic regime, otherwise the reaction rate is underestimated. This has been discussed in detail by Danckwerts [11] and Astarita [2].

The mechanism of simultaneous absorption of two gases which react among themselves in a very slow regime [kinetic regime] is simple but different from that of single gas absorption in a reacting liquid. When the solubilities of the two gases are not equal, a case may exist where the absorption of one gas is controlled by the kinetics whereas that of the other by its diffusion, thus making the mechanism complex. In order to obtain the kinetics of such reactions, therefore, it is necessary to ensure that absorption of both the gases is controlled by the kinetics, i.e. conditions 3.3 and 3.4 are satisfied.

In such situations it is important to establish criteria when the liquid is saturated throughout with the gases and the concentrations of the dissolved gases are not depleted by the reaction, and when the concentrations are depleted by the reaction, so that in addition to applying conditions 3.3 and 3.4, the data can also be tested by using the conditions for different regimes.

[a] Kinetic regime: In this regime the reaction rate is very ~~much~~ slow in comparison with the transport rate of the gas. As discussed earlier the rate of absorption expressed per unit volume is equal to the reaction rate in the kinetic regime. Then the rates of absorption of ethylene and hydrogen chloride, R_A and R_B respectively will be given by:

$$Z\,R_A = R_B = r = k\,A^{*m}\,B^{*n}\,C_o^p \qquad [3.5]$$

where k is the rate constant $\left[[\mathrm{cm}^3/\mathrm{g\ mole}]^2/\mathrm{sec}\right]$, C_o the catalyst concentration $[\mathrm{g\ mole}/\mathrm{cm}^3]$, r the reaction rate $[\mathrm{g\ mole}/\mathrm{cm}^3\ \mathrm{sec}]$, and m, n, p the orders of reaction with respect to A^*, B^* and C_o respectively.

The rates of diffusion of ethylene and hydrogen chloride are given by:

$$R_A' = k_L\underline{a}\,A^* \qquad [3.6]$$

$$R_B' = k_L\underline{a}\,B^* \qquad [3.7]$$

As mentioned earlier, in this case values of $k_L\underline{a}$ for ethylene and hydrogen chloride have been assumed to be equal, since the difference in their diffusivity values is small [2.2].

From Equations [3.5], [3.6] and [3.7] the following conditions, in addition to conditions [3.3] and [3.4] can be written for the kinetic regime:

$$\underline{l}\,k\,A^{*m-1}\,B^{*n}\,C_o^p \ll k_L\underline{a}, \quad m \neq 1 \qquad [3.8]$$

or

$$\underline{l}\,k\,B^{*n}\,C_o^p \ll k_L\underline{a}, \quad m = 1 \qquad [3.9]$$

and

$$\underline{l}\,k\,B^{*n-1}\,A^{*m}\,C_o^p \ll k_L\underline{a}, \quad n \neq 1 \qquad [3.10]$$

or

$$\underline{l}\,k\,A^{*m}\,C_o^p \ll k_L\underline{a}, \quad n = 1 \qquad [3.11]$$

where $\underline{l}$ represents the functional holdup of the liquid phase. The rates of absorption of ethylene and hydrogen chloride in this case will be represented by Equation [3.5].

[b] Diffusion regime: When the reaction is very fast in comparison with the diffusion rates, it ~~reaction~~ is said to be diffusion controlled. In this regime the rates of absorption of ethylene and hydrogen chloride will be represented by Equations [3.6] and [3.7], and need not be equal. The conditions for the diffusion regime can be written as follows:

$$\underline{l}\,k\,A^{*m-1}\,B^{*n}\,C_o^p \gg k_L\underline{a}, \quad m \neq 1 \qquad [3.12]$$

or

$$\underline{l}\,k\,B^{*n}\,C_o^p \gg k_L\underline{a}, \quad m = 1 \qquad [3.13]$$

$$\underline{l}\, k\, B^{*n-1} A^{*m} C_o^p \gg k_L\underline{a},\ n \neq 1 \qquad [3.14]$$

or

$$\underline{l}\, k\, A^{*m} C_o^p \gg k_L\underline{a},\ n = 1 \qquad [3.15]$$

and

$$\phi_A = \phi_B = 1 \qquad [3.16]$$

In this regime the mass transfer coefficient with and without chemical reaction is the same. An additional condition can also be given for this case to ensure that the reaction in the film is negligible:

$$\frac{D_A\, k\, B^{*n} C_o^p}{k_L^2} \ll 1 \qquad [3.17]$$

and

$$\frac{D_B\, k\, A^{*m} C_o^p}{k_L^2} \ll 1 \qquad [3.18]$$

3.3.3 Kinetics

The applicability of conditions [3.3], [3.4], [3.9], and [3.11], which ensure kinetic control, was verified for each run by ensuring that the pseudo first-order rate constants $\underline{l}\, k\, A^{*m} C_o^p$ and $\underline{l}\, k\, B^{*n} C_o^p$ are much lower than $k_L\underline{a}$ and the enhancement factors ϕ_A and ϕ_B are much less than unity. This can be clearly seen from Table 3.1. It can also be seen that while the absorption of hydrogen chloride is kinetically controlled at all temperatures and catalyst concentrations

TABLE 3.1

ABSORPTION AND REACTION OF ETHYLENE AND HYDROGEN CHLORIDE IN NITROBENZENE MEDIUM (CONTAINING A DISSOLVED $AlCl_3$ CATALYST)

Catalyst concentration $\frac{g\ mole}{cm^3}$	Reactant concentration		Rate of absorption $R_A \times 10^8$ $\frac{g\ mole}{cm^3,\ sec}$	Reaction rate constant $k \times 10^{-5}$ $\left(\frac{cm^3}{g\ mole}\right)^2$ / sec	$\underline{1}\ k B^* C_o$ 1/sec	$\underline{1}\ k A^* C_o$ 1/sec	Enhancement factor for ethylene ϕ_A	Enhancement factor for hydrogen chloride ϕ_B
	Ethylene $A^* \times 10^5$ $\frac{g\ mole}{cm^3}$	Hydrogen chloride $B^* \times 10^4$ $\frac{g\ mole}{cm^3}$						
1	2	3	4	5	6	7	8	9
				Temperature: 303°K				
~~9.360~~	~~1.980~~							
9.360	1.980	2.510	5.580	1.199	0.0019	0.00015	0.0188	0.00148
	2.820	1.572	4.830	1.164	0.0012	0.000214	0.0114	0.0020
	2.115	2.680	6.510	1.227	0.0020	0.00016	0.0205	0.0016
	3.310	1.168	4.080	1.127	0.00088	0.000092	0.0255	0.0008
	0.905	4.190	4.460	1.256	0.00318	0.000069	0.0328	0.00071
18.720	1.818	2.300	8.360	1.068	0.00349	0.000276	0.0306	0.0024
	1.925	2.440	9.300	1.058	0.00370	0.00024	0.0322	0.0025
	2.020	2.560	10.400	1.074	0.00388	0.00031	0.0344	0.0027
	2.705	1.362	7.800	1.130	0.00207	0.00041	0.0192	0.0038
	0.760	4.120	7.250	1.237	0.00625	0.00011	0.0635	0.0011
	3.520	0.810	6.140	1.150	0.00123	0.0053	0.0116	0.0050

1	2	3	4	5	6	7	8	9
28.080	1.500	1.900	9.300	1.162	0.0043	0.00034	0.0413	0.0032
	1.632	2.070	11.150	1.175	0.0047	0.00037	0.0455	0.0036
	1.755	2.221	13.400	1.224	0.0050	0.00040	0.0510	0.0040
	1.880	2.382	15.800	1.256	0.0054	0.00043	0.0560	0.0044
	0.675	4.090	8.730	1.126	0.0093	0.00015	0.0862	0.0014
	2.700	1.140	9.300	1.076	0.0026	0.00061	0.0230	0.0054
				Temperature: 313°K				
9.360	1.567	1.856	7.430	2.729	0.0034	0.00029	0.0316	0.00026
	1.560	2.015	8.180	2.780	0.0037	0.000286	0.0350	0.0027
	1.525	1.723	6.500	2.643	0.0032	0.000280	0.0284	0.0025
	0.950	2.882	8.550	3.336	0.00529	0.000170	0.0600	0.0029
	2.600	0.878	5.576	2.609	0.00161	0.00048	0.0143	0.0042
18.720	1.230	1.458	9.680	2.883	0.00535	0.00045	0.0525	0.0044
	1.282	1.670	11.320	2.824	0.00613	0.000471	0.0588	0.0045
	1.405	1.750	11.900	2.585	0.00643	0.000516	0.0565	0.0045
	1.060	1.382	8.550	3.117	0.00508	0.000389	0.0538	0.0041
	0.890	2.320	9.320	2.411	0.00852	0.000327	0.0698	0.0026
	0.703	2.735	9.680	2.689	0.0100	0.000258	0.0918	0.0023
	1.780	1.160	9.240	2.390	0.00426	0.00065	0.0346	0.0053

1	2	3	4	5	6	7	8	9
	2.090	1.006	9.800	2.490	0.00369	0.00076	0.0312	0.0065
28.080	1.035	1.280	11.300	3.037	0.00705	0.00057	0.0728	0.0058
	1.162	1.518	13.400	2.705	0.00836	0.00064	0.0769	0.0058
	1.262	1.648	16.750	2.868	0.00908	0.00069	0.0885	0.0067
	1.378	1.850	19.900	2.780	0.01020	0.00076	0.0963	0.0071
	0.438	3.185	12.100	3.089	0.0175	0.00024	0.1840	0.0025
	0.695	2.620	16.900	3.305	0.0144	0.00038	0.1620	0.0043
				Temperature: 323°K				
9.360	1.190	1.388	9.850	6.371	0.00555	0.000476	0.0552	0.0047
	1.230	1.518	11.340	6.489	0.00607	0.00049	0.0615	0.0049
	1.302	1.606	13.010	6.647	0.00642	0.00052	0.0666	0.0054
	1.065	1.313	8.360	6.387	0.00525	0.00042	0.0523	0.0042
	0.610	2.285	8.360	6.408	0.00914	0.00024	0.0914	0.00024
	2.165	0.618	7.430	5.933	0.00247	0.00086	0.0229	0.0080
18.720	0.956	1.180	14.300	6.771	0.00944	0.00076	0.0988	0.0080
	1.022	1.260	15.250	6.326	0.01008	0.00081	0.0995	0.0080
	1.065	1.313	16.750	6.399	0.01050	0.00085	0.1050	0.0085
	0.900	1.110	10.600	5.668	0.00888	0.00072	0.0785	0.0063
	0.470	2.215	11.320	5.808	0.01772	0.00037	0.1607	0.0034

1	2	3	4	5	6	7	8	9
	2.120	0.435	11.150	6.458	0.00348	0.00169	0.0350	0.0170
	1.730	0.564	11.900	6.515	0.00451	0.00138	0.0459	0.0140
28.080	0.942	1.070	15.060	5.321	0.0128	0.00113	0.1070	0.0093
	0.980	1.246	18.590	5.422	0.01495	0.00118	0.1270	0.0099
	1.073	1.363	24.160	5.883	0.01636	0.00128	0.150	0.0118
	0.465	2.190	16.730	5.851	0.0263	0.000558	0.240	0.0051
	0.313	2.540	13.010	5.823	0.0305	0.000375	0.270	0.0034
	0.727	1.038	11.710	5.526	0.0124	0.000872	0.100	0.0075
				<u>Temperature: 333^{o}K</u>				
9.360	0.940	0.942	13.20	15.930	0.00887	0.00088	0.0936	0.0093
	1.015	1.090	15.05	14.530	0.01027	0.00095	0.0988	0.0092
	1.088	1.168	18.59	15.630	0.0110	0.00102	0.1100	0.0106
	1.930	0.381	10.22	14.850	0.00359	0.00182	0.0353	0.0178
	0.434	1.756	10.59	14.850	0.01650	0.00041	0.1620	0.0040
18.720	0.736	0.791	16.35	15.000	0.01490	0.00138	0.1400	0.0138
	0.705	0.757	14.35	14.360	0.0143	0.00133	0.1300	0.0126
	0.740	0.765	13.95	13.160	0.0144	0.00139	0.1200	0.0121
	0.685	0.736	13.00	13.770	0.0139	0.00129	0.1200	0.0117

1	2	3	4	5	6	7	8	9
	0.671	0.720	11.51	12.730	0.0136	0.00126	0.1100	0.0106
	0.570	0.612	8.74	13.380	0.0115	0.00107	0.1000	0.0095
28.080	0.662	0.790	16.73	11.390	0.022	0.00187	0.1700	0.0141
	0.825	0.886	20.45	9.960	0.025	0.00233	0.1650	0.0154
	0.896	0.995	27.88	11.140	0.028	0.00253	0.2030	0.0187
	0.355	1.692	18.59	11.020	0.0478	0.00100	0.3500	0.0073
	1.610	0.366	18.03	10.900	0.0103	0.00455	0.07500	0.0328
	0.544	1.363	23.23	11.160	0.0385	0.00154	0.2850	0.0113
	0.247	2.035	13.01	9.220	0.0575	0.00069	0.3500	0.0042

studied, that of ethylene shows some diffusional resistance at higher temperatures and catalyst concentrations.

In order to determine the order of reaction with respect to each reactant and the activation energy, the reaction rate constant k in Equation [3.5] was substituted in terms of temperature and the activation energy, and using the resulting Equation [3.19] given below and all the data obtained except at 70°C at all catalyst concentrations and at 60°C at 0.28 M catalyst concentrations, the values of m, n, p and the activation energy E were computed:

$$\ln R_A = \ln k_{\infty} - \frac{E}{RT} + m \ln A^* + n \ln B^* + p \ln C_o \qquad [3.19]$$

The data at 70°C [at all catalyst concentrations] and 60°C [at 0.28 M catalyst concentration] were not used since condition [3.9] was not fully satisfied for the absorption of ethylene. The data were processed in a Honeywell-400 digital computer and the final equation obtained is:

$$R_A = 1.246 \times 10^{17} \; e^{\left(-\frac{16600}{RT}\right)} \; A^{*0.98} \; B^{*1.01} \; C_o^{0.94} \qquad [3.20]$$

which may be written as

$$R_A = 1.246 \times 10^{17} \; e^{\left(-\frac{16600}{RT}\right)} \; A^* B^* C_o \qquad [3.21]$$

Knowing the orders of reaction with respect to each reactant, the values of the reaction rate constant were calculated from the observed data by using Equation [3.5].

An Arrhenius plot of the temperature dependence of the second-order rate constant k_2 [$= k\ C_o$] is shown in Figure 3.3. It may be noticed that at lower temperatures and catalyst concentrations the reaction occurs in the kinetic regime. On the other hand, at higher temperatures [70° and 60°] the points do not fall on the extrapolated Arrhenius line, thus supporting the earlier conclusion that under these conditions the absorption of ethylene is accompanied by some diffusional resistance, and thus the values of k_2 calculated from Equation 3.5 are lower than the true values. The activation energy, as calculated from plot in Figure 3.3, is 16546 cal/g mole which agrees to within 1% with the value [16600 cal/g mole] given in Equation 3.21.

The effect of catalyst concentration on the second-order rate constant is shown in Figure 3.4 which is a log-log plot of k_2 vs catalyst concentration. It may be seen that the order is unity, which confirms the correctness of the order used in writing Equation 3.21. The linear dependence of the reaction rate constant on the catalyst concentration provides another confirmation of ~~the~~ kinetic control.

The results are also presented in the form of a plot of ϕ_A or ϕ_B vs $k_L\underline{a}/k\ B^{*n}\ C_o^{p}$ or $k_L\underline{a}/k\ A^{*m}\ C_o^{p}$ respectively [Figure 3.5] which gives a clear idea of the regimes. It may be mentioned that beyond the values of ϕ_A or $\phi_B = 0.1$, the reaction is accompanied by diffusional resistance and ~~is~~ tends towards the intermediate regime. For the reaction to be unambiguously kinetically controlled the ratio $k_L\underline{a}/k\ B^{*n}\ C_o^{p}$ or $k_L\underline{a}/k\ A^{*m}\ C_o^{p}$ should be more than 10.

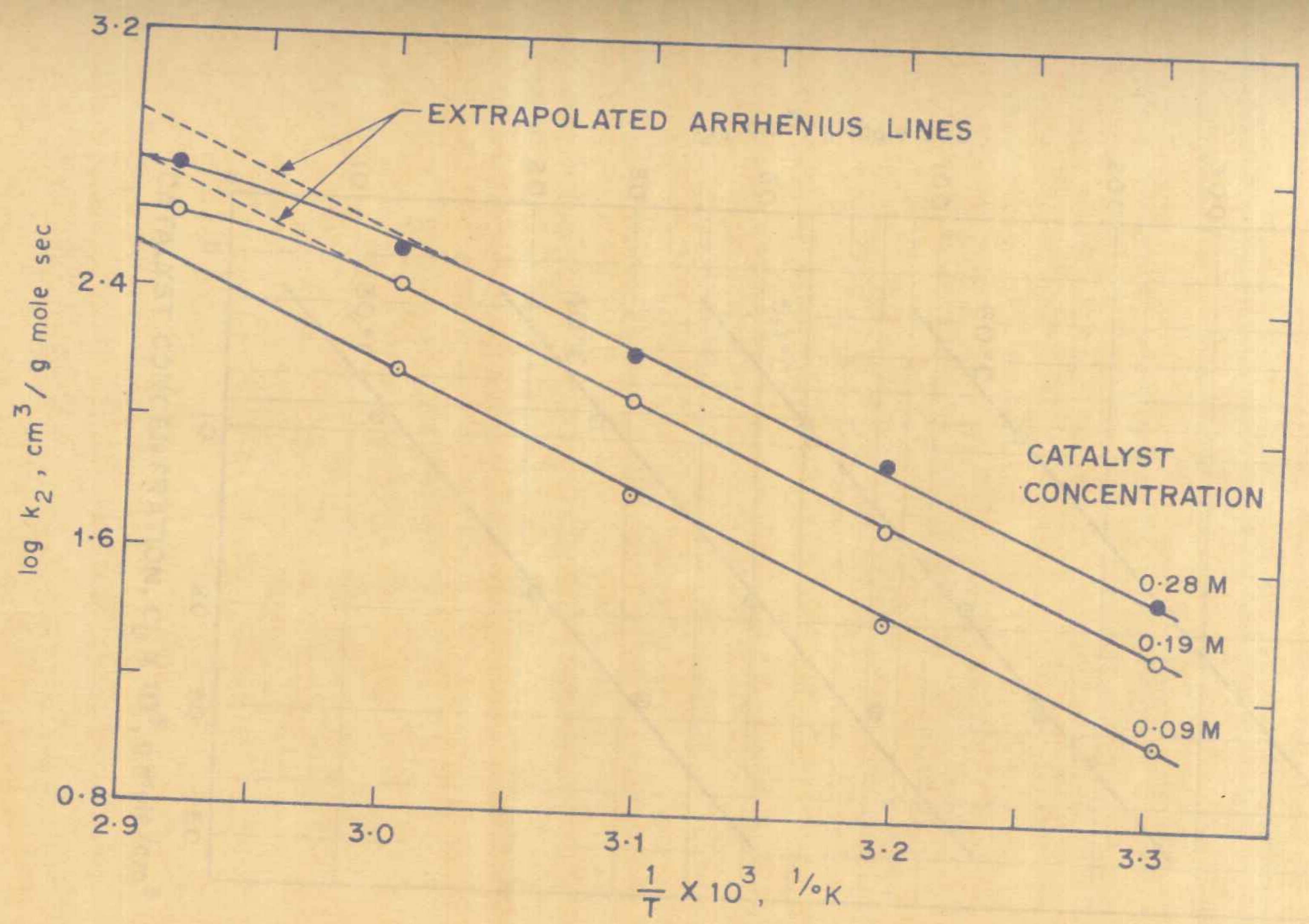


FIG. 3·3: TEMPERATURE DEPENDENCE OF THE SECOND-ORDER RATE CONSTANT

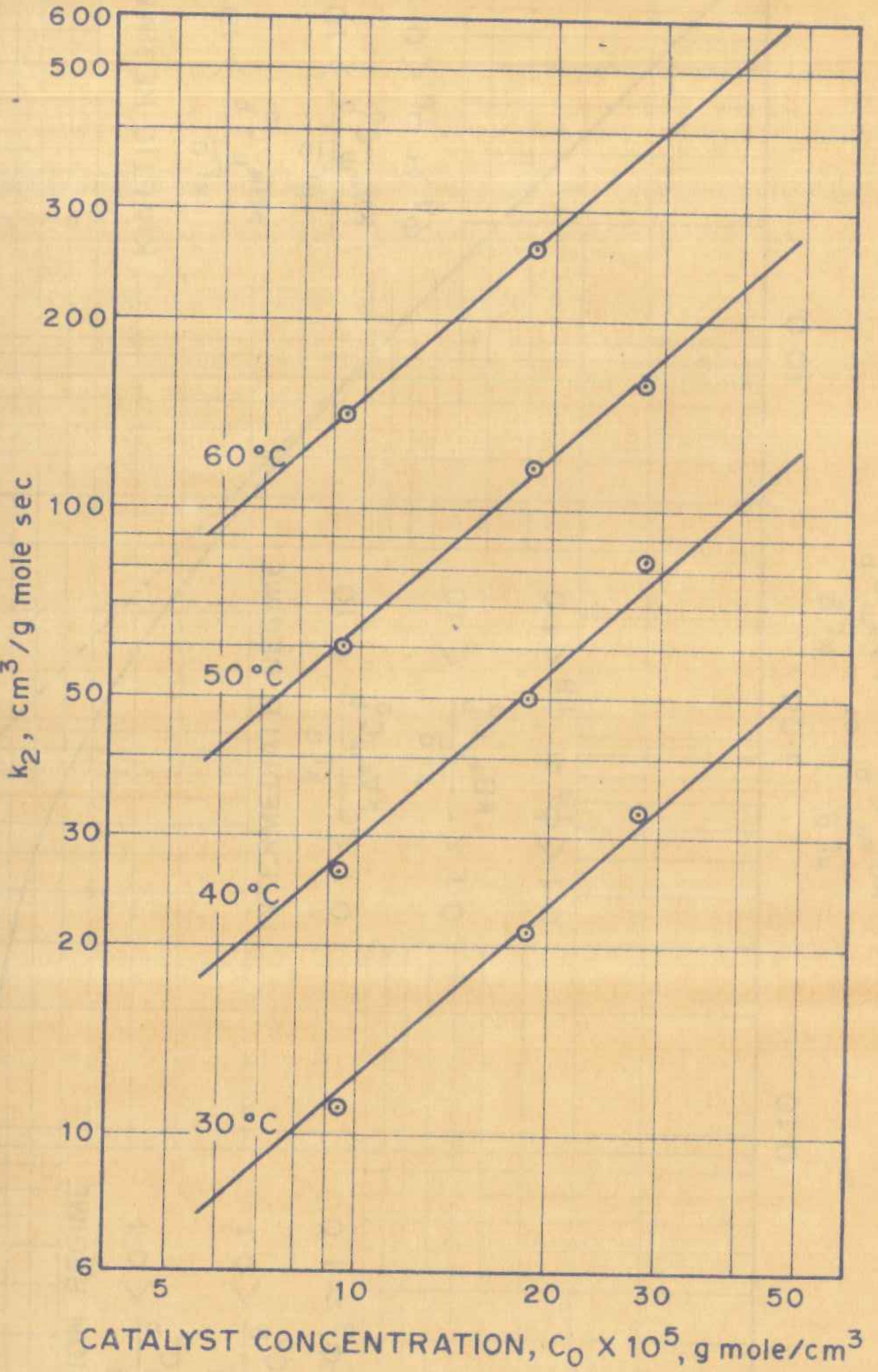


FIG. 3·4: EFFECT OF CATALYST CONCENTRATION ON THE REACTION RATE IN THE KINETIC REGIME

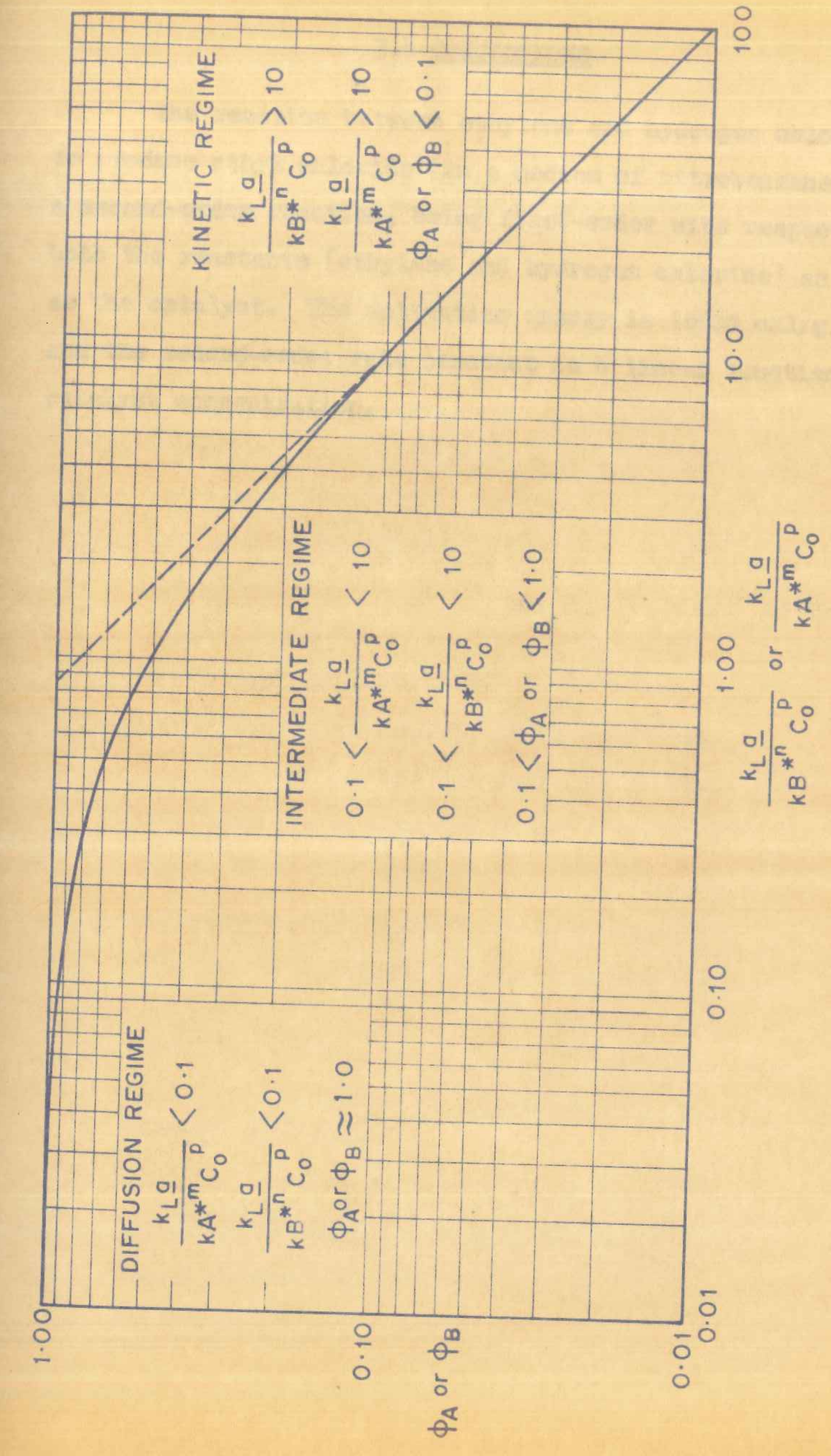


FIG. 3·5: TRANSITION FROM KINETIC TO THE DIFFUSIONAL REGIME

3.4 CONCLUSIONS

The reaction between ethylene and hydrogen chloride to produce ethyl chloride [in a medium of nitrobenzene] is a second-order reaction, being first-order with respect to both the reactants [ethylene and hydrogen chloride] as well as the catalyst. The activation energy is 16600 cal/g mole and the second-order rate constant is a linear function of catalyst concentration.

NOTATION

a	arbitrary constant
$\underline{a}$	effective interfacial area, cm^2/cm^3
A^*	solubility of ethylene in nitrobenzene, g mole/cm^3
b	arbitrary constant
B^*	solubility of hydrogen chloride in nitrobenzene, g mole/cm^3
c	arbitrary constant
C_o	concentration of aluminium chloride in nitrobenzene, g mole/cm^3
D	diffusion coefficient, cm^2/sec
D_A	diffusion coefficient of ethylene in nitrobenzene, cm^2/sec
D_B	diffusion coefficient of hydrogen chloride in nitrobenzene, cm^2/sec
E	activation energy of the reaction, cal/g mole
k	reaction rate constant, $[cm^3/g\ mole]^2$/sec
k_2	$[k\ C_o]$ second-order reaction rate constant, cm^3/g mole sec
k_∞	frequency factor, $[cm^3/g\ mole]^2$/sec
k_L	liquid film mass transfer coefficient, cm/sec
$\underline{l}$	fractional hold up of the liquid phase
m	order of reaction with respect to the concentration of ethylene
M	molecular weight, gm
n	order of reaction with respect to the concentration of hydrogen chloride
N_1	normality of HCl solution, $[g\ mole/cm^3]\ 10^3$
N_2	normality of sodium thiosulfate solution, $[g\ mole/cm^3]\ 10^3$
p	order of reaction with respect to the concentration of the catalyst

P	partial pressure of the gas under study, cm
Q	area of cross-section of the absorbing interface, cm^2
r	rate of a chemical reaction, g $mole/cm^3$ sec
R	universal gas constant, cal/g mole ^oK
R_A	specific rate of absorption of ethylene, g $mole/cm^3$ sec
R_B	specific rate of absorption of hydrogen chloride g $mole/cm^3$ sec
R_A'	rate of physical absorption of ethylene, g $mole/cm^3$ sec
R_B'	rate of physical absorption of hydrogen chloride, g $mole/cm^3$ sec
S	solubility, gm/Litre
t	time, sec
T	absolute temperature, ^oK
V_o	volume of the gas dissolved at STP, cm^3
V_1	volume of the solvent, cm^3
V	volume of the gas displaced in time t, cm^3
x	association parameter
x_1	blank titration reading, cm^3
x_2	back titration reading, cm^3
X	volume of the sample, cm^3
Z	stoichiometric coefficient
α_T	Bunsen's absorption coefficient at temperature T
β	$\alpha_T \left(\frac{T}{273}\right)\left(\frac{P}{760}\right)$ a constant in Equation 2.1
ν	molecular volume of the gas, cm^3
μ	viscosity of the solvent, centipoise
ϕ_A	enhancement factor for ethylene defined by Equation 3.1
ϕ_B	enhancement factor for hydrogen chloride defined by Equation 3.2

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PART - II

ABSORPTION OF PHOSPHINE IN AN AQUEOUS SOLUTION OF HYDROCHLORIC ACID AND FORMALDEHYDE: FORMATION OF TETRAKKIS- [HYDROXYMETHYL] PHOSPHONIUM CHLORIDE

CHAPTER - 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 LITERATURE SURVEY

Tetrakis [hydroxymethyl] phosphonium chloride [THPC] is a rather unusual and little investigated organophosphorus compound, but has recently attracted interest as an intermediate for certain resins which impart flame resistance to cotton fabrics. There is a lot of information available in the literature on the compounds of THPC, but little on the manufacturing process itself.

THPC was first reported by Hoffman in 1921 [5], who prepared it by the reaction of phosphine with aqueous formaldehyde and hydrochloric acid solution. He carried out the reaction at 80°C and found it to be so slow that it took two days to obtain 50 gm of THPC, but he was not sure of the structure of THPC which he established later [6]. With a view to improving this method Reeves et al [10] thought that at 80°C the vapour pressure of the solution interfered with the absorption of phosphine and thus carried out the reaction at lower temperatures [10-30°C], where the explosions were also avoided. These authors used an agitated contactor and found that at lower temperatures the absorption of phosphine was rapid. Gobain et al [4] have reported the formation of THPC by reacting Zn_3P_2 with formaldehyde in hydrochloric acid solution.

In the Hooker electrochemical process [1] THPC is prepared by passing phosphine in an aqueous solution of formaldehyde and hydrochloric acid under a slight positive pressure of the inert gas. The temperature was maintained above 10°C but below 25°C to prevent explosions, and good agitation was also maintained to promote rapid absorption of phosphine. The reaction was carried out to about 90% conversion, since it slows at the end and this was evaporated to obtain a crystalline product of about 95% purity. A patent by Flynn et al [3] in 1956 also describes the preparation of THPC by a method similar to those discussed above.

Reuter in 1959 [11] prepared THPC by treating phosphine with aqueous formaldehyde and hydrochloric acid solution in the presence of a heavy metal catalyst such as Hg, and reported that the addition of the catalyst increased the reaction velocity considerably at moderate temperatures without the use of rapid stirrers. He found that at 30-35°C the use of Hg catalyst decreased the time required for the absorption of phosphine by one half. Reuter also suggested the use of $AgNO_3$ and $PtCl_4$ as the catalysts for this reaction. Later in 1960 Roitburd et al [12] also reported the synthesis of THPC by reacting phosphine [obtained from aluminium phosphide and water], formaldehyde and hydrochloric acid and claimed 99.9% yield of THPC. Raver et al [9] have also suggested a method for the preparation of THPC in steps. These authors first obtained tetrakis [hydroxymethyl] phosphonium hydroxide [$(CH_2OH)_4$ POH] by passing PH_3 through three successive scrubbing towers containing 38% formaldehyde at 40-80°C under an overall pressure of 150-300 mm in the system. Tetrakis [hydroxymethyl] phosphonium hydroxide was further treated with hydrochloric acid to give THPC.

1.2 INDUSTRIAL APPLICATIONS OF THPC

THPC is widely used in the fire proofing of textiles. It reacts with amines, phenols, polybasic acids and anhydrides producing many useful polymers which are used as flame retardants. In fact THPC has recently attracted interest due to its use as an intermediate in the manufacture of certain resins and polymers which are used as flame retardants and thus has opened up a vast field of new flame resistant polymers.

THPC is also used in making some emulsions required for photographic printing. Its use in hair treatment [for fixing], photographic sensitizer, heat stabilizers for polyesters and polyethers has also been mentioned. THPC is also used in light fastening on dyes and pigments on textiles.

1.3 KINETICS AND MECHANISM

No attempt has been made so far to investigate the kinetics of this reaction and there is no information reported on the mechanism of the reaction, but it seems likely that the following steps would be involved:

$$HCHO + HCl \rightleftharpoons ClCH_2OH \qquad [1.1]$$

$$PH_3 + 4\ ClCH_2OH \rightarrow [CH_2OH]_4\ PCl + 3\ HCl \qquad [1.2]$$

$$PH_3 + HCl + 4\ HCHO \rightarrow [CH_2OH]_4\ PCl \qquad [1.3]$$

resulting in the overall reaction [Equation 1.3]. The first step has been shown as an equilibrium reaction in view of the literature report that the chloromethanol formed is not isolable [7]. This intermediate then reacts with PH_3 to give THPC. Thus the reaction appears to be a combination of two steps which suggest approximately first-order kinetics with respect to HCHO and PH_3.

1.4 SCOPE OF THE PRESENT WORK

The information available in the literature to date on the absorption of phosphine in an aqueous solution of formaldehyde and hydrochloric acid relates only to the manufacture of THPC and the kinetics and controlling mechanism have not been investigated.

The present work was therefore undertaken with the object of studying the mechanism of absorption of phosphine [in THPC formation] and establishing the kinetics of this industrially important reaction.

CHAPTER - 2

ANALYSIS OF THE REACTION

CHAPTER 2

ANALYSIS OF THE REACTION

2.1 GENERAL

Absorption and reaction of phosphine in an aqueous solution of formaldehyde and hydrochloric acid takes place according to the following reaction to give tetrakis [hydroxymethyl] phosphonium chloride [THPC]:

$$PH_3 + HCl + 4\ HCHO \rightarrow [CH_2OH]_4\ PCl \qquad [2.1]$$

The probable mechanism has been discussed in the previous section. This reaction is also significant theoretically in that it provides an example of gas-liquid reaction in which the gas [PH_3] reacts with two reactive components in the liquid phase [hydrochloric acid and formaldehyde]. The present work was undertaken with the object of studying the kinetics of this rather interesting system which is also of considerable industrial importance.

2.2 EXPERIMENTAL

2.2.1 Reactor assembly

One of the important considerations in any experimental programme associated with gas-liquid reactions is the choice of the experimental reactor. From preliminary rate data and a knowledge of the mass transfer coefficient, as described in the next section, it was observed that the reaction is essentially kinetically controlled. For gas-liquid reactions falling in this regime, agitated reactors are usually recommended. Thus an all-glass agitated reactor as described in Part I [Chapter 3] was used in the present work. The other important parts of the assembly are the capillary and the soap film flowmeters to measure inlet and outlet gas flow rates respectively. A diagrammatic sketch of the complete assembly is shown in Figure 2.1. A thermostatic bath was used for temperature control.

2.2.2 Materials

Formaldehyde [35% by wt] and hydrochloric acid [33% by wt] were used directly as obtained. Distilled water was used as solvent.

As the gaseous reactant PH_3 could not be obtained as such, it was prepared in the laboratory by reacting yellow phosphorus [300 gm] with calcium hydroxide slurry [made from 500 gm CaO] in a 5 litre flask. The reaction is:

$$P_4 + 2\,Ca[OH]_2 + 4\,H_2O \rightarrow 2\,Ca[H_2PO_2]_2 + 2\,H_2 \qquad [2.2]$$

$$P_4 + 2\,Ca[OH]_2 + 2\,H_2O \rightarrow 2\,CaHPO_3 + 2\,PH_3 \qquad [2.3]$$

Initially the system was flushed by nitrogen gas in view of the inflammability of PH_3 in contact with air. Then the reaction mixture was heated to 70-80°C on a water bath under good agitation and the liberated PH_3 collected and stored in a gas holder. PH_3 thus obtained was of 60% purity and the impurities were mainly traces of P_2H_4 [diphosphine] and hydrogen, the latter being an inert for the present system.

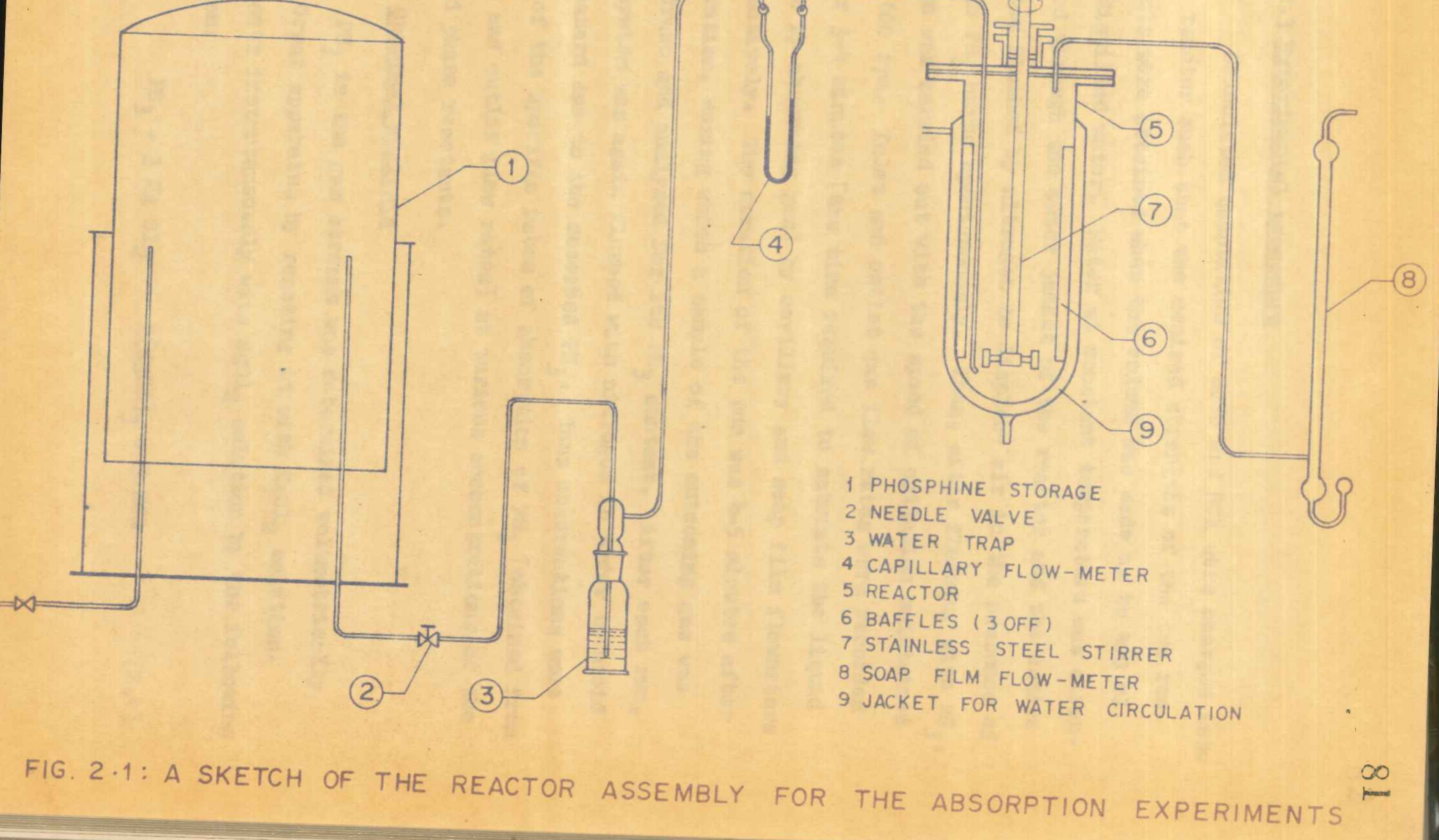

FIG. 2·1: A SKETCH OF THE REACTOR ASSEMBLY FOR THE ABSORPTION EXPERIMENTS

2.2.3 Experimental procedure

Calculated quantities of HCHO and HCl were charged into the reactor such that the desired strengths of the two reactants were obtained when the volume was made up to 400 ml by distilled water. Water at constant temperature was circulated through the outer jacket of the reactor and the entire system flushed by nitrogen to displace air in the presence of which PH_3 burns spontaneously. Then, after flushing with PH_3, a run was carried out with the speed of agitation maintained at 1600 rpm. Inlet and outlet gas flow rates were recorded after 3-4 minutes [the time required to saturate the liquid phase by absorbing gas] by capillary and soap film flowmeters respectively. The duration of the run was 4-5 minutes after saturation, during which a sample of the outcoming gas was withdrawn and analysed for its PH_3 content. After each run, the system was again flushed with nitrogen in order to avoid the hazard due to the desorbed PH_3. Thus observations were made of the specific rates of absorption of PH_3 [obtained from inlet and outlet flow rates] at various concentrations of the liquid phase reactants.

2.2.4 Chemical analysis

PH_3 in the gas streams was determined volumetrically in an Orsat apparatus by reacting it with $HgCl_2$ solution. PH_3 reacts instantaneously with $HgCl_2$ solution by the following reaction:

$$PH_3 + 3\,HgCl_2 \rightarrow P[HgCl]_3 + 3\,HCl \qquad [2.4]$$

and thus this method is quite accurate even for determining traces of PH_3.

2.3 PHYSICOCHEMICAL DATA FOR THE SYSTEM

2.3.1 Solubility

The solubility of PH_3 in water as well as in aqueous solutions of NaCl and H_2SO_4 has been well studied by Weston [13]; his results are presented in Table 2.1, the temperature dependence of the solubility being plotted in Figure 2.2. On the basis of these data it can be concluded that the reduction in the solubility of PH_3 in aqueous HCl solution would be insignificant [less than 2 to 3%], so that the solubility of PH_3 in water can be directly used to calculate the concentration of PH_3 in the liquid phase.

2.4 RESULTS AND DISCUSSION

2.4.1 Calculation of rates

The rates of absorption of PH_3 in an aqueous solution of HCl and HCHO were found to be very low, of the order of $1 - 7 \times 10^{-8}$ g mole/cm^3 sec; thus considerable precision was required in the calculation of these rates. In the experimental runs reported in the present work the rates were calculated by measuring the inlet and outlet flow rates of the gas phase, the composition of which was: PH_3, 60% and H_2, 40%. As mentioned earlier, no attempt was made to prepare pure PH_3 since this mixture could be directly used in the kinetic study. In view of the very low rates of absorption, the reduction

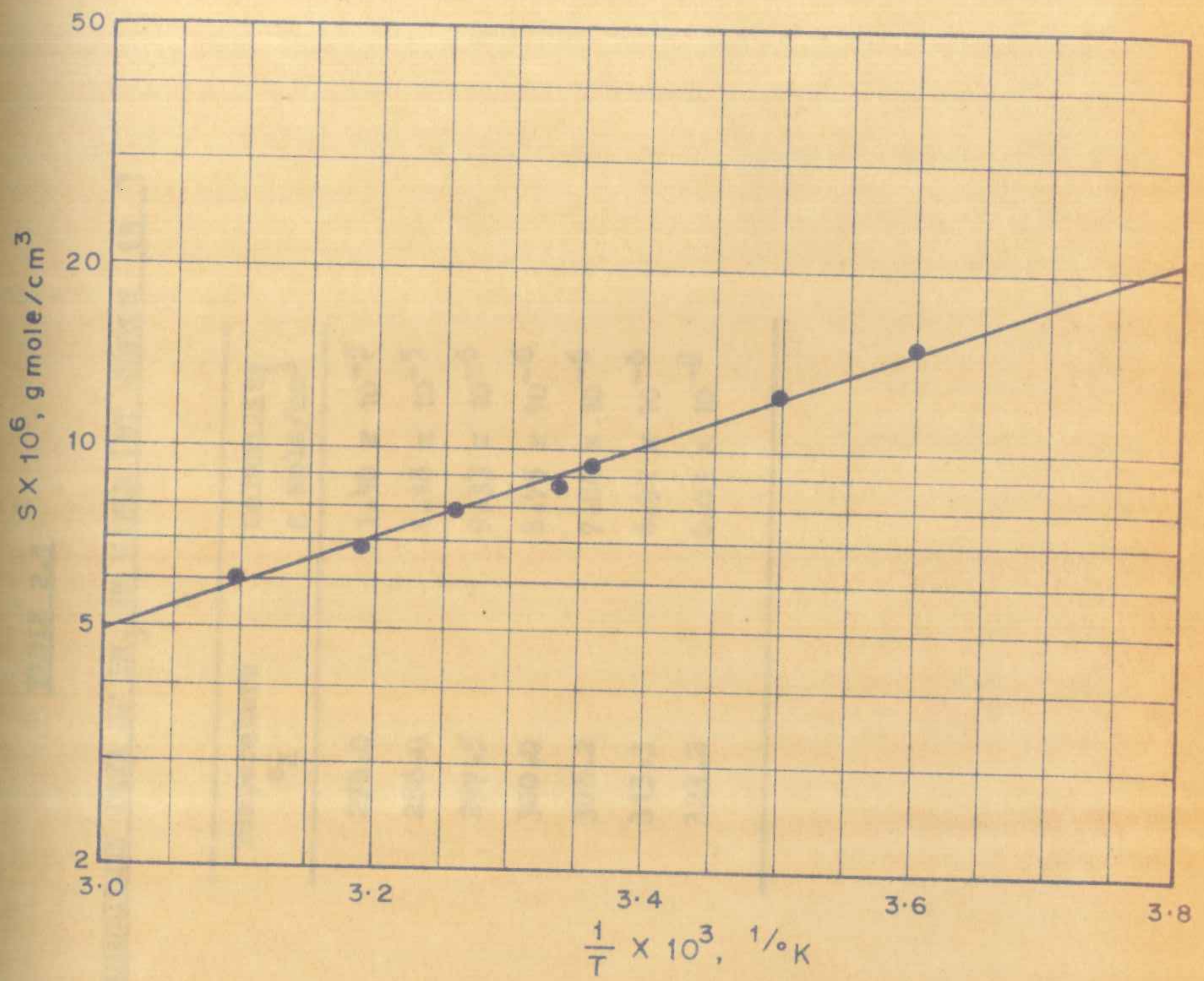

FIG.2·2: EFFECT OF TEMPERATURE ON THE SOLUBILITY OF PH_3 IN WATER

TABLE 2.1

SOLUBILITY DATA OF PH_3 IN WATER [BY WESTON 13]

Temperature ^{o}K	Solubility g mole/cm^3
278.0	1.40×10^{-5}
286.0	1.18×10^{-5}
297.5	9.33×10^{-6}
300.0	8.75×10^{-6}
306.2	7.86×10^{-6}
313.3	6.92×10^{-6}
323.2	6.03×10^{-6}

in the volume was very small and the rates thus calculated subject to error. It was therefore necessary to confirm the rate by analysing the exit gas for PH_3 and thus determining the amount of PH_3 reacting. Only those runs in which the rates determined by these two methods agreed to within 5% were considered for analysis of the results. From these rates and the duration of the run final concentrations of the liquid phase reactants were calculated and the average of the initial and the final concentrations was used in the final calculations. It may be mentioned here that the reaction being very slow and the duration of the run only 4-5 minutes, the change in concentrations of the liquid phase reactants is small enough not to affect the specific rate of absorption significantly.

In calculating the concentration of PH_3 in the liquid phase, the partial pressure of PH_3 at the reactor outlet was used, since at the speed of agitation employed in the present work the gas phase is expected to be completely backmixed. Then from a knowledge of this partial pressure and the solubility data discussed in the earlier section, the concentration of PH_3 in the liquid phase was calculated. The vapour pressure of water and the atmospheric pressure in Poona [710 mm Hg] were also taken into account during the calculation of the outlet partial pressure.

2.4.2 Organisation of experiments

The type of contactor to be used in the experimental studies normally varies with the regime in which the runs are sought to be carried out. Thus a preliminary experimental programme was organised to establish the regime involved in the concentration ranges that are practically feasible. In view of the slow rates of absorption of PH_3 observed, as a first step, kinetic control was assumed and experiments carried out to determine the maximum concentrations of the liquid phase reactants [HCl and HCHO] at which the absorption would be unambiguously in the kinetic regime. These experiments were carried out in the agitated contactor described earlier and the approximate values of the enhancement factor ϕ defined below were calculated:

$$\phi = \frac{R_A}{k_L \underline{a}\, A^*} \qquad [2.5]$$

where R_A represents the specific rate of absorption of PH_3, g mole/cm^3 sec; k_L the liquid film mass transfer coefficient, cm/sec; $\underline{a}$ the effective interfacial area, cm^2/cm^3; and A^* the solubility of PH_3 in the liquid phase, g mole/cm^3. The condition for kinetic control is:

$$\phi \ll 1 \qquad [2.6]$$

The application of this condition does not require a prior knowledge of either the rate constant or the reaction order and therefore provides a powerful basis for evaluating raw data and ensuring kinetic control.

In agitated contactors $k_L\underline{a}$ is usually in the range of 0.1 - 0.15 [sec^{-1}] [8]. Thus, for every run with specific value of A^*, the rate of absorption R_A can be found and the applicability of the condition verified. In all the preliminary runs carried out to broadly fix the concentration ranges of the liquid phase reactants, a stirrer speed of 1600 rpm was used. Having thus obtained the highest concentrations of HCl and HCHO consistent with kinetic control, as a supporting test, the effect of agitation was also studied at these concentrations, and the results are presented in Figure 2.3. It can be seen that beyond 1300 rpm, agitation has no effect. This ensures complete elimination of the mass transfer resistance at 1600 rpm [the speed of agitation employed in the bulk of the experiments].

Thus all experiments carried out at 1600 rpm in the concentration ranges determined should conform to the kinetic regime provided they also satisfy condition 2.6. Several experiments were carried out by the procedure discussed above in the temperature range 4 - 40°C and the results are presented in Table 2.2.

If preliminary runs are not made to make sure that the process is indeed in the kinetic regime and the absorption data are taken such that there is some diffusional resistance and condition 2.6 is not met satisfactorily, then the results interpreted on this basis would underestimate the reaction rate constant. Hence organisation of experiments and preliminary analysis of the data are very important. This has been discussed in detail by Astarita [2].

2.4.3 Regimes of control

In addition to applying condition 2.6 for correlating

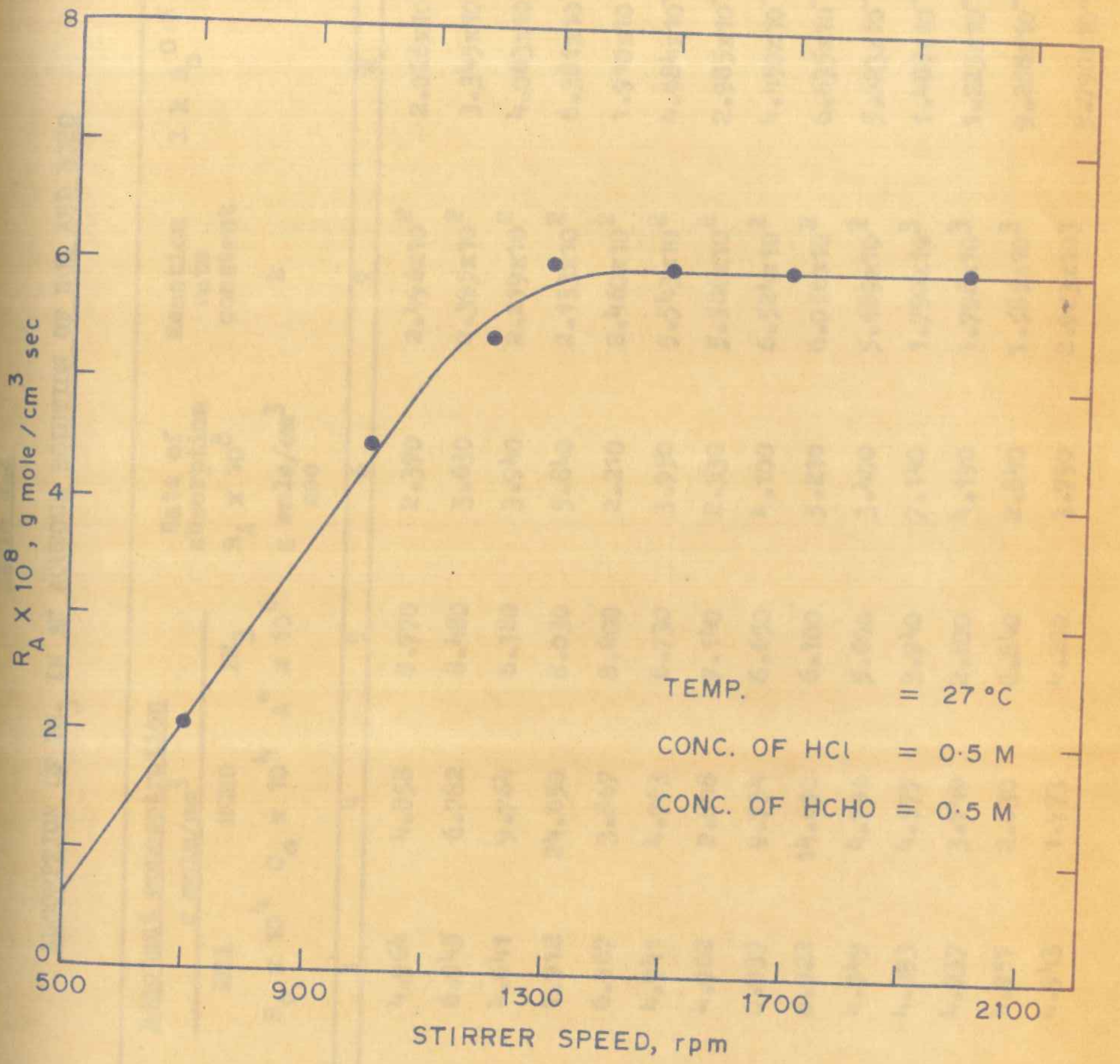

FIG. 2·3: EFFECT OF THE SPEED OF AGITATION ON THE RATE OF ABSORPTION OF PH_3

TABLE 2.2

ABSORPTION OF PH_3 IN AN AQUEOUS SOLUTION OF HCl AND HCHO

Run No.	Temp. ^oK	Reactant concentration g mole/cm^3 HCl $B_o \times 10^4$	HCHO $C_o \times 10^4$	PH_3 $A^* \times 10^6$	Rate of absorption $R_A \times 10^8$ g mole/cm^3 sec	Reaction rate constant k	$1\ k\ B_o^{0.5}\ C_o$	Enhancement factor
1	2	3	4	5	6	7	8	9
1	277	4.964	4.858	8.770	2.370	2.496×10^2	2.026×10^{-3}	0.019
2	277	6.945	6.782	8.480	3.630	2.395×10^2	3.345×10^{-3}	0.031
3	277	4.941	9.764	8.180	3.940	2.219×10^2	4.063×10^{-3}	0.034
4	277	1.912	24.650	8.030	5.840	2.133×10^2	6.381×10^{-3}	0.052
5	277	6.967	3.867	8.800	2.210	2.460×10^2	1.910×10^{-3}	0.018
6	286	4.941	4.763	6.730	3.950	5.543×10^2	4.984×10^{-3}	0.042
7	286	4.962	2.848	7.140	2.530	5.586×10^2	2.985×10^{-3}	0.025
8	286	0.939	9.754	6.650	4.100	6.524×10^2	4.450×10^{-3}	0.044
9	286	0.922	14.690	6.100	5.210	6.056×10^2	6.635×10^{-3}	0.061
10	286	4.949	4.796	5.600	3.400	5.689×10^2	5.023×10^{-3}	0.043
11	300	4.893	4.577	3.940	7.140	1.790×10^3	1.488×10^{-2}	0.120
12	300	4.937	3.749	2.800	4.190	1.798×10^3	1.225×10^{-2}	0.110
13	300	4.957	2.830	2.840	2.840	1.585×10^3	9.288×10^{-3}	0.071
14	300	4.943	1.773	4.200	3.790	2.923x103	5.790x10-3	0.065

1	2	3	4	5	6	7	8	9
15	300	4.974	0.896	4.410	1.740	1.975×10^3	2.940×10^{-3}	0.028
16	300	0.943	9.773	1.860	3.790	2.147×10^3	1.397×10^{-2}	0.145
17	300	0.453	9.810	2.250	3.160	2.127×10^3	9.720×10^{-3}	0.100
18	300	0.205	9.820	3.810	3.000	1.770×10^3	6.550×10^{-3}	0.056
19	300	1.949	4.796	3.060	3.400	1.655×10^3	9.880×10^{-3}	0.079
20	300	4.915	4.658	3.240	5.700	1.701×10^3	1.522×10^{-2}	0.126
21	300	4.946	4.783	2.360	3.620	1.445×10^3	1.562×10^{-2}	0.110
22	300	4.962	4.848	1.050	2.530	2.228×10^3	1.591×10^{-2}	0.172
23	300	4.941	4.764	2.450	3.940	1.520×10^3	1.557×10^{-2}	0.115
24	300	4.948	4.790	1.752	3.500	1.870×10^3	1.570×10^{-2}	0.143
25	313	1.945	1.782	2.700	3.640	5.424×10^3	9.890×10^{-3}	0.096
26	313	1.972	0.886	3.180	1.900	4.799×10^3	4.960×10^{-3}	0.043
27	313	1.981	0.522	3.280	1.260	5.226×10^3	2.930×10^{-3}	0.027
28	313	0.462	2.848	2.900	2.530	4.506×10^3	7.710×10^{-3}	0.062
29	313	0.219	2.876	3.110	2.060	4.919×10^3	5.362×10^{-3}	0.047

the data in the kinetic regime the data were also tested by using the equations and conditions for different regimes as summarised below. From the preliminary analysis it has been observed that the reaction is essentially slow, and the reaction is said to be in the slow reaction regime when it occurs entirely in the bulk of the liquid. Hence this discussion will be restricted to reaction in the bulk - and the fast reaction regime [in which reaction occurs in the film] need not be considered. The reaction in the bulk may be controlled either by the kinetics or by diffusion, and on this basis it can be classified in two regimes, viz. kinetic regime and diffusion regime.

[a] Kinetic regime: The reaction is said to be kinetically controlled when the reaction rate is very slow in comparison with the diffusion rate. In this situation the specific rate of absorption of the gas [in g mole/cm^3 sec] is the same as the reaction rate and the liquid phase is essentially saturated with the absorbing gas [i.e. there is no depletion in the concentration of the dissolved gas at any point in the liquid phase]. The concentration profiles for this regime are shown in Figure 2.4. In this regime the concentration of the gaseous species in the liquid phase is given by its solubility [which is the same as the interfacial concentration]. The specific rate of absorption R_A [g mole/cm^3 sec] is given by:

$$R_A = r = k\, A^{*a}\, B_o^{b}\, C_o^{c} \qquad [2.7]$$

where k is the rate constant [$(\mathrm{cm}^3/\mathrm{g\ mole})^{a+b+c-1}$ sec^{-1}];

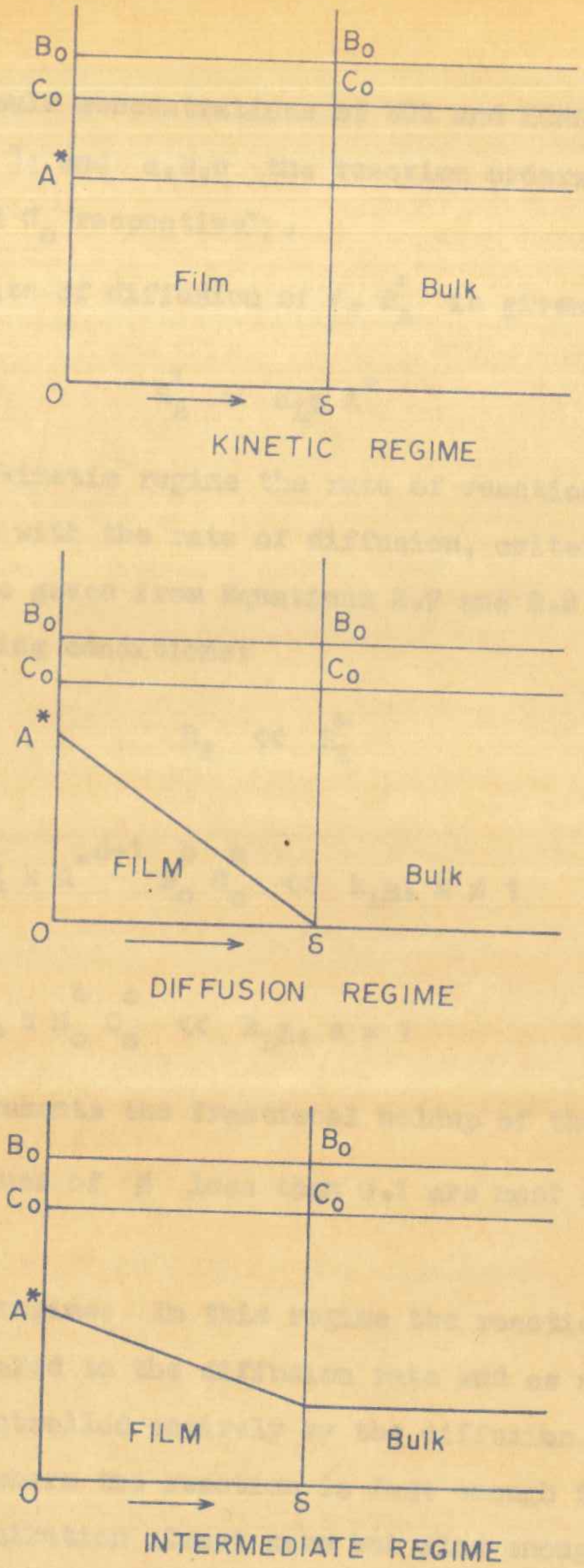

FIG. 2.4 : CONCENTRATION PROFILES OF THE REACTING SPECIES FOR VARIOUS REGIMES

B_o, C_o the bulk concentrations of HCl and HCHO respectively [g mole/cm^3]; and a,b,c the reaction orders with respect to A^*, B_o and C_o respectively.

The rate of diffusion of A, R'_A is given by

$$R'_A = k_L\underline{a}\, A^* \qquad [2.8]$$

Since in the kinetic regime the rate of reaction is very slow in comparison with the rate of diffusion, criteria for kinetic control can be given from Equations 2.7 and 2.8 in the form of the following conditions:

$$R_A \ll R'_A \qquad [2.9]$$

or

$$\underline{l}\, k\, A^{*a-1}\, B_o^b\, C_o^c \ll k_L\underline{a},\; a \neq 1 \qquad [2.10]$$

and

$$\underline{l}\, k\, B_o^b\, C_o^c \ll k_L\underline{a},\; a = 1 \qquad [2.11]$$

where $\underline{l}$ represents the fractional holdup of the liquid phase.

The values of $\emptyset$ less than 0.1 are most adequate for this regime.

[b] Diffusion regime: In this regime the reaction rate is very fast compared to the diffusion rate and as such the reaction is controlled entirely by the diffusion. This is the situation where the reaction is fast enough to maintain the bulk concentration almost zero but slow enough to occur in the film, and thus the concentration of the gaseous species

is not the same as that at the interface. The concentration profiles are shown in Figure 2.4. In this regime the rate of absorption of A is governed by its transport and is represented by Equation 2.8 and the condition is exactly the reverse, ie

$$R_A' << R_A \qquad [2.12]$$

or

$$k_L\underline{a} << \underline{1}\, k\, A^{*a-1} B_o^b C_o^c, \; a \neq 1 \qquad [2.13]$$

and

$$k_L\underline{a} << \underline{1}\, k\, B_o^b C_o^c, \; a = 1 \qquad [2.14]$$

It is also necessary to ensure that there is no reaction occurring in the film and as such the following condition has to be satisfied:

$$\frac{D_A\, k\, B_o^b C_o^c}{k_L^2} << 1 \qquad [2.15]$$

When the absorption is entirely diffusion controlled the mass transfer coefficients with and without chemical reaction are the same indicating that there is no enhancement in the absorption due to reaction. On this basis the following condition can also be postulated for the diffusion regime:

$$\phi = 1 \qquad [2.16]$$

[c] Intermediate regime: When the concentration of the gaseous species in the bulk is not the same as the interfacial

concentration but also not zero, a situation exists when the reaction and the diffusion rates are comparable and both are important. The concentration profiles for this regime are shown in Figure 2.4. The specific rate of absorption will be given by:

$$R_A = k_L\underline{a}\,[A^* - A_o] \qquad [2.17]$$

and

$$R_A = \underline{1}\,k\,A_o^a\,B_o^b\,C_o^c \qquad [2.18]$$

Eliminating the unknown A_o from Equations 2.17 and 2.18 we get the following relationship for the specific rate of absorption of A:

$$R_A = \frac{\underline{1}\,k\,A^*\,B_o^b\,C_o^c}{1 + \dfrac{\underline{1}\,k\,B_o^b\,C_o^c}{k_L\underline{a}}} \qquad [2.19]$$

Equations 2.7 and 2.8 are the two assymptotes of Equation 2.19 and the condition to be satisfied for the intermediate regime is:

$$\underline{1}\,k\,B_o\,C_o \approx k_L\underline{a},\ a = 1 \qquad [2.20]$$

When the values of $\emptyset$ are in the range 0.2 - 0.9 it is quite likely that the absorption would be in the intermediate regime. A diagrammatic presentation of all the three regimes is shown in Figure 2.5 which is a log-log plot of $\emptyset$ vs $\dfrac{k_L\underline{a}}{\underline{1}\,k\,B_o^b\,C_o^c}$.

From Figure 2.5 the transition from kinetic to the diffusion regime can be very clearly seen.

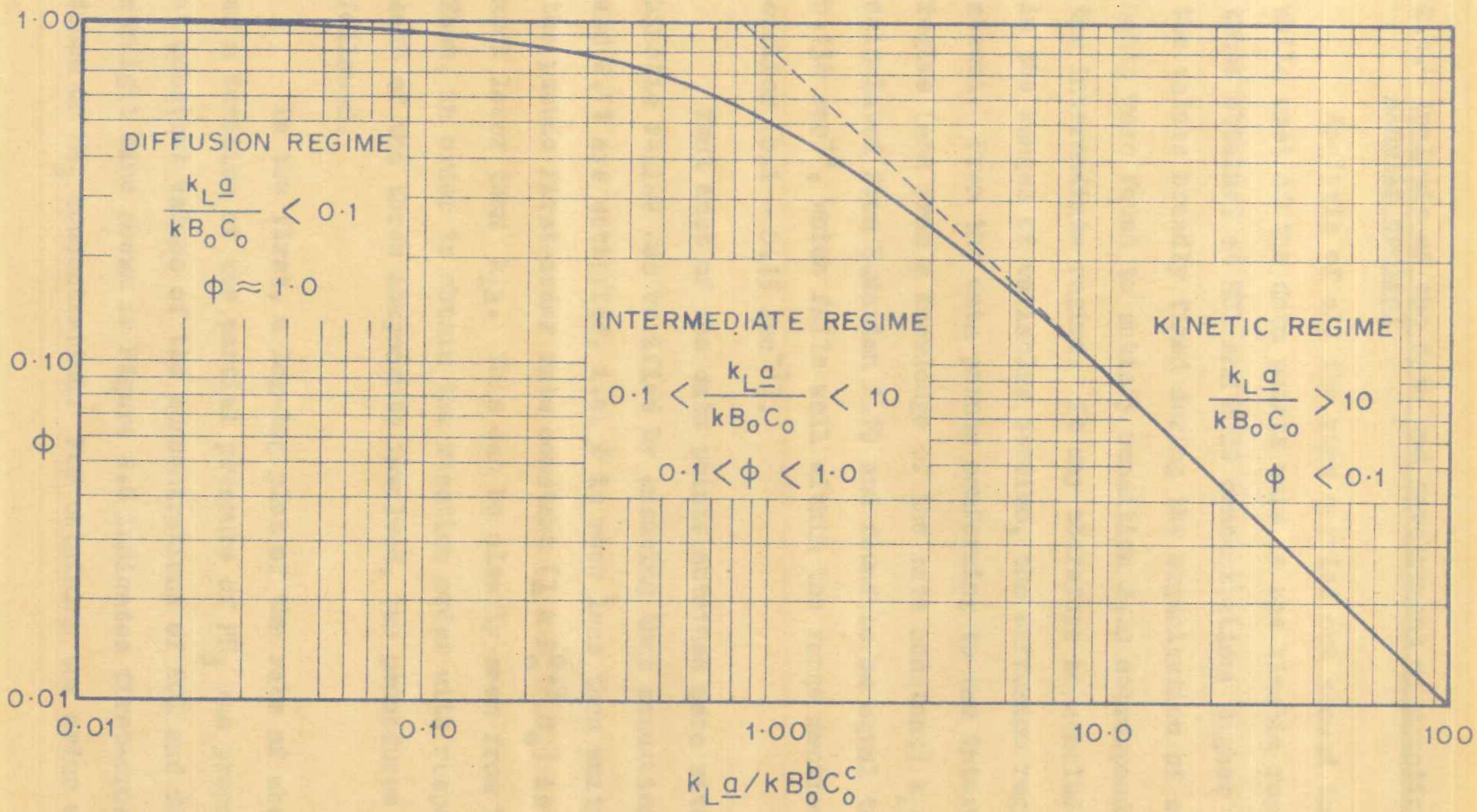

FIG. 2·5: TRANSITION FROM KINETIC TO THE DIFFUSIONAL REGIME

2.4.4 Analysis of the data and development of equation for kinetic control

Analysis of all the runs carried out showed that, while most of the data points were in the kinetic regime, those obtained at HCl and HCHO concentrations higher than the values broadly fixed during the organisation of experiments were found to satisfy condition 2.20 corresponding to the intermediate regime. It may therefore be concluded that in the ranges of variables studied, the diffusion regime is absent. From the data points conforming to the intermediate regime [and from a knowledge of the rate constant] $k_L\underline{a}$ was calculated from Equation 2.19 and found to be equal to 0.136 sec^{-1}, which falls well within the range mentioned earlier [0.1 - 0.15 sec^{-1}].

That most of the data points obtained were within the kinetic regime was verified by ensuring that conditions 2.6 and 2.11 are satisfied, i.e. ϕ is much less than unity and the pseudo first-order rate constant [$\underline{1}\ k\ B_o^{0.5}\ C_o$] is very much lower than $k_L\underline{a}$. This can be clearly seen from Table 2.2. Then, in order to obtain the reaction order with respect to each of the three components involved, two procedures were followed.

In the first, a log-log plot of the rate of absorption as a function of the partial pressure of PH_3 was prepared at constant values of the concentrations of HCl and HCHO. The straight line shown in Figure 2.6 indicates first-order dependence on PH_3 concentration. For obtaining the order with

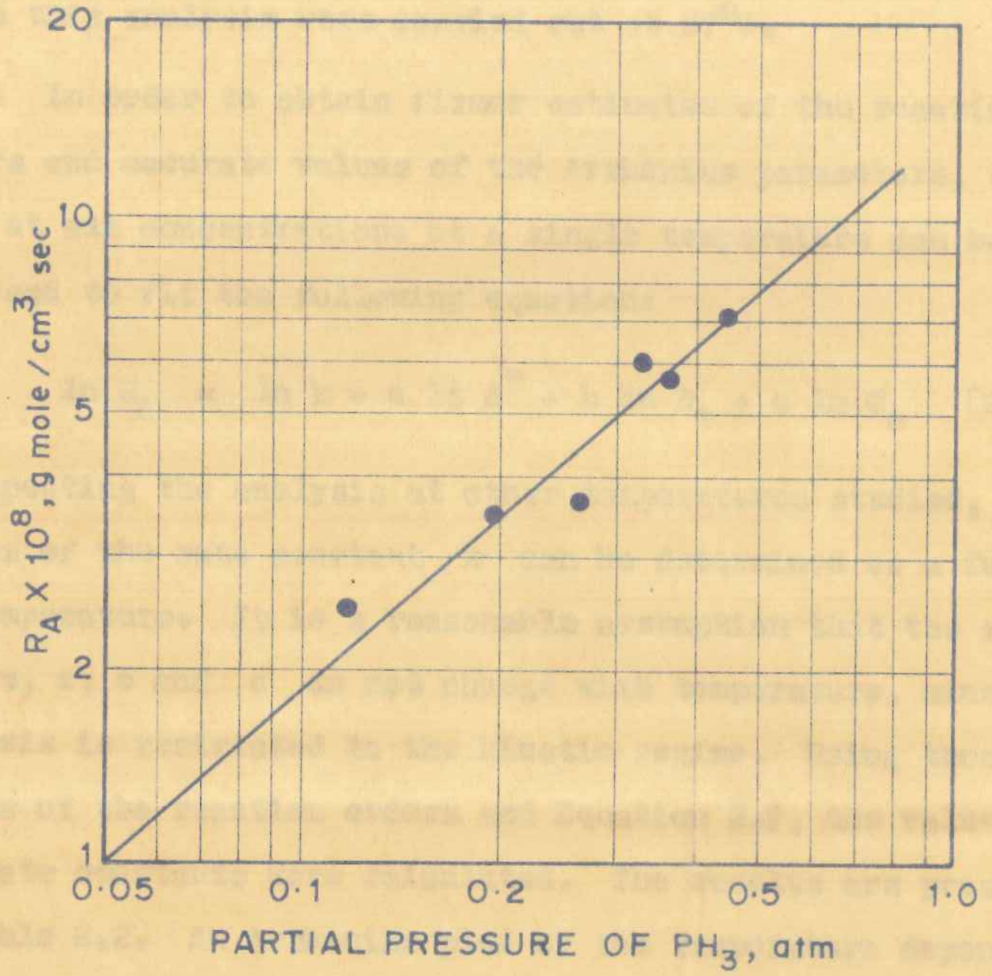

FIG. 2·6: EFFECT OF PARTIAL PRESSURE OF PH_3 ON THE RATE OF ABSORPTION respect to HCl and HCHO, log-log plots were prepared of $\frac{R_A}{A^*}$ vs concentrations B_o and C_o and the corresponding graphs are shown in Figure 2.7. It may be noticed that the reaction is first-order with respect to HCHO but approximately half-order with respect to HCl. All the experiments referred to in this analysis were carried out at 27°C.

In order to obtain firmer estimates of the reaction orders and accurate values of the Arrhenius parameters, the data at all concentrations at a single temperature can be analysed to fit the following equation:

$$\ln R_A = \ln k + a \ln A^* + b \ln B_o + c \ln C_o \qquad [2.21]$$

By repeating the analysis at other temperatures studied, the values of the rate constant k can be determined as a function of temperature. It is a reasonable assumption that the reaction orders, a, b and c do not change with temperature, since the analysis is restricted to the kinetic regime. Using these values of the reaction orders and Equation 2.7, the values of the rate constants were calculated. The results are presented in Table 2.2. An Arrhenius plot of the temperature dependence of the reaction rate constants is shown in Figure 2.8, from the slope of which the activation energy was calculated and found to be 14740 cal/g mole. The complete rate equation is then given by

$$R_A = 8.57 \times 10^{13} \; e^{\left(-\frac{14740}{RT}\right)} \; A^* \, B_o^{0.5} \, C_o \qquad [2.22]$$

In the second method [which is statistically more

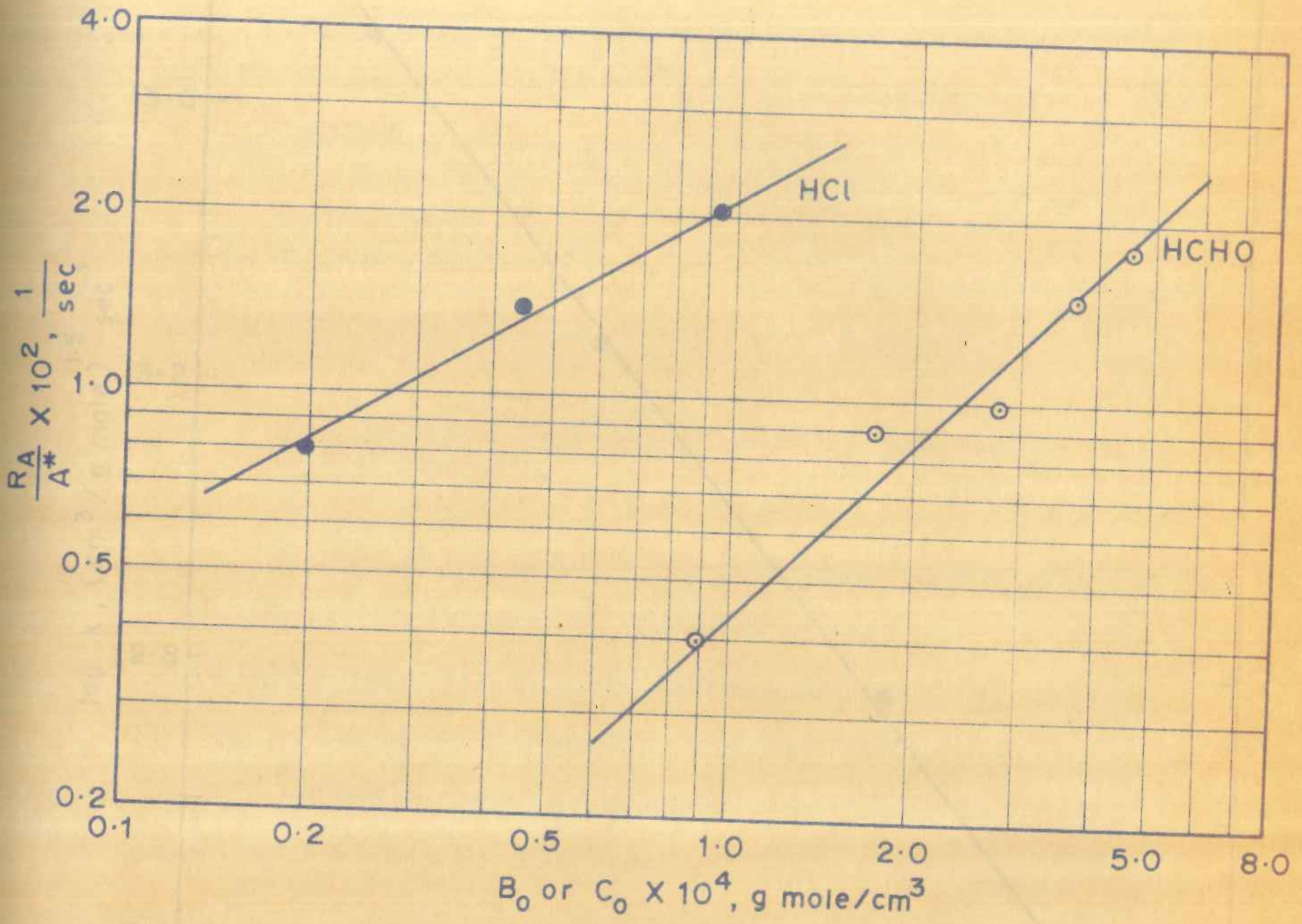

FIG. 2·7: EFFECT OF HCl AND HCHO CONCENTRATIONS ON THE RATE OF ABSORPTION OF PH_3

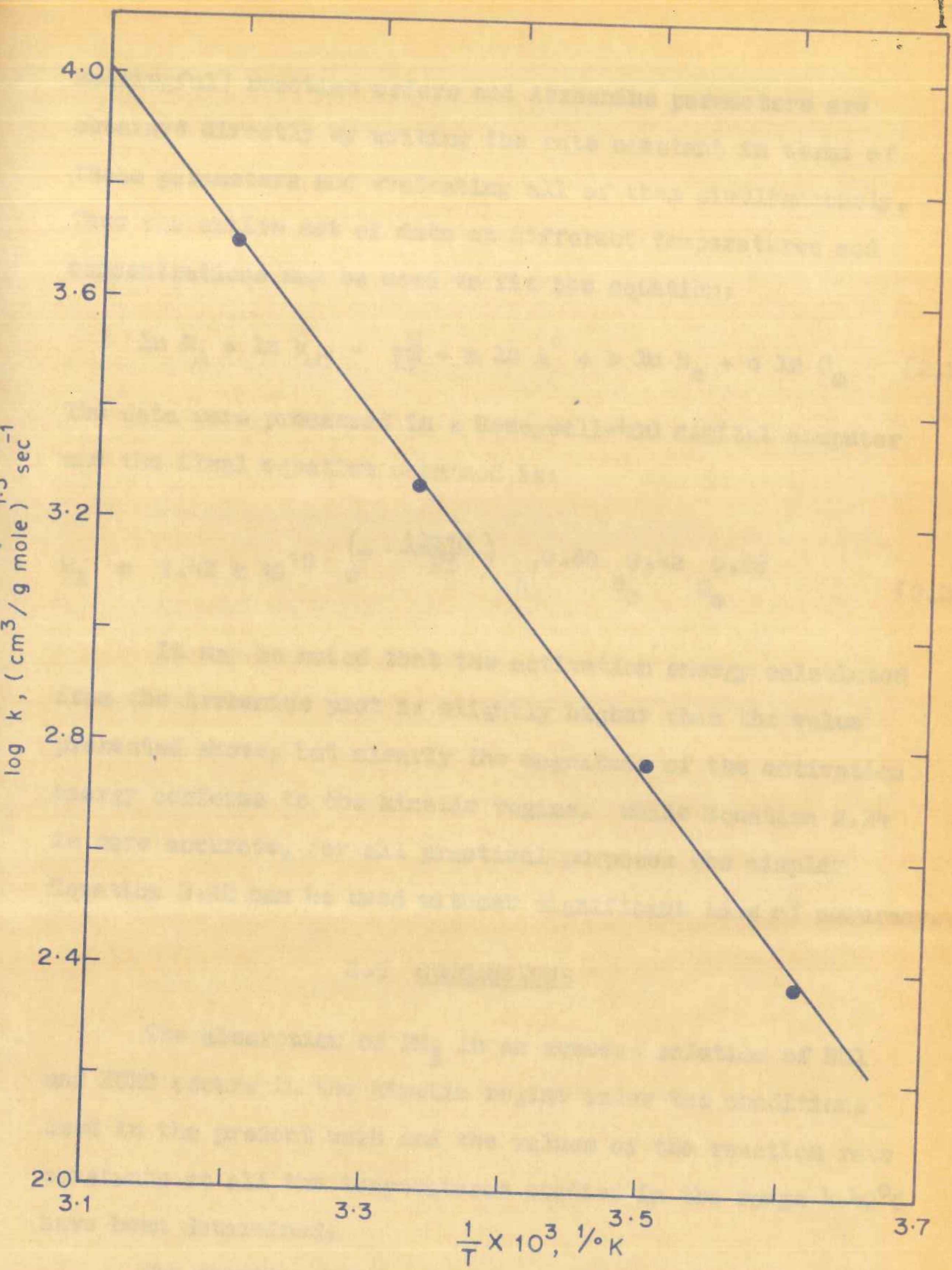

FIG. 2·8: TEMPERATURE DEPENDENCE OF THE REACTION RATE CONSTANT meaningful] reaction orders and Arrhenius parameters are obtained directly by writing the rate constant in terms of these parameters and evaluating all of them simultaneously. Thus the entire set of data at different temperatures and concentrations may be used to fit the equation:

$$\ln R_A = \ln k_{\infty} - \frac{E}{RT} + a \ln A^{*} + b \ln B_o + c \ln C_o \qquad [2.23]$$

The data were processed in a Honeywell-400 digital computer and the final equation obtained is:

$$R_A = 1.42 \times 10^{10} \, e^{\left(-\frac{12018}{RT}\right)} \, A^{*0.80} \, B_o^{0.42} \, C_o^{0.88} \qquad [2.24]$$

It may be noted that the activation energy calculated from the Arrhenius plot is slightly higher than the value presented above, but clearly the magnitude of the activation energy conforms to the kinetic regime. While Equation 2.24 is more accurate, for all practical purposes the simpler Equation 2.22 can be used without significant loss of accuracy.

2.5 CONCLUSIONS

The absorption of PH_3 in an aqueous solution of HCl and HCHO occurs in the kinetic regime under the conditions used in the present work and the values of the reaction rate constants at all the temperatures studied in the range 4-40°C have been determined.

The reaction has been found to be approximately first-order with respect to PH_3 [exact order: 0.80] and HCHO [exact order: 0.88], and approximately half-order with respect to HCl [exact order: 0.42].

NOTATION

a	order of reaction with respect to concentration of PH_3
$\underline{a}$	effective interfacial area, cm^2/cm^3
A^*	solubility of PH_3 in water, g mole/cm^3
A_o	concentration of PH_3 in the liquid bulk, g mole/cm^3
b	order of reaction with respect to the concentration of HCl
B_o	concentration of HCl in the liquid bulk, g mole/cm^3
c	order of reaction with respect to the concentration of HCHO
C_o	concentration of HCHO in the liquid bulk, g mole/cm^3
D_A	diffusion coefficient of PH_3 in water, cm^2/sec
E	activation energy of the reaction, cal/g mole
k	reaction rate constant, $[cm^3/g\ mole]^{1.5}$/sec
k_∞	Arrhenius frequency factor, $[cm^3/g\ mole]^{1.5}$/sec
k_L	liquid film mass transfer coefficient, cm/sec
$\underline{l}$	fractional hold up of the liquid phase
r	rate of a chemical reaction, g mole/cm^3 sec
R_A	specific rate of absorption of PH_3, g mole/cm^3 sec
R'_A	rate of physical absorption, g mole/cm^3 sec
R	universal gas constant, cal/g mole ^oK
T	absolute temperature, ^oK
ø	enhancement factor, defined by Equation 2.5

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PART - III

THEORETICAL STUDIES IN COMPLEX GAS-LIQUID SYSTEMS

CHAPTER - 1

COMPLEX GAS-LIQUID REACTIONS: A SURVEY

CHAPTER 1

COMPLEX GAS-LIQUID REACTIONS: A SURVEY

1.1 INTRODUCTION

The problem of absorption of one or more gases accompanied by a chemical reaction is of importance in industrial operations. A primary use is in removing some unwanted gases selectively from a mixture. Theoretical and experimental studies on the absorption of a single gas accompanied by a simple irreversible chemical reaction have been attempted for many systems and the topic is well discussed by Danckwerts [6] and Astarita [2]. But many industrially important problems involve the absorption of one or more gases accompanied by complex chemical reactions, and there is surprisingly little information available in the literature on this subject. Recently Ramachandran and Sharma [19] have reviewed the subject of simultaneous absorption of two gases.

In the present chapter all the information on the absorption of one or more gases accompanied by complex chemical reactions has been compiled together and discussed under the following four categories:

[1] reversible reactions;

[2] consecutive reactions;

[3] parallel reactions; and

[4] combination of reversible, consecutive and parallel reactions.

Models for the various types of complex reactions considered by previous authors are summarised in Table 1.1.

TABLE 1.1

SURVEY OF MODELS FOR COMPLEX REACTIONS

Reactions 1	Solution 2	Example 3	Reference 4
$A[g] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E$ [finite rate]	$\phi_A = [1 - q_A] \dfrac{1 + r_E K}{1 + r_E K \dfrac{\tanh\sqrt{\bar{M}_1}}{\sqrt{\bar{M}_1}}}$ $\bar{M}_1 = M\left(1 + \dfrac{1}{r_E K}\right)$		18,11,7
$A[g] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E$ [instantaneous]	$\phi_A = [1 - q_A]\,[1 + r_E K]$		18,12
$A[g] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2E$ [instantaneous]	$\phi_A = [1 - q_A]\left(1 + \dfrac{r_E\sqrt{K/A^*}}{2\left(1 + \sqrt{q_A}\right)}\right)$		12
$A[g] + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E$ [finite rate]	$\phi_A = [1 - q_A] + r_c\,[q_c - c_i]$ $\phi_A = [1 - q_A] \dfrac{1 + K r_E \left[C_i + \dfrac{C_i - C_o}{A^* - A_o} A_o \left(1 - \operatorname{sech}\sqrt{M'}\right)\right]}{1 + K r_E C_i \dfrac{\tanh\sqrt{M'}}{\sqrt{M'}}}$ $M' = k_1\left(\dfrac{C_i}{D_A} + \dfrac{1}{K D_E}\right)\delta^2$		18
$A[g] + C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E$ [instantaneous]	$\phi_A = [1 - q_A]\left(1 + \dfrac{r_c C_o}{A^* + \dfrac{r_c}{K r_E}}\right)$	Absorption of H_2S in amine solution; Absorption of O_2 in haemoglobin.	12

TABLE 1.1 CONTINUED

1	2	3	4
$Z_A\ A[g] + Z_c\ C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z_E\ E + Z_F\ F$ [finite rate]	$\phi_A = \dfrac{[1-q_A]\left(1+\frac{r_E}{\nu_E T}\right)+\frac{r_E}{\nu_E}\left(\frac{q_A}{T}-q_E\right)[1-\text{sech}\ M'']}{1+\frac{r_E}{E\ T}\ \frac{\tanh\sqrt{M''}}{\sqrt{M''}}}$ $M'' = M\left(\frac{c_i}{q_c}\right)^n\left(1+\frac{m+1}{p+1}\ \frac{E}{r_E}\ T\right)$ $T = \dfrac{K\ e_i^{p-1}\ f_i^{q}}{c_i^{n}}\ ,\quad M = \dfrac{2}{m+1}\ \dfrac{Z_A\ k_1\ A^{*m-1}\ C_o^{n}}{D_A}\ \delta^2$	Absorption of Cl_2 in water	13
$Z_A\ A[g] + Z_c\ C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z_E\ E + Z_F\ F$ [instantaneous]	$\phi_A = [1-q_A]\left(1+\frac{r_E}{\nu_E}\ \frac{e_i-q_E}{1-q_A}\right)$ $c_i = q_c - \frac{\nu_C}{\nu_E}\ \frac{r_E}{r_\theta}\ [e_i - q_E],\quad f_i = q_F + \frac{\nu_F\ r_E}{\nu_E\ r_F}\ [e_i - q_E]$ $K = E_i^{p}\ F_i^{q}\ /\ A^{*m}\ C_i^{n}$	Absorption of CO_2 in amine solution Absorption of H_2S in amine solution	26
$A[g] + C \rightleftharpoons E_1 + E_2$ $B[g] + C \rightleftharpoons F_1 + F_2$ [instantaneous]	$\phi_A = 1 + \frac{1}{2}\sqrt{\frac{K_A}{A^*}}\left(\sqrt{K_A\ A^*\ K_B\ B^*} + 2\sqrt{K_A\ A^*\ K_B\ B^* + 4\ C_o} - \sqrt{K_A\ A^*} - \sqrt{K_B\ B^*}\right)$	Simultaneous absorption of H_2S and CO_2 in amine solutions	20
$A[g] + C \rightleftharpoons E_1 + F_2$ $B[g] + C \rightleftharpoons F_1 + F_2$ [finite rate]	-	Simultaneous absorption of CO and C_2H_4 in ammoniacal $CuCl_2$ solution	21
$Z_A\ A[g] + Z_{E_1}\ E \rightleftharpoons Z_c\ C[g] + Z_{F_1}\ F$ $Z_{F_2}\ F + Z_B\ B[g] \rightleftharpoons Z_{E_2}\ E$ [finite rate]	$\phi_A = \dfrac{[1-q_A]\left(1+\frac{r_c}{\nu_c\ T_1}\right)+\frac{r_c}{\nu_c}\left(\frac{q_A}{T_1}-q_c\right)\left(1-\text{sech}\sqrt{\bar{M}}\right)}{1+\frac{r_c}{\nu_c\ T_1}\ \frac{\tanh\sqrt{\bar{M}}}{\sqrt{\bar{M}}}}$	Simultaneous absorption of SO_2 and O_2 in V_2O_5 solution	27

TABLE 1.1 CONTINUED

1	2	3	4
	$\bar{M} = M\left(\frac{e_i}{q_E}\right)^n \left(1 + \frac{\nu_c}{r_C} T_1\right)$ $T_1 = K_2 c_i^{p-1} q_E^{q-n} \frac{\left[\left(q_F/q_E\right) + 1 - \left(e_i/q_E\right)\right]^q}{\left(e_i/q_E\right)^n}$ $\phi_A = 1 - q_A + \frac{r_B}{\nu_{F_1}} [q_E - e_i] + \frac{r_B b^*}{\nu_B} \left[\phi_B - \frac{\nu_{E_2}}{\nu_{E_1}}\left(1 - q_B\right)\right]$ $\phi_A = 1 - q_A + \frac{r_c}{\nu_c} [c_i - q_c]$ $\phi_B = \left[\frac{\frac{\bar{M}_3}{\bar{M}_2} + \left(1 - \frac{\bar{M}_3}{\bar{M}_2}\right) \cosh\sqrt{\bar{M}_2} - q_B}{\sinh\sqrt{\bar{M}_2}}\right]\sqrt{\bar{M}_2}$		
$A[g] + C \rightarrow E$ $E + C \rightarrow$ Products [finite rate]	$R_A = \frac{A^* \sqrt{D_A k_1 C_i^n}}{\tanh\left(\sqrt{D_A k_1 C_i^n / k_L}\right)}$ $\frac{E_i}{A^*} = \frac{k_1/k_2}{[D_E/D_A][k_1/k_2] - 1} \left[\sqrt{\frac{k_1}{k_2} \frac{D_E}{D_A}} \frac{\tanh\sqrt{D_E k_2 C_i^n / k_L [D_A/D_E]}}{\tanh\sqrt{D_A k_1 C_i^n / k_L}} - 1\right]$		22
$Z_A A[g] + Z_E E \rightarrow Z_C C +$ Products $Z_B B[g] + Z_C C \rightarrow Z_E E$ [finite rate]	$\phi_A = \frac{\sqrt{M [e_i/q_E]^n} \left[1 - q_A \operatorname{sech}\sqrt{M [e_i/q_E]^n}\right]}{\tanh\sqrt{M [e_i/q_E]^n}}$ $\phi_B = \sqrt{M_1'}\left(1 - q_B \operatorname{sech}\sqrt{M_1'}\right) \Big/ \tanh\sqrt{M_1'}$	Simultaneous absorption of C_2H_4 and O_2 in $CuCl_2$ solution	14

TABLE 1.1 CONTINUED

1	2	3	4
	$M_1' = M K_2 \frac{m+1}{p+1} \frac{\nu_B}{r_B} q_E^{q-n} b^{*p-1} \left[\frac{q_c''}{q_E} + \frac{\nu_c''}{\nu_E} \frac{r_E}{r_C} \left(1 - \frac{e_i}{q_E}\right)\right]^q$ $\phi_A = 1 - q_A + \frac{r_E}{\nu_E}\left(q_E - e_i\right) + \frac{r_B}{\nu_B} b^* \left[\phi_B - \left(1 - q_B\right)\right]$		
$Z_A A[g] + Z_E E \rightarrow Z_c C$ $Z_A A[g] Z_c' C \rightarrow$ Products [finite rate]	$\phi_A = \frac{\sqrt{M_2}\left(1 - q_A \operatorname{sech}\sqrt{M_2}\right)}{\tanh\sqrt{M_2}}$ $\phi_A = 1 - q_A + \frac{r_E}{\nu_E}\left(1 + \frac{\nu_c}{\nu_c'}\right)\left(q_E - e_i\right) - \frac{r_c}{\nu_c'} c_i$ $M_2 = M\left[\left(\frac{e_i}{q_E}\right)^n + \frac{m+1}{p+1} K_2 q_E^{q-n-1} c_i\right]$	Absorption of Cl_2 in trichloroethylene solution	14
$A[g] \xrightarrow{k_1} B[g] + E$ $B[g] \xrightarrow{k_2}$ Products [finite rate]	$R_B = \left\{B^* \sqrt{D_B k_2} / \tanh\left[\sqrt{\left(k_2/D_B\right)}\delta\right]\right\} + \frac{k_1 A^* D_A D_B}{D_B k_1 - D_A k_2} \left[\frac{1}{D_B B^*} \frac{B^* \sqrt{D_B k_2}}{\tanh \sqrt{k_2/D_B}\,\delta} - \frac{1}{D_A A^*} \frac{A^* \sqrt{D_A k_1}}{\tanh \sqrt{k_1/D_A}\,\delta}\right]$	Simultaneous absorption of $COCl_2$ and CO_2 in water	24
$A[g] + E \xrightarrow{k_1} C +$ Prod. [instantaneous] $B[g] + C \xrightarrow{k_2} E$ [finite rate]	$R_A = \frac{D_E E_o}{\delta} + \frac{B^* \sqrt{D_B k_1}}{\tanh \sqrt{k_1/D_B}\,\delta} - \frac{D_B B^*}{\delta}$	Simultaneous absorption of C_2H_4 and O_2 in $PdCl_2$ solution	23

TABLE 1.1 CONTINUED

1	2	3	4
A[g] + C → E [instantaneous] E + C → Products [finite rate]	$R_A = \dfrac{C_o \left(D_c/D_E \right) \sqrt{D_E\, k_2}}{2 \sqrt{k_2/D_E}\, [\delta-\lambda] - \tanh \sqrt{k_2/D_E}\, [\delta-\lambda]}$		22
Z_A A[g] + Z_E E → Products Z_B B[g] + Z_E E → Products [finite rate]	$\phi_A = \dfrac{\sqrt{M \left(e_i/q_E \right)^n} \left[1 - q_A \operatorname{sech} \sqrt{M \left(e_i/q_E \right)^n} \right]}{\tanh \sqrt{M \left(e_i/q_E \right)^n}}$ $\phi_B = \dfrac{\sqrt{M_3} \left(1 - q_B \operatorname{sech} \sqrt{M_3} \right)}{\tanh \sqrt{M_3}}$ $M_3 = M \left(e_i/q_E \right)^q \left(\dfrac{m+1}{p+1} \dfrac{\nu_B}{r_B} q_E^{q-n} b^{*p-1} K_2 \right)$ $\phi_A = 1 - q_A + \dfrac{r_E}{\nu_E} \left(q_E - e_i \right) - \dfrac{r_B}{\nu_B} b^* \left[\phi_B - \left(1 - q_B \right) \right]$	Simultaneous absorption of CO_2 and Cl_2 in aqueous NaOH solution	15
Z_A A[g] + Z_E E → Products Z_A A[g] + Z_c C → Products [finite rate]	$\phi_A = \dfrac{\sqrt{M_4} \left(1 - q_A \operatorname{sech} \sqrt{M_4} \right)}{\tanh \sqrt{M_4}}$ $\phi_A = 1 - q_A + \dfrac{r_E}{\nu_E} \left(q_E - e_i \right) + \dfrac{r_c}{\nu_c} \left(q_c - c_i \right)$ $M_4 = M \left(\dfrac{e_i}{q_E} \right)^n . \left[1 + \dfrac{m+1}{p+1} K_2 \dfrac{c_i^q}{e_i^n} \right]$	Absorption of CO_2 in Na_2CO_3 and monoethanolamine solution	15

TABLE 1.1 CONTINUED

1	2	3	4
$A[g] + 2B \rightarrow C + E$ $A'[g] + B \rightarrow E + F$ $A'[g] + C \rightarrow F + G$ $G + B \rightarrow C + E$ [instantaneous]	-	Simultaneous absorption of H_2S and CO_2 in aqueous NaOH solution	17
$Z_A\ A[g] + Z_B\ B[g] \rightarrow Z_X\ X$ $Z_B\ B[g] + Z_c\ C \rightleftharpoons Z_E\ E + Z_F\ F$ $Z_A\ A[g] + Z_E\ E \rightarrow Z_Y\ Y$	$\phi_A - \left(\frac{r_B\ b^*}{\nu_B}\right)\phi_B = 1 - \left(\frac{r_B\ b^*}{\nu_B}\right) - \frac{r_E}{\nu_E}\ e_i$ $\phi_A = M\left[\frac{2}{[n+1][\phi_A+\phi_B]} + \frac{m+1}{u+1}K_1\left(\frac{e_i^{v}}{b^{*n}\ \phi_A}\right)\right]$ $\phi_B = M\left(\frac{\nu_B}{r_B\ b^*}\right)\left[\frac{2}{[n+1][\phi_A+\phi_B]} + \left(\frac{m+1}{p+1}\right)K_2\left(\frac{b^{*p-n}\ c_i^{q}}{\phi_B}\right) + \left(\frac{m+1}{p'+1}\right)K_3\left(\frac{e_i^{p'-1}\ f_i^{q'}}{b^{*n-1}}\right)\left(\frac{\nu_E\ r_B}{\nu_B\ r_E}\left(\frac{1}{\phi_B} + \frac{\phi_B}{2} - 1\right) + \frac{\nu_E}{r_E\ b^*}\left(1 - \frac{1}{\phi_A} - \frac{\phi_A}{2}\right) - \frac{e_i}{b^*}\right)\right]$	Simultaneous absorption of C_2H_4 [or any olefin] and Cl_2 in water	Present work

1.2 REVERSIBLE REACTIONS

This class of complex reactions has been studied to a far greater extent than any of the other categories listed above. Essentially two types of reversible gas-liquid reactions have been studied: [1] absorption of a single gas accompanied by a reversible reaction [instantaneous or with a finite rate]; and [2] simultaneous absorption of two or more gases accompanied by reversible reactions.

1.2.1 Absorption of a single gas accompanied by reversible reaction [instantaneously or with a finite rate]

This problem was first considered by Peaceman [18] who obtained the film theory solutions for the enhancement factor ϕ, which is defined as the ratio of the mass transfer coefficient with chemical reaction to the physical mass transfer coefficient. Peaceman [18] considered the following schemes:

[a] $A \rightleftharpoons E$ [finite rate] [2.1]

[b] $A \rightleftharpoons nE$ [instantaneous] [2.2]

[c] $A + C \rightleftharpoons E$ [finite rate] [2.3]

Danckwerts and Kennedy [7] have also considered scheme [2.1] in obtaining a solution for ϕ based on the penetration theory. Both the analyses were based on the assumption that the diffusitities of A and E are equal. Olander [12] has analysed scheme [2.1] based on instantaneous reversible reaction using both the film and penetration theories. Toor and Chiang [28] have also made a similar analysis.

All the previous workers assumed a system with an equilibrium reversible reaction, which is invalid unless the molecular diffusion of the reactants and the products are extremely slow compared with the reaction rates. This has been pointed out by Huang and Kuo [11], who obtained analytical solutions for a non-equilibrium situation based on the film, film-penetration and surface renewal theories considering the reaction $A \rightleftharpoons E$.

Secor and Beutler [26] have obtained film and penetration theory solutions for the scheme:

$$Z_A A + Z_C C \rightleftharpoons Z_E E + Z_F F \qquad [2.4]$$

based on the assumption that the reaction is instantaneous. These authors have also solved the problem numerically based on the penetration model for the [m, n] - [p, q]th order reversible reactions. Later Onda et al [13] obtained approximate analytical solutions for scheme [2.4] with a finite rate based on the film theory and using the approximations suggested by Hikita and Asai [9]. These solutions have been compared with numerical solutions and found to be in good agreement, thus proving the validity of the approximations. Onda et al [16] subsequently also obtained the penetration and surface renewal theory solutions for this scheme [for finite reaction], and proposed a generalised solution whose parameters have different definitions for the three theories.

1.2.2 Simultaneous absorption of two or more gases accompanied by reversible reactions

Simultaneous absorption of two gases accompanied by a reversible chemical reaction with the liquid phase reactant was first considered by Ramachandran [20] assuming the reactions of both gases to be instantaneous. Ramachandran considered the scheme:

$$\begin{aligned} A[g] + C[1] &\rightleftharpoons E_1[1] + E_2[1] \\ B[g] + C[1] &\rightleftharpoons F_1[1] + F_2[1] \end{aligned} \qquad [2.5]$$

and obtained analytical solutions for the rates of absorption of the two gases based on the penetration theory for the case of equal diffusivities of all the species. Ramachandran has also discussed the theoretical aspects of the simultaneous absorption of hydrogen sulfide and carbon dioxide in amine solutions based on the above model. For a particular limiting case Astarita [3] has given a more general solution than Ramachandran for the same scheme.

Ramachandran [21] has also considered a situation where absorption of two gases is followed by simultaneous mass transfer and reversible chemical reaction, and has obtained approximate analytical solutions based on the film theory. This treatment is an extension of absorption accompanied by reversible reaction, which has been discussed by Onda et al [13].

The problem of absorption of two gases where one of the gases reacts instantaneously and irreversibly in the liquid while the second gas undergoes a reversible reaction of finite rate has also been analysed by Ramachandran [21] assuming a linearised concentration profile of the liquid phase reactant.

Later Shah and Kenney [27] considered the simultaneous absorption of sulfur dioxide and oxygen to give a gaseous product sulfur trioxide and analysed the problem based on the following scheme:

$$\begin{array}{ccccc} Z_A\,A[g] & +\,Z_{E_1}\,E & \rightleftharpoons & Z_c\,C[g] & +\,Z_{F_1}\,F \\ SO_2 & V_2O_5 & & SO_3 & V_2O_4 \\ & & & & \\ Z_{F_2}\,F & +\,Z_B\,B[g] & \rightleftharpoons & Z_{E_2}\,E & \\ V_2O_4 & \frac{1}{2}\,O_2 & & V_2O_5 & \end{array} \qquad [2.6]$$

These authors have obtained approximate film theory solutions for the enhancement factors ϕ_A and ϕ_B of the gases A and B for a general order reaction and compared the results with the numerical solutions obtained based on the penetration theory. This problem is also a combination of reversible and consecutive steps.

Theoretical analysis of reversible reactions other than those discussed here has not been worked out, and there are many industrially important systems involving reversible steps on which theoretical studies have not been attempted. Also, none of the above models has been verified by any elaborate experimental programme. Thus there appears to be a wide scope to study such systems experimentally and gain a clearer understanding of absorption accompanied by complex reactions.

Besides the investigation of Holryd and Kenney [10] who studied the oxidation of sulfur dioxide and Shah and Kenney [27] who tried to correlate the data with the theoretical model, there is practically no reported work along these lines.

1.3 CONSECUTIVE REACTIONS

Absorption of one or more gases may be followed by consecutive reactions of different types. Thus: [1] product of the first reaction is a reactant for the second reaction; [2] product of the first reaction is a reactant for the second reaction which regenerates the reactant for the first reaction; [3] one of the steps is instantaneous or reversible.

Brian et al [4] have analysed gas absorption accompanied by a two-step reaction of the type:

$$\begin{aligned} A[g] + C &\rightarrow E \\ E + C &\rightarrow \text{products} \end{aligned} \qquad [2.7]$$

and have obtained numerical solutions based on the film and penetration theories. This solution shows interesting trends in the enhancement factor ϕ vs $\sqrt{M}$ curve; it goes through a maximum as the parameter $\sqrt{M}$ increases and then approaches its ultimate asymptote. Later Ramachandran [22] obtained film theory analytical solutions for this scheme for the rate of absorption of A and considered the case when both the steps are fast and the case when the first step is instantaneous.

Van de Vusse [29] has discussed the problem of yield and selectivity for different consecutive chemical reactions such as:

$$\begin{aligned} A[g] + E &\rightarrow C \\ A[g] + C &\rightarrow \text{products} \end{aligned} \qquad [2.8]$$

Further Onda et al [14] have analysed this problem considering a general stoichiometry and have obtained approximate film theory solutions for the general order case. These authors have compared the approximate solution with the numerical solution thus proving the validity of the approximations. Their solution, presented in the form of plots of ϕ vs $\sqrt{M}$, shows an interesting trend where ϕ goes through a maximum and further increases as $\sqrt{M}$ increases to approach the upper asymptote. This is a unique behaviour, not observed in the case of a single gas absorption. Onda et al [16] have also obtained penetration and surface renewal theory solutions for this problem and have formulated a generalized solution of this case for all theories.

A typical problem was analysed by Onda et al [14,16] where they considered the scheme:

$$\begin{aligned} Z_A\, A[g] + Z_E\, E &\rightarrow Z_C\, C + \text{products} \\ Z_B\, B[g] + Z_C\, C &\rightarrow Z_E\, E \end{aligned} \qquad [2.9]$$

and obtained approximate film, penetration and surface renewal theory solutions and also generalised a solution for this case for all the three theories. The film theory solution has been compared with the numerical solution and excellent agreement found between the two. This solution shows a typical trend of ϕ_A vs $\sqrt{M}$, where ϕ_A increases indefinitely as $\sqrt{M}$ is increased due to the regeneration of the species C.

Ramachandran et al [23] have also obtained approximate film theory solutions for scheme [2.9] considering the second step as an instantaneous one and the first as a fast reaction. These authors [24] have also analysed on the basis of film theory a problem where the product of the first reaction yields a second gas which reacts further to give products.

1.4 PARALLEL REACTIONS

Absorption of one or more gases may also be followed by parallel steps and some cases which have been considered so far are discussed below.

1.4.1 Absorption of a single gas accompanied by chemical reaction with several nonvolatile reactants in the liquid phase

Onda et al [15,16] have considered a problem where a single gas reacts with two liquid phase reactants simultaneously. These authors presented the problem in the form of the following scheme:

$$\begin{aligned} Z_A\, A[g] + Z_E\, E &\rightarrow \text{products} \\ Z_A\, A[g] + Z_C\, C &\rightarrow \text{products} \end{aligned} \qquad [2.10]$$

and have obtained approximate analytical solutions based on the film, penetration and surface renewal theories and also proposed a generalised solution for all theories as discussed in the case of reversible and consecutive reactions. The film theory solution has been compared with the numerical solution, the excellent agreement obtained proving the validity of the approximations. In this analysis the authors have assumed that both the reaction steps are followed by simultaneous diffusion and chemical reaction; thus the analysis is valid only for this particular regime. It should also be mentioned that this analysis is valid only for sparingly soluble gases, since the absorption of highly soluble gases is always accompanied by some resistance in the gas phase which has been assumed to be insignificant in the analysis. It is also possible to have a situation where the first step is instantaneous and this case has not been analysed so far.

1.4.2 <u>Simultaneous absorption of two or more gases with chemical reaction</u>

Roper et al [25] have obtained an analytical solution based on the film theory for the case where two gases are absorbed in the liquid phase and react instantaneously with the nonvolatile liquid phase reactant. Later Goettler et al [8] also studied the problem and considered the transition from fast to instantaneous reaction regime. Onda et al [15] have analysed this problem considering a general stoichiometry when reactions of both the gases are followed by finite kinetics. The scheme considered by these authors is:

$$\begin{aligned} Z_A\,A[g] + Z_E\,E &\rightarrow \text{products} \\ Z_B\,B[g] + Z_E\,E &\rightarrow \text{products} \end{aligned} \qquad [2.11]$$

Approximate analytical solutions [15,16] based on the film, penetration and surface renewal theories and a general solution for all the three theories have been obtained. The film theory results have been compared with the computer solution which shows good agreement, thus proving the validity of the Hikita and Asai's approximations for this case too. Their solution is valid only when both the gases are sparingly soluble. If one of the gases is highly soluble, the analysis will not be strictly valid as the absorption will have significant resistance in the gas phase. In this case also a situation may exist where absorption of one of the gases is in the instantaneous regime and that of the other in the fast reaction regime. This problem has not been analysed so far.

1.5 COMBINATION OF REVERSIBLE, CONSECUTIVE AND PARALLEL REACTIONS

There are many industrially important systems which involve the absorption of one or more gases accompanied by reversible, consecutive and parallel steps simultaneously. Due to the practical significance of this problem, a few cases have been discussed here.

In this problem [present work] two gases A and B dissolve in a liquid C and react to give product X. Simultaneously B reacts reversibly with C to give products E and F, one of which [E] reacts with the second dissolved gas A to give product Y. This ~~scheme~~ is represented by scheme 2.12.

$$\begin{aligned} A[g] + B[g] &\rightarrow X \\ B[g] + C &\rightleftharpoons E + F \qquad [2.12] \\ A[g] + E &\rightarrow Y \end{aligned}$$

A theoretical analysis of this problem has been attempted based on the film theory and has been discussed in detail in Section 2.3. The chlorohydrination of olefins, where chlorine and olefin dissolve in water to produce the chlorohydrin [Y] and the corresponding dichloride [X] provides a striking example of industrial importance conforming to the above scheme.

Onda et al [17] have also considered the simultaneous absorption of two gases followed by instantaneous consecutive and parallel reactions simultaneously, which is represented by the scheme:

$$\begin{aligned} A[g] + 2B &\rightarrow C + E \\ A'[g] + B &\rightarrow E + F \\ A'[g] + C &\rightarrow F + G \qquad [2.13] \\ G + B &\rightarrow C + E \end{aligned}$$

These authors have analysed the problem based on the penetration theory. Simultaneous absorption of hydrogen sulfide and carbon dioxide in aqueous sodium hydroxide solution is followed by several steps as indicated in Equation 2.13. Using this system the penetration model for the above scheme was verified experimentally.

1.6 SCOPE OF PRESENT WORK

From the survey of complex reactions discussed above, it may be concluded that only in a few cases theoretical models have been developed for complex systems of industrial importance. Hence it was the purpose of this investigation to provide a theoretical analysis of a scheme which conforms to an industrially important system: chlorohydrination of olefins. This analysis will be useful in the design of plants for chlorohydrins [used subsequently in the production of the corresponding epoxides, such as ethylene oxide and propylene oxide], and in general for products of absorption of two gases in a liquid accompanied by a complex reaction. The approximate solution given for the latter problem is more realistic than the solutions proposed by previous workers. A precise statement of the problem is given in Chapter 2 [Section 2.1].

CHAPTER - 2

SIMULTANEOUS ABSORPTION OF TWO GASES ACCOMPANIED BY A COMPLEX CHEMICAL REACTION

CHAPTER 2

SIMULTANEOUS ABSORPTION OF TWO GASES ACCOMPANIED BY A COMPLEX CHEMICAL REACTION

2.1 INTRODUCTION

In the present work the problem of simultaneous absorption of two gases with a complex chemical reaction accompanied by the combination of reversible, consecutive and parallel steps simultaneously has been considered. This problem is unique in that the two absorbing gases also react between themselves in the liquid phase. Several industrially important reactions follow this complex scheme, and a theoretical analysis of such a scheme would therefore be very useful for design purposes. A typical system is the simultaneous absorption of propylene [or any olefin] and chlorine in water. This is an industrially important reaction in the manufacture of propylene oxide, where propylene chlorohydrin [an intermediate] is prepared by passing propylene and chlorine in water.

The complex reaction scheme considered is:

$$Z_A\ A + Z_B\ B \xrightarrow{k_1} Z_X\ X \qquad [2.1]$$

$$Z_B\ B + Z_C\ C \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Z_E\ E + Z_F\ F \qquad [2.2]$$

$$Z_A\ A + Z_E\ E \xrightarrow{k_4} Z_Y\ Y \qquad [2.3]$$

In this scheme two gases A and B dissolve in a liquid C and react to give product X. Simultaneously, dissolved B reacts with C reversibly to give products E and F, one of which [E] reacts with the second dissolved gas A to give product Y. A theoretical analysis of this problem has been attempted based on the film theory. In the film theory, well discussed by Danckwerts [6] and Astarita [2], it is assumed that close to the fluid interface there exists a stagnant film of thickness δ. Mass transfer by convection within the film is assumed to be insignificant, and the process of diffusion takes place solely by molecular diffusion; as such there is no accumulation of mass at any point in the film.

The assumptions involved in the present analysis are:

[1] the film theory is valid for the system;

[2] gas side resistance to the absorption is insignificant and the concentrations of the gaseous species at the gas-liquid interface are constant;

[3] the components in the liquid phase are nonvolatile;

[4] heat effects are negligible;

[5] the reaction terms in the mass balance equations can be linearised in terms of the interfacial concentrations; and

[6] concentration profiles of the gaseous species can be expressed in terms of the enhancement factors [enhancement factor ϕ represents the ratio of mass transfer coefficient with chemical reaction to the physical mass transfer coefficient].

The theoretical analysis of this sytem was taken up in two parts:

[a] <u>Two gases dissolving in a liquid and reacting between themselves</u>

The first reaction of the complex scheme corresponds to this case, the theoretical analysis of which has been undertaken with the objective of improving upon the existing methods of analysing such a reaction [Section 2.2].

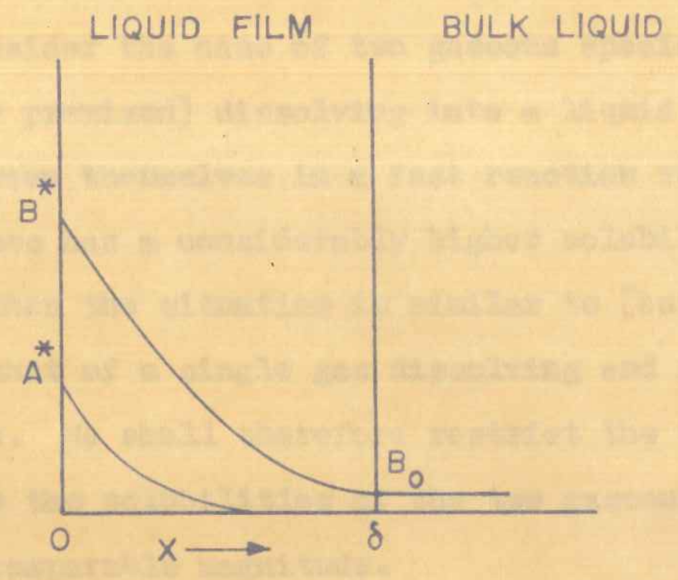
[b] Analysis of the complex scheme

Using the analysis of reaction [2.1] of the complex scheme mentioned under [a], a complete theoretical analysis has been attempted of the complex reaction, with the object of developing expressions for enhancement during absorption [Section 2.3].

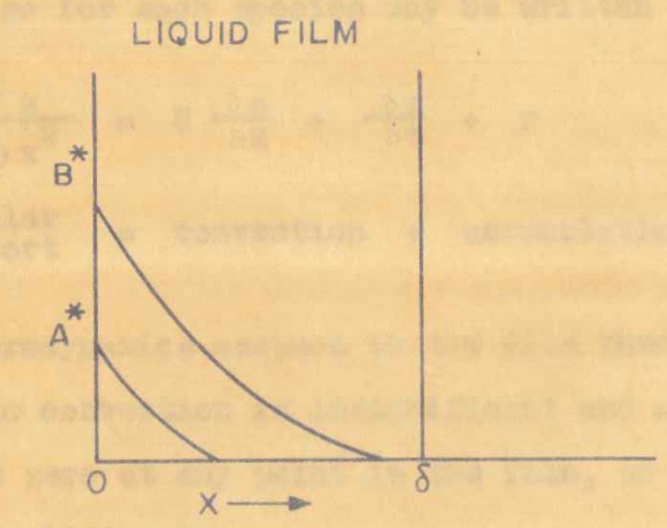
2.2 AN APPROXIMATE SOLUTION TO THE ABSORPTION AND REACTION OF TWO GASES IN A LIQUID

2.2.1 General considerations

The problem of simultaneous absorption of two gases which react between themselves has been analysed by previous workers using both the penetration and film theories. Roper, Hatch and Pigford [25] used the penetration theory to obtain numerical solutions and have considered a transition from slow to fast reaction regimes while Ramachandran and Sharma [19] derived an approximate analytical solution based on the film theory. The latter workers assumed a linear profile for the gaseous species in the film in obtaining the solution, and as such deviations from the numerical solutions of Roper, Hatch and Pigford were quite large [of the order of 30-35%]. In the present work an analytical solution has been presented on the basis of a nonlinear profile which conforms very closely to the numerical solution. The concentration profiles are shown in Figure 2.1.



(i) B_o HAS A FINITE VALUE



(ii) B_o IS ZERO

FIG. 2·1: CONCENTRATION PROFILES FOR THE ABSORPTION AND REACTION OF TWO GASES AMONG THEMSELVES IN A FAST REACTION REGIME

2.2.2 Formulation of the problem

Let us consider the case of two gaseous species A and B [which are premixed] dissolving into a liquid phase and reacting between themselves in a fast reaction regime. If one of the gases has a considerably higher solubility than the other, then the situation is similar to [but not identical with] that of a single gas dissolving and reacting in a liquid phase. We shall therefore restrict the treatment to the case where the solubilities of the two gaseous species involved are of comparable magnitude.

The differential material balance equations representing the phenomenon of simultaneous diffusion and chemical reaction in a liquid phase for each species may be written in the form:

$$D\frac{\partial^2 s}{\partial x^2} = U\frac{\partial s}{\partial x} + \frac{\partial s}{\partial t} + r \qquad [2.4]$$

$$\text{molecular transport} = \text{convection} + \text{accumulation} + \text{reaction rate}$$

but for the hydrodynamics assumed in the film theory, the transport due to convection is insignificant and also the accumulation is zero at any point in the film, so that Equation 2.4 simplifies to:

$$D\frac{d^2 s}{d x^2} = r \qquad [2.5]$$

The material balance for each species based on the film theory [i.e. Equation 2.5] can then be represented by the following differential equations:

$$D_A \frac{d^2 A}{d x^2} = Z_A k A^m B^n \qquad [2.6]$$

$$D_B \frac{d^2 B}{d x^2} = Z_B k A^m B^n \qquad [2.7]$$

where A and B represent the concentrations of the species A and B in the liquid phase [g mole/cm^3]; m, n the orders of reactions with respect to A and B; k the reaction rate constant $[(\text{cm}^3/\text{g mole})^{m+n-1} \text{sec}^{-1}]$; Z_A, Z_B the stoichiometric coefficients; D_A, D_B the diffusion coefficients for A and B respectively [cm^2/sec]; and x the distance from the interface [cm].

The boundary conditions are:

$$x = 0 \qquad A = A^* \qquad B = B^* \qquad [2.8]$$

$$x = \delta \qquad A = 0 \qquad B = B_o \qquad [2.9]$$

where δ is the film thickness [cm]; A^*, B^* the concentrations of A and B at the gas-liquid interface [g mole/cm^3]; and B_o is the concentration of B in the bulk [g mole/cm^3].

2.2.3 Approximate solution [based on an exponential profile]

From Equations 2.6 and 2.7 we have

$$\frac{D_A}{Z_A} \frac{d^2 A}{d x^2} = \frac{D_B}{Z_B} \frac{d^2 B}{d x^2} \qquad [2.10]$$

Equation 2.10 can be solved with the boundary conditions 2.8 and 2.9 in terms of the enhancement factors ϕ_A and ϕ_B defined as:

$$\phi_A = -\frac{\delta}{A^*}\left(\frac{d\,A}{d\,x}\right)_{x\,=\,0} \qquad [2.11]$$

$$\phi_B = -\frac{\delta}{[B^* - B_o]}\left(\frac{d\,B}{d\,x}\right)_{x\,=\,0} = -\frac{\delta}{B^*}\left(\frac{d\,B}{d\,x}\right)_{\substack{x\,=\,0\\ B_o=\,0}} \qquad [2.12]$$

Integrating Equation 2.10 we have:

$$\frac{D_A}{Z_A}\,\frac{d\,A}{d\,x} = \frac{D_B}{Z_B}\,\frac{d\,B}{d\,x} + \text{constant} \qquad [2.13]$$

$$\text{At } x = 0,\ \text{constant} = -\frac{D_B}{Z_B}\left(\frac{d\,B}{d\,x}\right)_{x\,=\,0} + \frac{D_A}{Z_A}\left(\frac{d\,A}{d\,x}\right)_{x\,=\,0} \qquad [2.14]$$

Integrating Equation 2.13 further and using the boundary conditions 2.8 and 2.9, we get the following relationship between the enhancement factors ϕ_A and ϕ_B:

$$\phi_A - \phi_B\,\frac{r_B}{\nu_B}\,[b^* - q_B] = 1 - \frac{r_B}{\nu_B}\,[b^* - q_B] \qquad [2.15]$$

Where $q_B = 0$, i.e. when the concentration of B is zero at $x = \delta$, Equation 2.15 reduces to:

$$\phi_A - \phi_B\,\frac{r_B}{\nu_B}\,b^* = 1 - \frac{r_B}{\nu_B}\,b^* \qquad [2.16]$$

Equation 2.15 is rigorous and does not involve any approximation. However, in order to obtain numerical values of ϕ_A and ϕ_B as functions of the various other parameters of the equations involved, a second equation is required either for ϕ_A or ϕ_B. It is in the development of this equation that suitable approximations will have to be made, and the accuracy of the final values will depend largely on the extent of validity of these approximations.

Equation 2.6 is a nonlinear differential equation and thus cannot be solved as such; but it can be linearised to obtain a solution for ϕ_A by making the following approximations:

$$A^m = \frac{2}{m+1} A^{*\,m-1} A \qquad [2.17]$$

$$B^n = \frac{2}{n+1} B^{*\,n-1} B \qquad [2.18]$$

$$A = A^* e^{-\phi_A [x/\delta - x]} \qquad [2.19]$$

$$B = B_o + [B^* - B_o] e^{-\phi_B [x/\delta - x]} \qquad [2.20]$$

$$\text{or} \quad B = B^* e^{-\phi_B [x/\delta - x]} \quad , \text{ at } B_o = 0 \qquad [2.21]$$

Approximations 2.17 and 2.18 have been suggested by Hikita and Asai [9] and have been widely used to linearise problems; they have been shown to be valid for many gas-liquid systems involving simultaneous diffusion and chemical reaction.

Approximations 2.19 and 2.20, on the other hand, have been introduced in the present work. Since the concentration profiles of the gaseous species reacting in the film are known to be usually exponential in nature, the assumption of a linear profile by Ramachandran and Sharma [19] is unrealistic. Hence the approximations represented by Equations 2.19 and 2.20 for the species A and B should provide a more valid solution. These approximations are written in terms of the enhancement factors ϕ_A and ϕ_B defined by Equations 2.11 and 2.12, as the nature of the profiles depends entirely on the enhancement during absorption. It can be seen that these nonlinear approximations also satisfy the boundary conditions 2.8 and 2.9. Approximation 2.20 has been suggested in terms of the interfacial and bulk concentration of B, as in the case of absorption and reaction of two gases between themselves in a liquid medium, a situation may exist when the more soluble gas has some finite concentration in the bulk. This approximation is likely to give errors at higher values of B_o, but the present analysis is restricted to the case where solubilities of both the gases are of comparable magnitude and the situation of higher values of B_o is unlikely. Still this term has been included in the interest of generality.

The linearised form of Equation 2.6 based on the above approximations is:

$$D_A \frac{d^2 A}{d x^2} = \frac{4 Z_A k A^{*m} B^{*n}}{[m + 1] [n + 1]} \left[\frac{B_o}{B^*} e^{- \phi_A [x/\delta - x]} + \left(1 - \frac{B_o}{B^*}\right) e^{- [\phi_A + \phi_B] [x/\delta - x]} \right] \qquad [2.22]$$

Equation 2.22 can be solved using boundary conditions 2.8 and 2.9 to give an expression for the enhancement factor ϕ_A.

Integrating Equation 2.22 with reference to x we have:

$$D_A \frac{dA}{dx} = \frac{4 Z_A k A^{*m} B^{*n}}{[m+1][n+1]} \left[\frac{B_o}{B^*} e^{-\phi_A [x/\delta - x]} \left(\frac{[\delta - x]^2}{-\phi_A \delta} \right) + \left(1 - \frac{B_o}{B^*}\right) e^{-[\phi_A + \phi_B][x/\delta - x]} \left(\frac{[\delta - x]^2}{-[\phi_A + \phi_B]\delta} \right) \right] + \text{constant} \qquad [2.23]$$

$$\text{at } x = \delta, \frac{dA}{dx} = 0, \quad \text{constant} = 0 \qquad [2.24]$$

at $x = 0$, Equation 2.23 reduces to

$$-D_A \left(\frac{dA}{dx}\right)_{x=0} = \frac{4 Z_A k A^{*m} B^{*n}}{[m+1][n+1]} \left[\frac{B_o \delta}{B^* \phi_A} + \left(1 - \frac{B_o}{B^*}\right) \frac{\delta}{[\phi_A + \phi_B]} \right] \qquad [2.25]$$

From the definition of ϕ_A in Equation 2.11 we have

$$\phi_A = \frac{4 Z_A k A^{*m-1} B^{*n} \delta^2}{[m+1][n+1] D_A} \left[\frac{B_o}{B^* \phi_A} + \left(1 - \frac{B_o}{B^*}\right) \frac{1}{[\phi_A + \phi_B]} \right] \qquad [2.26]$$

Equation 2.26 may be presented in terms of the dimensionless parameters as:

$$\phi_A = M \left[\frac{q_B}{b^* \phi_A} + \frac{1 - [q_B/b^*]}{\phi_A + \phi_B} \right], \quad q_B > 0 \qquad [2.27]$$

Where $q_B = 0$, Equation 2.27 reduces to:

$$\phi_A = \frac{M}{\phi_A + \phi_B} \qquad [2.28]$$

where

$$M = \frac{4}{[m+1]\,[n+1]} \; \frac{Z_A \, k \, A^{*m-1} \, B^{*n} \, \delta^2}{D_A} \qquad [2.29]$$

Values of ϕ_A and ϕ_B can be calculated from Equations 2.16 and 2.28 by a trial-and-error method at different values of b^*, r_B and ν_B.

When $B^* >> A^*$ [i.e. very high b^*], it is likely that there will not be a concentration gradient of B in the film, so that $[q_B/b^*]$ will approach unity and the absorption of A will be in the fast pseudo m^{th} order regime. In this situation Equation 2.27 reduces to Equation 2.30 which is the well known expression for ϕ_A as given by Danckwerts [6], provided $n = 1$:

$$\phi_A = \sqrt{M} \qquad [2.30]$$

where

$$M = \frac{2}{m+1} \; \frac{Z_A \, k' \, A^{*m-1} \, \delta^2}{D_A} \qquad [2.31]$$

Where $n \neq 1$, k' will be replaced by k'' given by $[2\,k'/n+1]$.

2.2.4 Linear approximation

Ramachandran and Sharma [19] linearised Equation 2.6 when m, n, Z_A are unity, assuming the concentration profiles of A and B as:

$$A = A^* - \frac{R_A}{D_A}\,x \qquad [2.32]$$

$$B = B^* - \frac{R_B}{D_B}\,x \qquad [2.33]$$

The solution of linearised Equation 2.6 obtained in terms of the rate of absorption of A and B is:

$$R_A = k\, A^* B^* \lambda - \frac{k \lambda^2}{2}\left[\frac{R_B\, A^*}{D_B} + \frac{R_A\, B^*}{D_A}\right] + \frac{k \lambda^3}{3\, D_A}\, \frac{R_A\, R_B}{D_A\, D_B} \qquad [2.34]$$

Equation 2.34 can be expressed in terms of the enhancement factors ϕ_A, ϕ_B and dimensionless parameter M as:

$$\phi_A = M\left[\frac{1}{\phi_A} - \frac{\phi_A + \phi_B}{2\, \phi_A^2} + \frac{\phi_B}{3\, \phi_A^2}\right] \qquad [2.35]$$

2.2.5 Verification of the proposed exponential approximation for a pseudo m^th^ order reaction

In order to verify the applicability of the approximation, the solution of a single gas undergoing a pseudo m^th^ order reaction has been compared with that obtained by substituting Equation 2.19. The basic mass balance equation for this case is represented by the following differential equation:

$$D_A \frac{d^2 A}{d x^2} = k_1\, A^m \qquad [2.36]$$

with boundary conditions:

$x = 0$ $A = A^*$ [2.37]

$x = \delta$ $A = 0$ [2.38]

The analytical solution obtained without approximating for the profile of A is:

$$\phi_A = \frac{\sqrt{M}}{\tanh \sqrt{M}} \qquad [2.39]$$

or

$$\phi_A = \sqrt{M}, \text{ at higher values of } M \qquad [2.40]$$

By substituting Equation 2.19 in Equation 2.36 for A the following equation is obtained:

$$D_A \frac{d^2 A}{d x^2} = \frac{2 k_1 A^{*^m}}{m + 1} e^{- \phi_A x/\delta - x} \qquad [2.41]$$

Solution of Equation 2.41 with the boundary conditions 2.37 and 2.38 for the enhancement factor ϕ_A is:

$$\phi_A = \sqrt{M} \qquad [2.42]$$

Similarly solution of Equation 2.36 using Ramachandran and Sharma's approximation [Equation 2.32] for ϕ_A is:

$$\phi_A = \sqrt{0.5\, M}$$

or [2.43]

$$\phi_A \quad 0.7 \sqrt{M}$$

It is interesting to note from Equations 2.40 and 2.42, that the approximate and analytical solutions [without approximation] are in perfect agreement, thus proving the validity of the approximation at higher values of $\sqrt{M}$ [which is the conditions for a pseudo m^th^ order reaction]. On the other hand, a comparison of Equations 2.40 and 2.43 clearly shows that Ramachandran and Sharma's approximation gives a consistent error of about 30% even at higher values of $\sqrt{M}$.

The approximate solution has been compared with the numerical solution of Roper, Hatch and Pigford [25] in Table 2.1 . It can be seen that the agreement is good, the maximum error being about 15% for values of $\sqrt{M} < 3$. Direct comparison of the solution at higher values of $\sqrt{M}$ [i.e. of enhancement] could not be made in the absence of numerical values, but the validity of the approximation in the high $\sqrt{M}$ range as brought out by its applicability to the pseudo m^{th} order case for a single gas lends clear support to the basic correctness of the approximation at higher values of $\sqrt{M}$ also. In fact the errors at higher $\sqrt{M}$, which constitutes the region of practical interest, are likely to be negligible. The results have also been presented graphically as ϕ_A or ϕ_B vs. $\sqrt{M}$ [Figure 2.2] for the numerical, Ramachandran and Sharma's and the present approximate solutions, which gives a clear picture of errors over the entire range of $\sqrt{M}$. From Table 2.1 it may be noted that Ramachandran and Sharma's solution gives errors of 30-35% at values of $\sqrt{M} < 3$. It may therefore be concluded that the linear approximation gives a consistent error of about 30% over the entire range of $\sqrt{M}$.

The approximation suggested in this work can be used in practical computations not only because of its validity at all values of enhancement, but also because it may be regarded as providing a logical extension of the pseudo m^{th} order case for a single gas to the mn^{th} order for two gases dissolving and reacting among themselves.

TABLE 2.1

ENHANCEMENT FACTORS ϕ_A AND ϕ_B AT DIFFERENT VALUES OF $\sqrt{M}$.

$$\text{AT } \frac{B^*}{A^*} = 3, \ \frac{D_A}{D_B} = \frac{Z_A}{Z_B} = 1, \ B_o = 0, \ m = n = 1$$

$\sqrt{M}$	Numerical solution		Present approximate solution		Ramachandran-Sharma solution	
	ϕ_A	ϕ_B	ϕ_A	ϕ_B	ϕ_A	ϕ_A
1.50	1.30	1.10	1.08	1.03	0.84	0.95
2.00	1.70	1.20	1.50	1.16	1.20	1.06
2.25	1.90	1.23	1.72	1.24	1.35	1.12
2.50	2.10	1.25	1.93	1.31	1.52	1.17
2.75	2.35	1.30	2.15	1.35	1.70	1.23
3.00	2.55	1.36	2.40	1.46	1.87	1.29

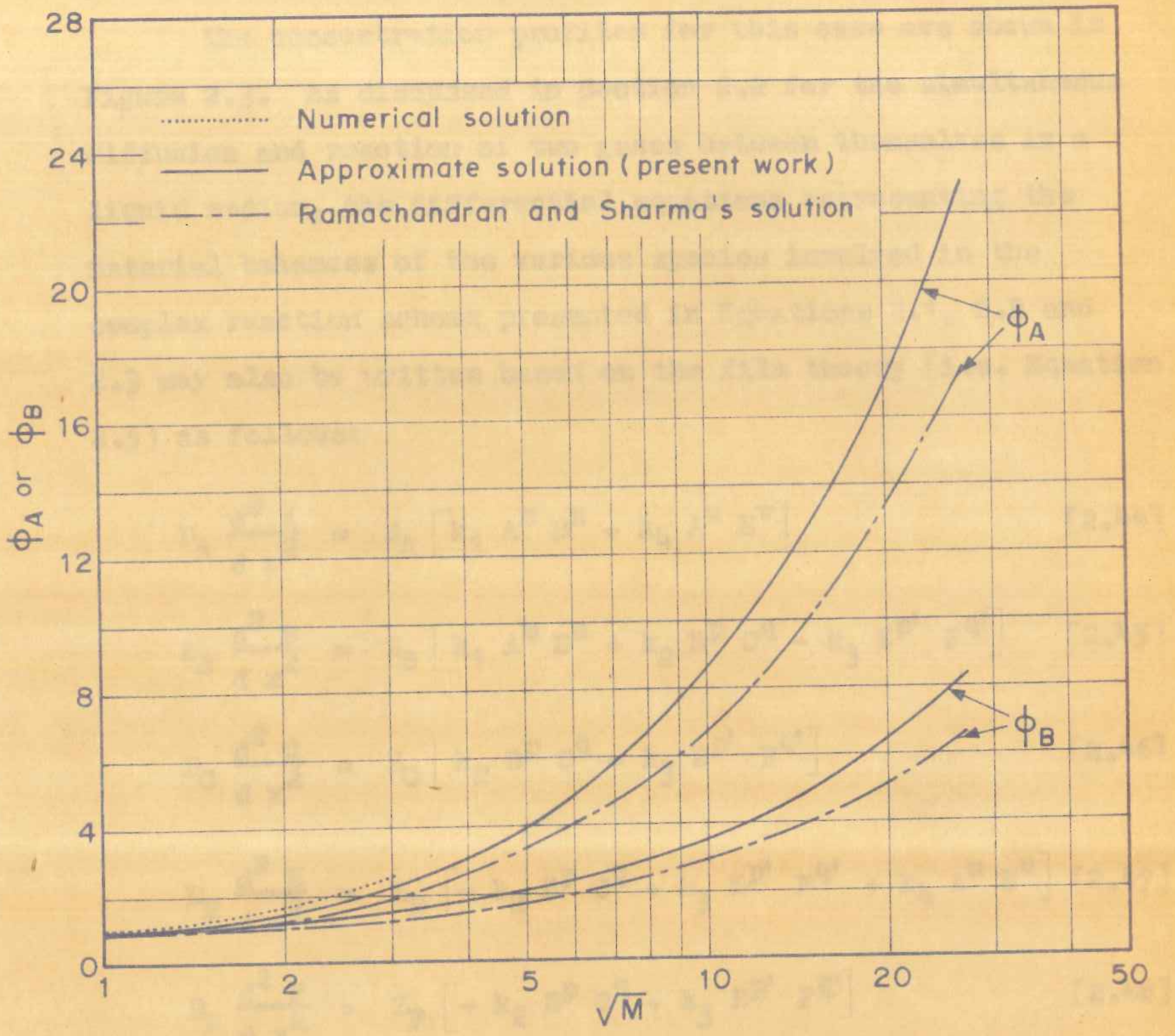


FIG. 2·2: COMPARISON OF THE SOLUTIONS OF THE (1,1)-st ORDER REACTION

2.3 ANALYSIS OF THE COMPLEX SCHEME

2.3.1 Formulation of the problem

The concentration profiles for this case are shown in Figure 2.3. As discussed in Section 2.2 for the simultaneous diffusion and reaction of two gases between themselves in a liquid medium, the differential equations representing the material balances of the various species involved in the complex reaction scheme presented in Equations 2.1, 2.2 and 2.3 may also be written based on the film theory [i.e. Equation 2.5] as follows:

$$D_A \frac{d^2 A}{d x^2} = Z_A \left[k_1 A^m B^n + k_4 A^u E^v \right] \qquad [2.44]$$

$$D_B \frac{d^2 B}{d x^2} = Z_B \left[k_1 A^m B^n + k_2 B^p C^q - k_3 E^{p'} F^{q'} \right] \qquad [2.45]$$

$$D_C \frac{d^2 C}{d x^2} = Z_C \left[k_2 B^p C^q - k_3 E^{p'} F^{q'} \right] \qquad [2.46]$$

$$D_E \frac{d^2 E}{d x^2} = Z_E \left[- k_2 B^p C^q + k_3 E^{p'} F^{q'} + k_4 A^u E^v \right] \qquad [2.47]$$

$$D_F \frac{d^2 F}{d x^2} = Z_F \left[- k_2 B^p C^q + k_3 E^{p'} F^{q'} \right] \qquad [2.48]$$

The boundary conditions are:

$x = 0$

$$A = A^*, \; B = B^*, \; C = C_i, \; E = E_i, \; F = F_i \qquad [2.49]$$

$$\frac{d C}{d x} = \frac{d E}{d x} = \frac{d F}{d x} = 0$$

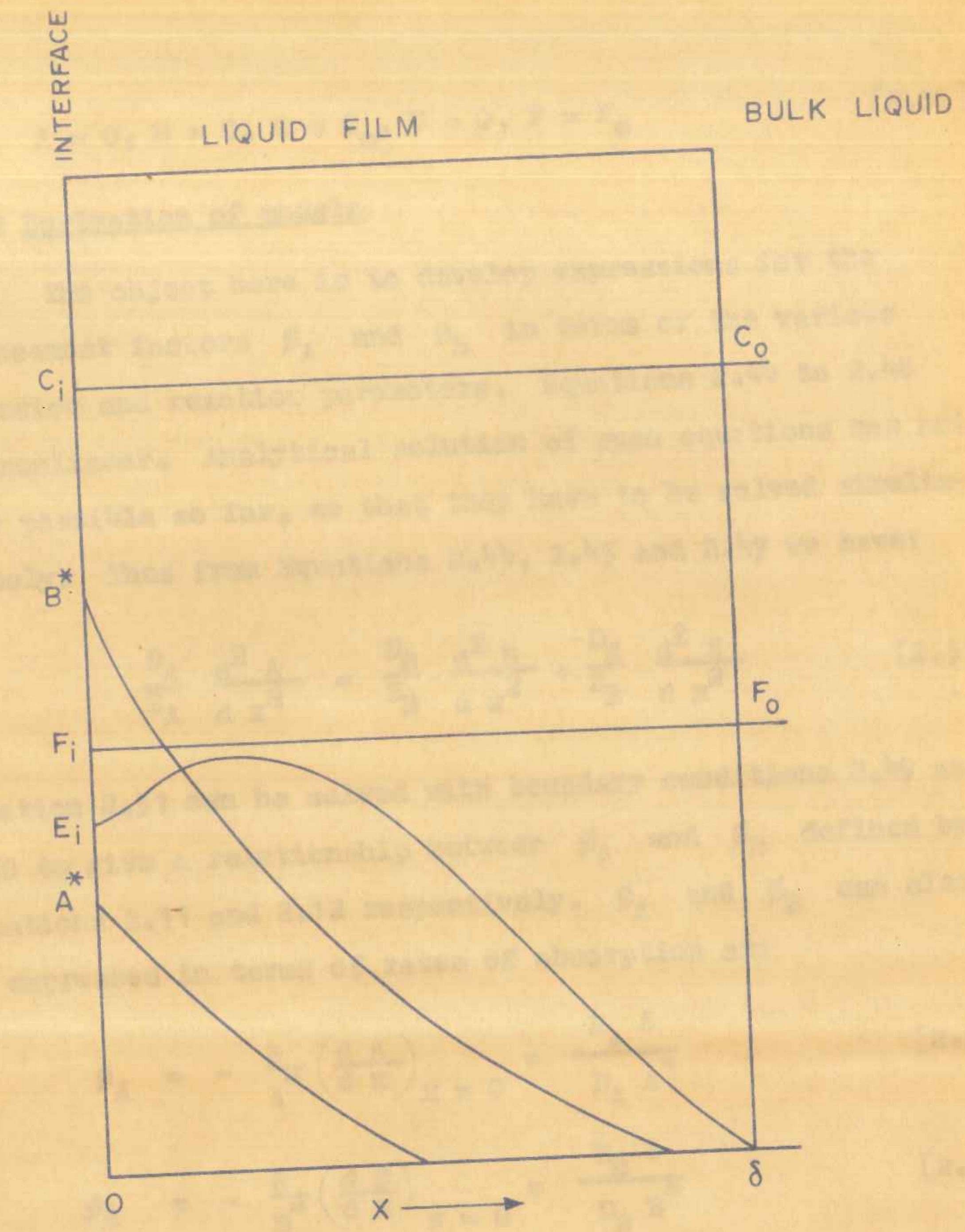


FIG. 2·3: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR THE FAST REACTION REGIME

$x = \delta$

$$A = 0,\ B = 0,\ C = C_o,\ E = 0,\ F = F_o \qquad [2.50]$$

2.3.2 Derivation of models

The object here is to develop expressions for the enhancement factors ϕ_A and ϕ_B in terms of the various diffusion and reaction parameters. Equations 2.44 to 2.48 are nonlinear. Analytical solution of such equations has not been possible so far, so that they have to be solved simultaneously. Thus from Equations 2.44, 2.45 and 2.47 we have:

$$\frac{D_A}{Z_A}\,\frac{d^2 A}{d\,x^2} = \frac{D_B}{Z_B}\,\frac{d^2 B}{d\,x^2} + \frac{D_E}{Z_E}\,\frac{d^2 E}{d\,x^2} \qquad [2.51]$$

Equation 2.51 can be solved with boundary conditions 2.49 and 2.50 to give a relationship between ϕ_A and ϕ_B defined by Equations 2.11 and 2.12 respectively. ϕ_A and ϕ_B can also be expressed in terms of rates of absorption as:

$$\phi_A = -\frac{\delta}{A^*}\left(\frac{d\,A}{d\,x}\right)_{x=0} = \frac{R_A\,\delta}{D_A\,A^*} \qquad [2.52]$$

$$\phi_B = -\frac{\delta}{B^*}\left(\frac{d\,B}{d\,x}\right)_{x=0} = \frac{R_B\,\delta}{D_B\,B^*} \qquad [2.53]$$

where the rates of absorption R_A and R_B are defined as:

$$R_A = -D_A\left(\frac{d\,A}{d\,x}\right)_{x=0} \qquad [2.54]$$

$$R_B = -D_B\left(\frac{d\,B}{d\,x}\right)_{x=0} \qquad [2.55]$$

Integrating Equation 2.51 twice and using boundary conditions 2.49 and 2.50 the following relationship between E, A, and B may be obtained:

$$E = E_i + \frac{\nu_E}{r_E}[A - A^*] - \frac{\nu_E}{\nu_B}\frac{r_B}{r_E}[B - B^*] + \frac{\nu_E}{r_E}\left[\frac{R_A}{D_A} - \frac{r_B}{\nu_B}\frac{R_B}{D_B}\right] x \qquad [2.56]$$

Setting Equation 2.56 at $x = \delta$, and using boundary conditions 2.49 and 2.50, the following relationship between ϕ_A and ϕ_B has been obtained:

$$\phi_A - \left[\frac{r_B\, b^*}{\nu_B}\right]\phi_B = 1 - \left[\frac{r_B\, b^*}{\nu_B}\right] - \frac{r_E}{\nu_E}\, e_i \qquad [2.57]$$

Equation 2.57 is rigorous and does not involve any approximation. However, in order to compute ϕ_A and ϕ_B for different values of the various parameters, other expressions for ϕ_A and ϕ_B are required. These expressions can be derived from Equations 2.44 and 2.45 using boundary conditions 2.49 and 2.50. A detailed analysis based on this general strategy is presented below for the case where all reactions are of general order and are complete in the film. A few special cases are then considered.

General order reactions [all complete in the film]: As discussed earlier, analytical solution of Equation 2.44 has not been possible, and it is this step that suitable approximations will have to be made in order to linearise Equation 2.44 and enable an approximate solution for ϕ_A. The approximations proposed in Section 2.2 have been used to linearise the problem.

In addition it has also been assumed that the interfacial concentrations of the liquid phase [nonvolatile] components are constant, viz. $E = E_i$. This has been suggested by Hikita and Asai [9] and has been widely used to linearise problems involving complex reactions, and has been proved to be valid for many gas-liquid systems accompanied by simultaneous diffusion and chemical reaction. This approximation with respect to E envisages the reaction between A and E [reaction 2.3] to be substantially complete at the interface so that the concentration of E involved is E_i. The second reaction involving the product F does not come into the picture in this analysis, but must be considered while deriving an expression for ϕ_B [given later in this section]. Using this approximation and those already listed in Section 2.2 [Equation 2.17 to 2.21] the following linearised form of Equation 2.44 may be written:

$$D_A \frac{d^2 A}{d\, x^2} = \frac{4\, Z_A\, k_1\, A^{*m}\, B^{*n}}{[m+1]\,[n+1]}\, e^{-[\phi_A + \phi_B]\,[x/\delta - x]} + \frac{2}{u+1}\, Z_A\, k_4\, A^{*u}\, E_i^{v}\, e^{-\phi_A\,[x/\delta - x]} \qquad [2.58]$$

Integration of this equation leads to

$$D_A \frac{d\, A}{d\, x} = \frac{4\, Z_A\, k_1\, A^{*m}\, B^{*n}}{[m+1]\,[n+1]}\, e^{-[\phi_A + \phi_B]\,[x/\delta - x]} \left(\frac{[\delta - x]^2}{-[\phi_A + \phi_B]\,\delta}\right) + \frac{2}{u+1}\, Z_A\, k_4\, A^{*u}\, E_i^{v}\, e^{-\phi_A\,[x/\delta - x]} \left(\frac{[\delta - x]^2}{-\phi_A\,\delta}\right) + \alpha_1 \qquad [2.59]$$

At $x = \delta$, this reduces to $\alpha_1 = 0$, and at $x = 0$ to

$$- D_A \left(\frac{d\,A}{d\,x}\right)_{x=0} = \frac{4\,Z_A\,k_1\,A^{*m}\,B^{*n}}{[m+1]\,[n+1]}\;\frac{\delta}{[\phi_A + \phi_B]} + \frac{2\,Z_A\,k_4\,A^{*u}\,E_i^{v}}{[u+1]}\;\frac{\delta}{\phi_A} \qquad [2.60]$$

The rate of absorption of the gas A defined by Equation 2.54 may be written as:

$$R_A = \frac{4\,Z_A\,k_1\,A^{*m}\,B^{*n}\,\delta}{[m+1]\,[n+1]\,[\phi_A + \phi_B]} + \frac{2\,Z_A\,k_4\,A^{*u}\,E_i^{v}\,\delta}{[u+1]\,\phi_A} \qquad [2.61]$$

From the definition of ϕ_A in terms of R_A given in Equation 2.52, we can write the following expression for ϕ_A:

$$\phi_A = \frac{4\,Z_A\,k_1\,A^{*m-1}\,B^{*n}\,\delta^2}{[m+1][n+1][\phi_A + \phi_B]\,D_A} + \frac{2\,Z_A\,k_4\,A^{*u-1}\,E_i^{v}\,\delta^2}{[u+1]\,\phi_A\,D_A} \qquad [2.62]$$

which in dimensionless form becomes

$$\phi_A = M\left[\frac{2}{[n+1]\,[\phi_A + \phi_B]} + \frac{[m+1]}{[n+1]}\,K_1\,\frac{e_i^{v}}{b^{*n}\,\phi_A}\right] \qquad [2.63]$$

where

$$M = \frac{2\,Z_A\,k_1\,A^{*m-1}\,B^{*n}\,\delta^2}{[m+1]\,D_A} \qquad [2.64]$$

$$K_1 = \frac{k_4}{k_1}\,A^{*u+v-m-n} \qquad [2.65]$$

It may be noted that the above derivations are based on the assumption that all the reactions involved are completed in the film, the condition for this being:

$$\phi_A = \sqrt{M \frac{2\,\phi_A}{[n+1]\,[\phi_A + \phi_B]} + \frac{[m+1]\,K_1\,e_i^{v}}{[u+1]\,b^{*n}}} > 1 \qquad [2.66]$$

In deriving an expression for ϕ_B, the complication arising out of reaction 2.2 should be considered. According to this reaction the nonvolatile intermediates E and F react to regenerate B. Since E and F are present throughout the film it is inconceivable that the reaction would be complete at the interface. Thus, as far as E is concerned, the rigorous Equation 2.56 should be used for expressing the concentration of this intermediate rather than the approximation $E = E_i$ employed for the analysis of the enhancement of A. It must also be noted that E undergoes a second reaction according to 2.3 so that a concentration maximum in the film may be expected. All these considerations were negligible in the case of the enhancement of A, since E is involved in the enhancement of A only through reaction 2.3 and therefore the assumption $E = E_i$ would be valid [the reaction being substantially complete at the interface]. A similar situation exists in the case of the intermediate F as applied to the enhancement of B, since it is only involved in a single reaction concerning B which is largely restricted to the surface. Thus the approximation $F = F_i$ would be valid.

In addition, since F is not involved in any other reaction and also does not react with any of the gases A and B at the interface, it may be reasonably assumed that there is no depletion in its concentration throughout the film.

Thus, using the approximation $F = F_2 =$ constant, the approximations given by Equations 2.17 to 2.21, and Equation 2.56 for E, the following linearised form of Equation 2.45 may be written:

$$D_B \frac{d^2 B}{d x^2} = \frac{4 Z_B k_1 A^{*m} B^{*n}}{[m+1][n+1]} e^{-[\emptyset_A + \emptyset_B] x/\delta - x} + \frac{2 Z_B k_2 B^{*p} C_i^{q}}{[p+1]} e^{-\emptyset_B x/\delta - x} +$$

$$\frac{2 Z_B k_3 E_i^{p'-1} F_i^{q'}}{[p'+1]} \left[B^* \frac{\nu_E r_B}{\nu_B r_E} e^{-\emptyset_B x/\delta - x} - A^* \frac{\nu_E}{r_E} e^{-\emptyset_A x/\delta - x} - \frac{\nu_E}{r_E}\left(\frac{R_A}{D_A} - \frac{R_B}{D_B} \frac{r_B}{\nu_B}\right) x - \left(E_i - \frac{\nu_E}{r_E} A^* + \frac{\nu_E r_B}{\nu_B r_E} B^*\right)\right] \qquad [2.67]$$

Integrating Equation 2.67 we get:

$$D_B \frac{d B}{d x} = \frac{4 Z_B k_1 A^{*m} B^{*n}}{[m+1][n+1]} e^{-[\emptyset_A + \emptyset_B] x/\delta - x} \left(\frac{[\delta - x]^2}{[\emptyset_A + \emptyset_B]\delta}\right) -$$

$$\frac{2 Z_B k_2 B^{*p} C_i^{q}}{[p+1]} e^{-\emptyset_A x/\delta - x} \left(\frac{[\delta - x]^2}{\emptyset_B \delta}\right) + \frac{2 Z_B k_3 E_i^{p'-1} F_i^{q'}}{[p'+1]}$$

$$\Bigg[- B^{*} \frac{\nu_E\, r_B}{\nu_B\, r_E}\; e^{-\phi_B\, x/\delta-x \left(\frac{[\delta-x]^2}{\phi_B\, \delta}\right)} + A^{*} \frac{\nu_E}{r_E}\; e^{-\phi_A\, x/\delta-x \left(\frac{[\delta-x]^2}{\phi_A\, \delta}\right)}$$

$$- \frac{\nu_E}{r_E}\left(\frac{R_A}{D_A} - \frac{R_B}{D_B}\,\frac{r_B}{\nu_B}\right)\frac{x^2}{2} - \left(E_1 - \frac{\nu_E}{r_E} A^{*} + \frac{\nu_E\, r_B}{\nu_B\, r_E} B^{*}\right) x \Bigg] + \alpha_2 \qquad [2.68]$$

At $x = \delta$ Equation 2.68 enables the evaluation of α_2:

$$\alpha_2 = \frac{2\, Z_B\, k_3\, E_1^{p'-1}\, F_1^{q'}}{[p' + 1]} \Bigg[\frac{\nu_E}{r_E}\left(\frac{R_A}{D_A} - \frac{R_B}{D_B}\,\frac{r_B}{\nu_B}\right)\frac{\delta^2}{2} +$$

$$\left(E_1 - \frac{\nu_E}{r_E} A^{*} + \frac{\nu_E\, r_B}{\nu_B\, r_E} B^{*}\right) \delta \Bigg] \qquad [2.69]$$

Substituting the value of α_2 in Equation 2.68 and rearranging at $x = 0$, we get the following expression for the rate of absorption of B [defined by Equation 2.55]:

$$R_B = - D_B \left(\frac{d\, B}{d\, x}\right)_{x = 0}$$

$$= \frac{4\, Z_B\, k_1\, A^{*m}\, B^{*n}\, \delta}{[m+1][n+1][\phi_A+\phi_B]} + \frac{2\, Z_B\, k_2\, B^{*p}\, C_1^{q}\, \delta}{[p+1]\, \phi_B} + \frac{2\, Z_B\, k_3\, E_1^{p'-1}\, F_1^{q'}\delta}{[p' + 1]}$$

$$\Bigg[B^{*} \frac{\nu_E\, r_B}{\nu_B\, r_E}\,\frac{1}{\phi_B} - A^{*} \frac{\nu_E}{r_B}\,\frac{1}{\phi_A} - \frac{\nu_E}{r_E}\left(\phi_A\, A^{*} - \phi_B\, B^{*} \frac{r_B}{\nu_B}\right) -$$

$$\left(E_1 - \frac{\nu_E}{r_E} A^{*} + \frac{\nu_E\, r_B}{\nu_B\, r_E} B^{*}\right)\Bigg] \qquad [2.70]$$

From the definition of ϕ_B given in Equation 2.53 Equation 2.70 can be expressed for ϕ_B as:

$$\phi_B = M\left(\frac{\nu_B}{r_B\, b^*}\right)\Bigg[\frac{2}{[n+1]}\,\frac{1}{[\phi_A+\phi_B]} + \frac{[m+1]}{[p+1]}\,\frac{k_2}{k_1}\,\frac{B^{*\,p-n}\,C_1^{\,q}}{A^{*\,m}}\,\frac{1}{\phi_B} + \frac{[m+1]}{[p'+1]}\,\frac{k_3}{k_1}\,\frac{E_1^{\,p'-1}\,F_1^{\,q}}{B^{*\,n-2}\,A^{*\,m}}\left[\frac{\nu_E\, r_B}{\nu_B\, r_E}\left(\frac{1}{\phi_B}+\frac{\phi_B}{2}-1\right) + \frac{\nu_E}{r_E\, b^*}\left(1-\frac{1}{\phi_A}-\frac{\phi_A}{2}\right)-\frac{B_1}{B^*}\right]\Bigg] \tag{2.71}$$

where M is defined by Equation 2.64. Using dimensionless parameters this becomes:

$$\phi_B = M\left(\frac{\nu_B}{r_B\, b^*}\right)\Bigg[\frac{2}{[n+1][\phi_A+\phi_B]} + \frac{[m+1]}{[p+1]}\,K_2\,\frac{b^{*\,p-n}\,c_1^{\,q}}{\phi_B} + \frac{[m+1]}{[p'+1]}\,K_3\,\frac{e_1^{\,p'-1}\,f_1^{\,q'}}{b^{*\,n-1}}\left[\frac{\nu_E\, r_B}{\nu_B\, r_E}\left(\frac{1}{\phi_B}+\frac{\phi_B}{2}-1\right) + \frac{\nu_E}{r_E\, b^*}\left(1-\frac{1}{\phi_A}-\frac{\phi_A}{2}\right)-\frac{e_1}{b^*}\right]\Bigg] \tag{2.72}$$

where

$$K_2 = \frac{k_2}{k_1}\,A^{*\,p+q-m-n} \tag{2.73}$$

$$K_3 = \frac{k_3}{k_1}\,A^{*\,p'+q'-m-n} \tag{2.74}$$

The values of the enhancement factors ϕ_A and ϕ_B can be calculated from Equations 2.57, 2.63 and 2.72 by a trial-and-error method.

Limiting cases

Case-1: $K_3 = 0$

When $K_3 = 0$, i.e. the reversible step in the complex scheme is absent, Equation 2.72 for ϕ_B reduces to:

$$\phi_B = M\left(\frac{\nu_B}{r_B\ b^*}\right)\left[\frac{2}{[n+1][\phi_A+\phi_B]} + \frac{[m+1]}{[n+1]} K_2 \frac{b^{*\,p-n}\ c_i^{\,q}}{\phi_B}\right] \qquad [2.75]$$

Enhancement factors ϕ_A and ϕ_B for this case can then be calculated from Equations 2.57, 2.63 and 2.75 by a trial-and-error method.

Case-2: $m = n = p = q = p' = q' = u = v = 1, \quad K_3 \neq 0$

When the reaction orders for all species are unity, Equation 2.57 still holds as it is, but Equations 2.63 and 2.72 for ϕ_A and ϕ_B are simplified as:

$$\phi_A = M\left[\frac{1}{[\phi_A+\phi_B]} + K_1 \frac{e_i}{b^*\ \phi_A}\right] \qquad [2.76]$$

$$\phi_B = M\left(\frac{\nu_B}{r_B\ b^*}\right)\left[\frac{1}{[\phi_A + \phi_B]} + K_2 \frac{c_i}{\phi_B} + K_3\ f_i \left[\frac{\nu_E\ r_B}{\nu_B\ r_E}\left(\frac{1}{\phi_B} + \frac{\phi_B}{2} - 1\right) + \frac{\nu_E}{r_E\ b^*}\left(1 - \frac{1}{\phi_A} - \frac{\phi_A}{2}\right) - \frac{e_i}{b^*}\right]\right] \qquad [2.77]$$

where

$$M = \frac{Z_A \; k_1 \; B^* \; \delta^2}{D_A} \qquad [2.78]$$

$$K_1 = \frac{k_4}{k_1} \qquad [2.79]$$

$$K_2 = \frac{k_2}{k_1} \qquad [2.80]$$

$$K_3 = \frac{k_3}{k_1} \qquad [2.81]$$

For this case ϕ_A and ϕ_B can be calculated as functions of $\sqrt{M}$ and other parameters such as r_B, ν_B, b^* from Equations 2.57, 2.76 and 2.77 by a trial-and-errror method.

Case-3: $m = n = p = q = p' = q' = u = v = 1, \; K_3 = 0$

For this case Equation 2.72 may be simplified as:

$$\phi_B = M \left(\frac{\nu_B}{r_B \; b^*} \right) \left[\frac{1}{[\phi_A + \phi_B]} + \frac{K_2 \; c_i}{\phi_B} \right] \qquad [2.82]$$

Enhancement factors ϕ_A and ϕ_B can be calculated by using Equations 2.57, 2.76 and 2.82.

2.3.3 Some special cases

[a] Solubility of B is much greater than of A [i.e. $B^* >> A^*$]

In all the analysis worked out for this complex scheme, it has been assumed that the gas phase resistance for the absorption is insignificant, but in this particular case this assumption is unlikely to be valid and there can be a significant resistance in the gas phase to the absorption of the more soluble gas; and it is also likely that the absorption of the less soluble gas would be followed by a pseudo-order reaction. The concentration profiles are shown in Figure 2.4.

Let us consider a situation where $B^* >> A^*$ [i.e. gas B is much more soluble than gas A]. The term $k_1 B^n$ in Equation 2.44 for species A may be replaced by k_1'. Then, linearising Equation 2.44 as discussed earlier, we get:

$$D_A \frac{d^2 A}{d x^2} = \frac{2}{m+1} Z_A k_1' A^{*m-1} A + \frac{2}{u+1} Z_A k_4 A^{*u-1} E_1^v A$$

or

$$\frac{d^2 A}{d x^2} = \left[\frac{2 Z_A k_1' A^{*m-1}}{[m+1] D_A} + \frac{2 Z_A k_4 A^{*u-1} E_1^v}{[u+1] D_A} \right] A \qquad [2.83]$$

Equation 2.83 is a linear differential equation and can be solved with the boundary conditions 2.49 and 2.50 to give the following expression for the concentration profile of A in the liquid film:

$$A = \frac{A^* \operatorname{Sinh} \sqrt{M_1} [\delta - x]}{\operatorname{Sinh} \sqrt{M_1} \delta} \qquad [2.84]$$

where

$$M_1 = \frac{2 Z_A k_1' A^{*m-1}}{[m+1] D_A} + \frac{2 Z_A k_4 A^{*u-1} E_1^v}{[u+1] D_A} \qquad [2.85]$$

Differentiating Equation 2.84 and setting $x = 0$ we have

$$-\left(\frac{d A}{d x}\right)_{x=0} = \frac{A^* \sqrt{M_1}}{\tanh \sqrt{M_1} \delta} \qquad [2.86]$$

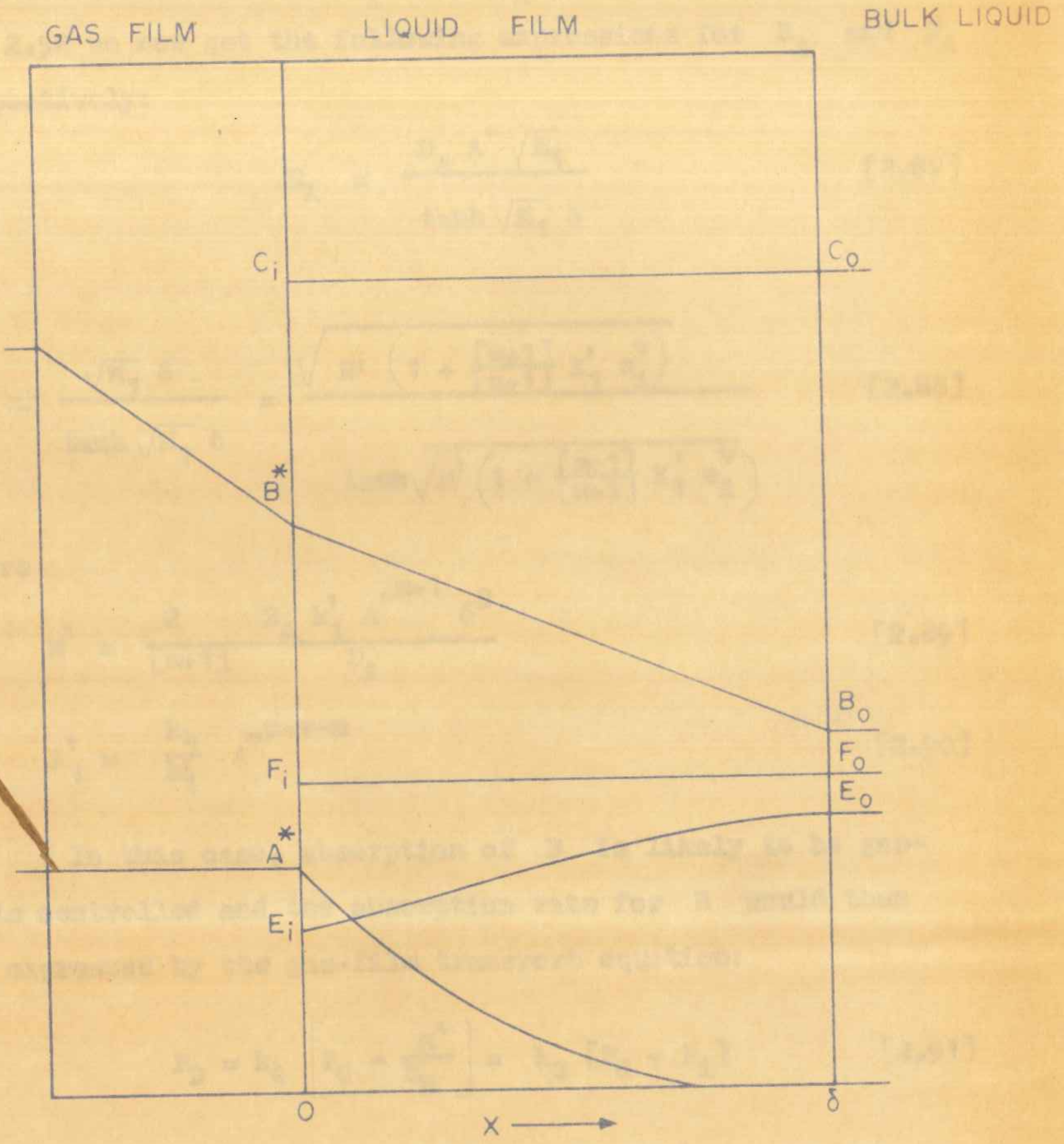


FIG. 2·4: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (a) $\left[\text{viz. } B^* \gg A^*\right]$

From the definitions of R_A and ϕ_A given in Equations 2.54 and 2.52 we now get the following expressions for R_A and ϕ_A respectively:

$$R_A = \frac{D_A A^* \sqrt{M_1}}{\tanh \sqrt{M_1}\, \delta} \qquad [2.87]$$

$$\phi_A = \frac{\sqrt{M_1}\, \delta}{\tanh \sqrt{M_1}\, \delta} = \frac{\sqrt{M' \left(1 + \frac{[m+1]}{[u+1]} K_1' e_i^v\right)}}{\tanh \sqrt{M' \left(1 + \frac{[m+1]}{[u+1]} K_1' e_i^v\right)}} \qquad [2.88]$$

where

$$M' = \frac{2}{[m+1]} \frac{Z_A k_1' A^{*m-1} \delta^2}{D_A} \qquad [2.89]$$

$$K_1' = \frac{k_4}{k_1'} A^{*u+v-m} \qquad [2.90]$$

In this case, absorption of B is likely to be gas-film controlled and the absorption rate for B would then be expressed by the gas-film transport equation:

$$R_B = k_G \left[P_G - \frac{B^*}{H_B}\right] = k_G [P_G - P_i] \qquad [2.91]$$

or

$$R_B = k_L [B^* - B_o]$$

where H_B is the Henry's law constant for gas B.

It is also possible that the reaction of the gas A with the intermediate E would be followed by pseudo u^{th}

order reaction, in which case ϕ_A will be given by:

$$\phi_A = \frac{\sqrt{M'\left(1 + \frac{[m+1]}{[u+1]} K_1'\right)}}{\tanh\sqrt{M'\left(1 + \frac{[m+1]}{[u+1]} K_1'\right)}} \qquad [2.92]$$

where

$$K_1' = \frac{k_4}{k_1'} A^{*u-m} \qquad [2.93]$$

[b] When A and B both react in the liquid bulk

The concentration profiles for this situation are shown in Figure 2.5. All the three steps are slow enough to occur in the bulk liquid and this is possible only when the following conditions would be satisfied for no reaction in the film [when reaction orders and stoichiometric coefficients are unity]:

$$\frac{\sqrt{D_A k_1 B^*}}{k_{L_A}} \ll 1, \qquad [2.94]$$

$$\frac{\sqrt{D_A k_4 E_o}}{k_{L_A}} \ll 1 \text{ and} \qquad [2.95]$$

$$\frac{\sqrt{D_B k_2 C_o}}{k_{L_B}} \ll 1 \qquad [2.96]$$

If the concentrations of A and B at the interface and the bulk are different, the diffusion as well as the kinetics will be important.

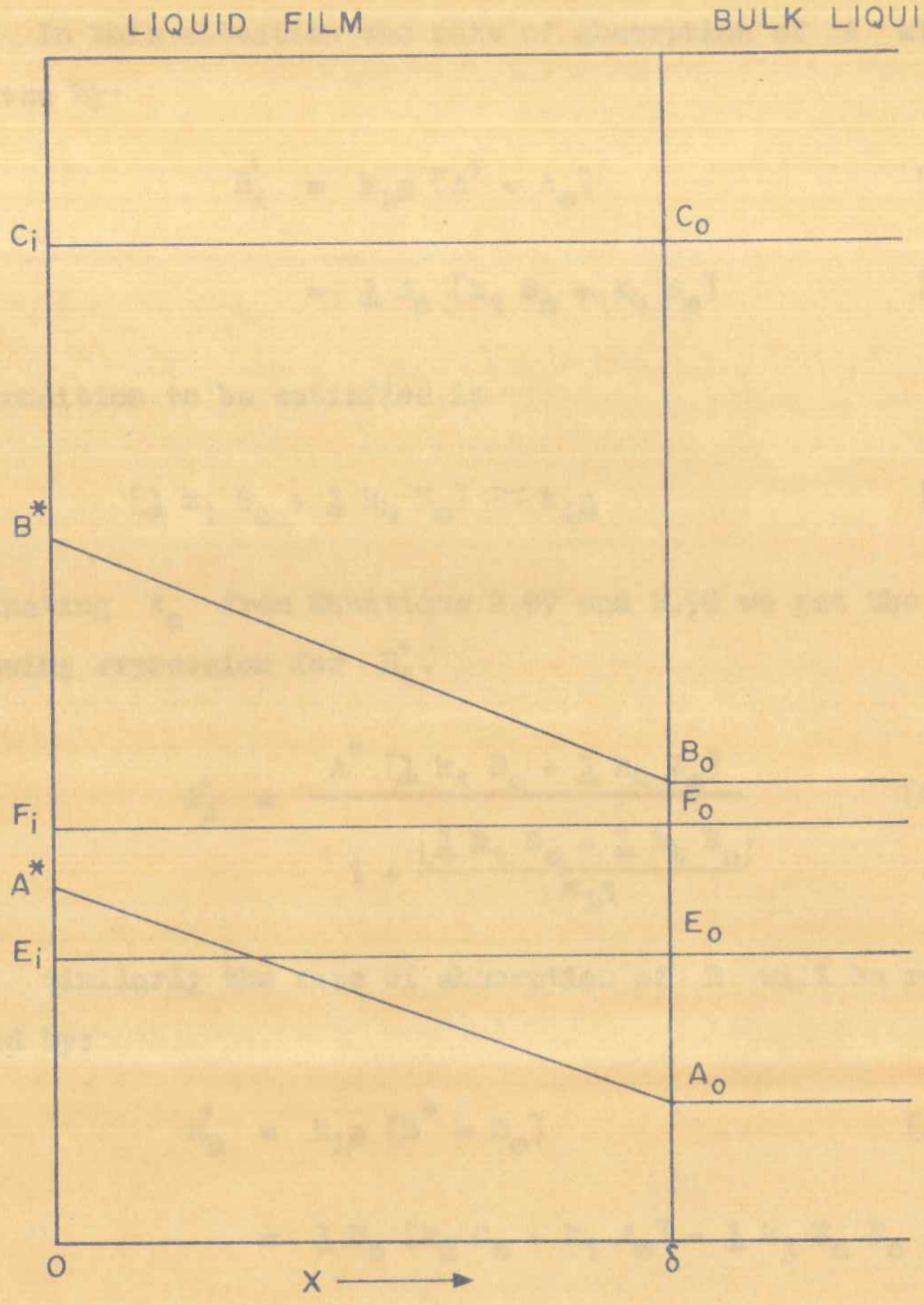


FIG. 2·5: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (b) [SLOW REACTION REGIME]

In this situation the rate of absorption of A will be given by:

$$R'_A = k_L\underline{a}\,[A^* - A_o] \qquad [2.97]$$

$$= \underline{l}\,A_o\,[k_1\,B_o + k_4\,E_o] \qquad [2.98]$$

The condition to be satisfied is

$$[\underline{l}\,k_1\,B_o + \underline{l}\,k_4\,E_o] \approx k_L\underline{a} \qquad [2.99]$$

Eliminating A_o from Equations 2.97 and 2.98 we get the following expression for R'_A.

$$R'_A = \frac{A^*\,[\underline{l}\,k_1\,B_o + \underline{l}\,k_4\,E_o]}{1 + \dfrac{[\underline{l}\,k_1\,B_o + \underline{l}\,k_4\,E_o]}{k_L\underline{a}}} \qquad [2.100]$$

Similarly the rate of absorption of B will be represented by:

$$R'_B = k_L\underline{a}\,[B^* - B_o] \qquad [2.101]$$

$$= \underline{l}\,B_o\,[k_2\,C_o + k_1\,A_o] - \underline{l}\,k_3\,E_o\,F_o \qquad [2.102]$$

Eliminating B_o from Equations 2.101 and 2.102 we have the following expression for R'_B:

$$R'_B = \frac{[\,\underline{l}\,k_2\,B^*\,C_o + \underline{l}\,k_1\,A_o\,B^* - \underline{l}\,k_3\,E_o\,F_o]}{1 + \dfrac{[\underline{l}\,k_2\,C_o + l\,k_1\,A_o]}{k_L\underline{a}}} \qquad [2.103]$$

The condition to be satisfied is:

$$\left[\underline{1}\,k_1\,A_o + \underline{1}\,k_2\,C_o - \underline{1}\,k_3\,\frac{E_o\,F_o}{B^*}\right] \approx k_L\underline{a} \qquad [2.104]$$

In Equations 2.100 and 2.103 A_o and B_o can be substituted in terms of the rates of absorption R_A' and R_B' to give the following relationships:

$$R_A' = \frac{A^*\left[\underline{1}\,k_1\,B^* - \left(\frac{\underline{1}\,k_1\,R_A'}{k_L\underline{a}}\right) + \underline{1}\,k_4\,E_o\right]}{1 + \frac{\left[\underline{1}\,k_1\,B^* - \left(\frac{\underline{1}\,k_1\,R_B'}{k_L\underline{a}}\right) + \underline{1}\,k_4\,E_o\right]}{k_L\underline{a}}} \qquad [2.105]$$

and

$$R_B' = \frac{\left[\underline{1}\,k_2\,B^*\,C_o + \underline{1}\,k_1\,A^*\,B^* - \left(\frac{\underline{1}\,k_1\,B^*\,R_A'}{k_L\underline{a}}\right) - \underline{1}\,k_3\,E_o\,F_o\right]}{1 + \frac{\left[\underline{1}\,k_2\,C_o + \underline{1}\,k_1\,A^* - \left(\frac{\underline{1}\,k_1\,R_A'}{k_L\underline{a}}\right)\right]}{k_L\underline{a}}} \qquad [2.106]$$

R_A' and R_B' can be calculated from Equations 2.105 and 2.106 by a trial-and-error method.

[c] <u>The first two steps occur in the bulk and the third step in the film</u>

In this case reactions of B would occur in the bulk but that of A with the intermediate E will occur in the film; as such the bulk concentration of A will be zero and the first reaction will not occur. The concentration profiles for this case are shown in Figure 2.6. To have this situation the following conditions must be satisfied:

$$\frac{\sqrt{D_A\,k_1\,B^*}}{k_{L_A}} \ll 1 \qquad [2.107]$$

$$\frac{\sqrt{D_B\,k_2\,C_o}}{k_{L_B}} \ll 1 \qquad [2.108]$$

$$1 < \frac{\sqrt{D_A\,k_4\,E_o}}{k_{L_A}} < 1 + \frac{E_o}{A^*} \qquad [2.109]$$

The rate of absorption of A is then represented by:

$$R_A' = \frac{\underline{a}\,A^*\sqrt{D_A\,k_4\,E_o}}{\tanh\sqrt{\frac{D_A\,k_4\,E_o}{k_L}}} \qquad [2.110]$$

Since there is no concentration of A available in the bulk to react with B_o, the first reaction step would be absent. The rate of absorption of B is given by:

$$R_B' = k_L\underline{a}\,[B^* - B_o] \qquad [2.111]$$

or

$$R_B' = \underline{1}\,k_2\,B_o^*\,C_o - \underline{1}\,k_3\,E_o\,F_o \qquad [2.112]$$

Eliminating B_o from Equations 2.111 and 2.112 we get the

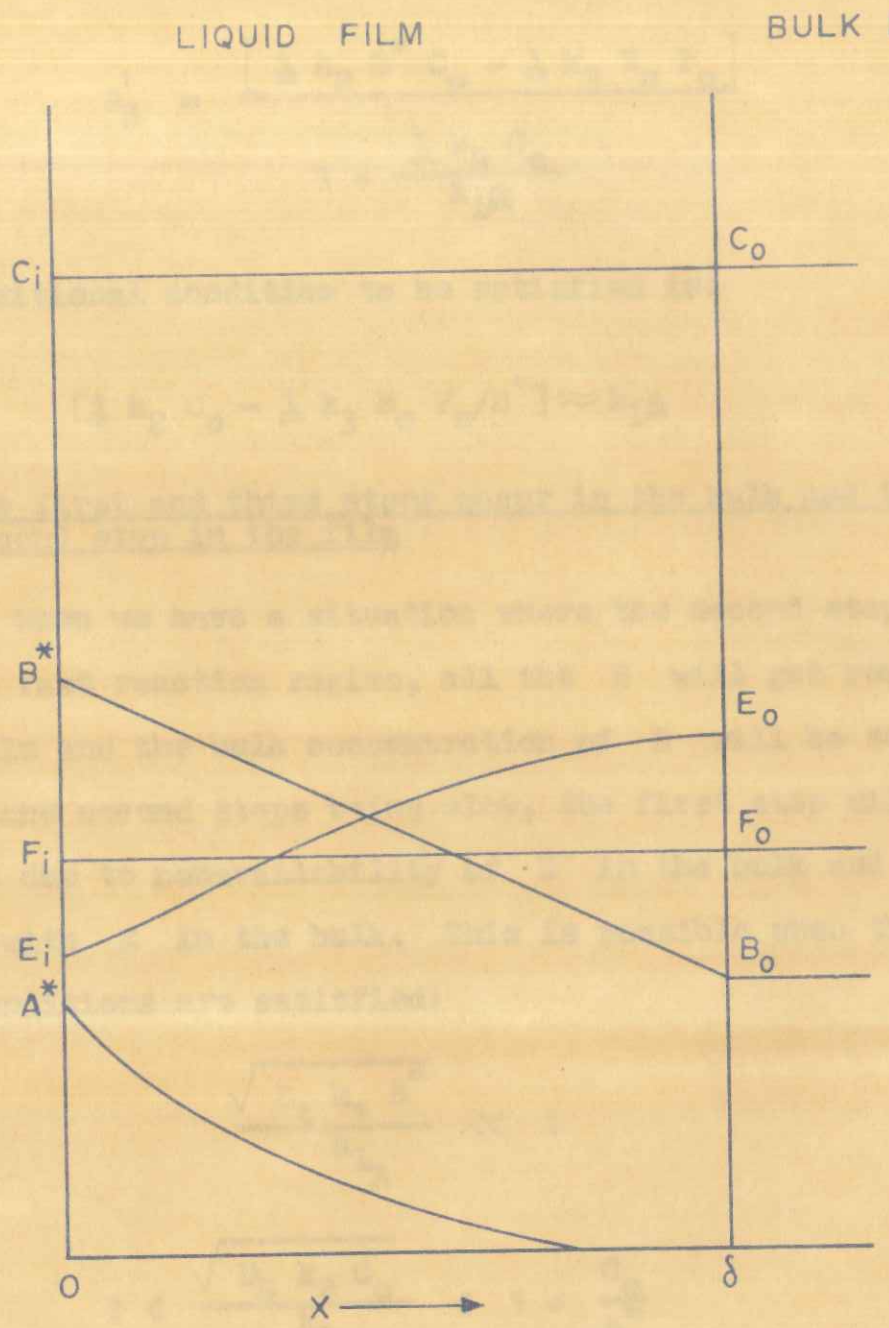


FIG. 2·6: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (c) following expression for R'_B:

$$R'_B = \frac{\left[\underline{l}\, k_2\, B^*\, C_o - \underline{l}\, k_3\, E_o\, F_o\right]}{1 + \dfrac{\underline{l}\, k_2\, C_o}{k_L\underline{a}}} \qquad [2.113]$$

The additional condition to be satisfied is:

$$[\underline{l}\, k_2\, C_o - \underline{l}\, k_3\, E_o\, F_o/B^*] \approx k_L\underline{a} \qquad [2.114]$$

[d] <u>The first and third steps occur in the bulk and the second step in the film</u>

When we have a situation where the second step occurs in the fast reaction regime, all the B will get reacted in the film and the bulk concentration of B will be zero. The first and second steps being slow, the first step will be absent due to nonavailability of B in the bulk and A will react with E in the bulk. This is possible when the following conditions are satisfied:

$$\frac{\sqrt{D_A\, k_1\, B^*}}{k_{L_A}} \ll 1 \qquad [2.115]$$

$$1 < \frac{\sqrt{D_B\, k_2\, C_o}}{k_{L_B}} < 1 + \frac{C_o}{B^*} \qquad [2.116]$$

$$\frac{\sqrt{D_A\, k_4\, E_o}}{k_{L_A}} \ll 1 \qquad [2.117]$$

The rate of absorption of A is given by

$$R'_A = k_L\underline{a}\, [A^* - A_o] \qquad [2.118]$$

$$= \underline{l}\, k_4\, A_o\, E_o \qquad [2.119]$$

Eliminating A_o from Equations 2.118 and 2.119 we get the following expression for R'_A:

$$R'_A = \frac{\underline{l}\, k_4\, A^*\, E_o}{\left[1 + \dfrac{\underline{l}\, k_4\, C_o}{k_L \underline{a}}\right]} \qquad [2.120]$$

The condition to be satisfied is:

$$\underline{l}\, k_4\, E_o \approx k_L \underline{a} \qquad [2.121]$$

T The rate of absorption of B is given by:

$$R_B \simeq \underline{a}\, [A^* - A_o] \sqrt{D_A\, k_2\, C_o} \qquad [2.122]$$

Equation 2.122 is valid only when B reacts with C. For a pseudo first-order mechanism, that is, when the concentrations of E and F at the interface are almost equal to their respective bulk concentrations. The concentration profiles of the reacting species for this case are shown in Figure 2.7.

[e] Reaction of B with C is instantaneous and reactions of A are in the fast reaction regime

In a situation where B reacts instantaneously with C it is likely that the absorption of B would be entirely gas-film controlled. The concentration profiles for this case are shown in Figure 2.8. The concentration of B at the interface will be zero and as such there will be no B available in the film to react with A, and reaction step [2.1] will be absent. This situation is likely provided the following conditions are satisfied:

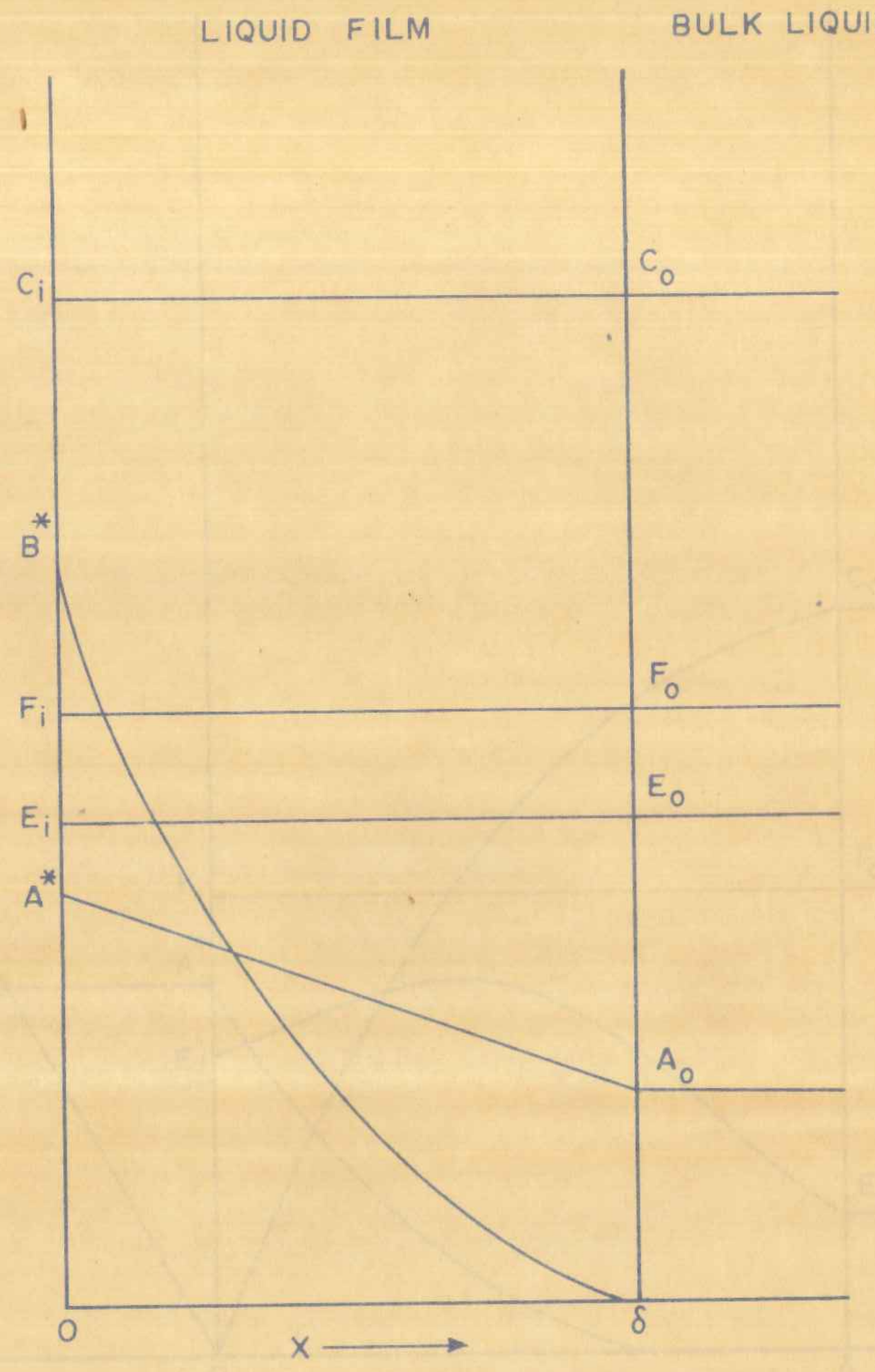


FIG. 2·7: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (d)

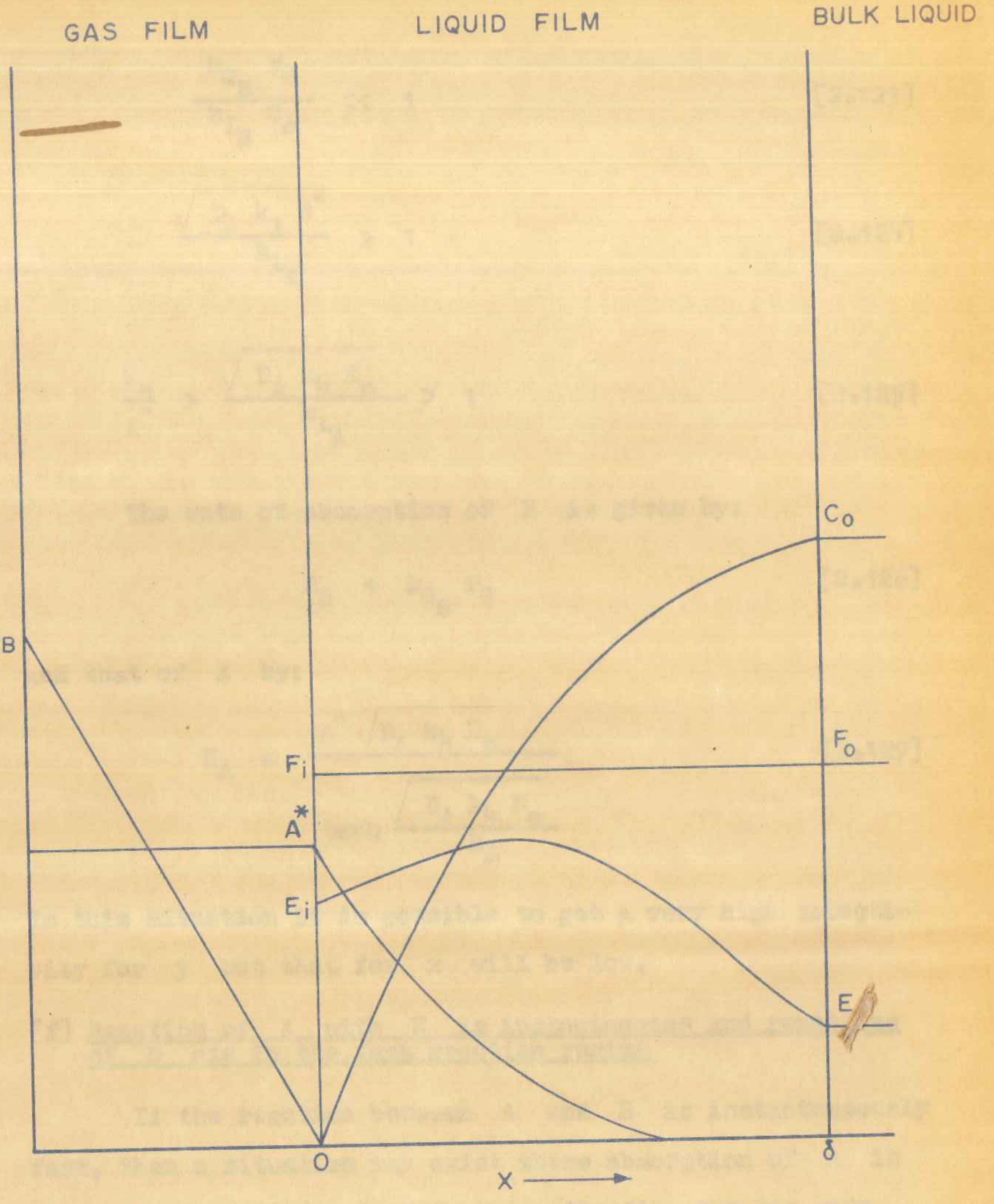


FIG. 2·8: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (e)

$$\frac{k_{G_B}\ P_G}{k_{L_B}\ C_o} \ll 1 \qquad [2.123]$$

$$\frac{\sqrt{D_A\ k_1\ B^*}}{k_{L_A}} > 1 \qquad [2.124]$$

$$\frac{E_o}{A^*} > \frac{\sqrt{D_A\ k_4\ E_o}}{k_{L_A}} > 1 \qquad [2.125]$$

The rate of absorption of B is given by:

$$R_B = k_{G_B}\ P_G \qquad [2.126]$$

and that of A by:

$$R_A = \frac{A^* \sqrt{D_A\ k_4\ E_o}}{\tanh \frac{\sqrt{D_A\ k_4\ E_o}}{k_L}} \qquad [2.127]$$

In this situation it is possible to get a very high selectivity for y but that for x will be low.

[f] Reaction of A with E is instantaneous and reactions of B are in the fast reaction regime

If the reaction between A and E is instantaneously fast, then a situation may exist where absorption of A is gas film controlled, since in this situation the gas side resistance would be very small compared to the liquid film resistance. B reacts with C in the fast reaction regime and the concentration profiles of the reacting species are shown in Figure 2.9. This is a typical case where there is no A available in the film to react with B and as such the selectivity of X will be very low; on the other hand, the selectivity of Y will be very high. For this situation to obtain, the following conditions must be satisfied:

$$k_{G_A} P_G \ll k_L E_o \qquad [2.128]$$

$$\frac{\sqrt{D_A k_1 B^*}}{k_{L_A}} > 1 \qquad [2.129]$$

$$\frac{C_o}{A^*} > \frac{\sqrt{D_B k_2 C_o}}{k_{L_B}} > 1 \qquad [2.130]$$

$$\frac{\sqrt{D_A k_4 E_o}}{k_L} \gg 1 + \frac{E_o}{A^*} \qquad [2.131]$$

The rate of absorption of A is given by:

$$R_A = k_{G_A} P_{G_A} \qquad [2.132]$$

and that of B by

$$R_B = B^* \sqrt{D_B k_2 C_o} \qquad [2.133]$$

Equation 2.133 is valid provided the reaction is pseudo first-order and there is no depletion in the concentration of the liquid phase reactants at the interface.

2.3.4 Discussion

The values of ϕ_A and ϕ_B were computed by a trial-

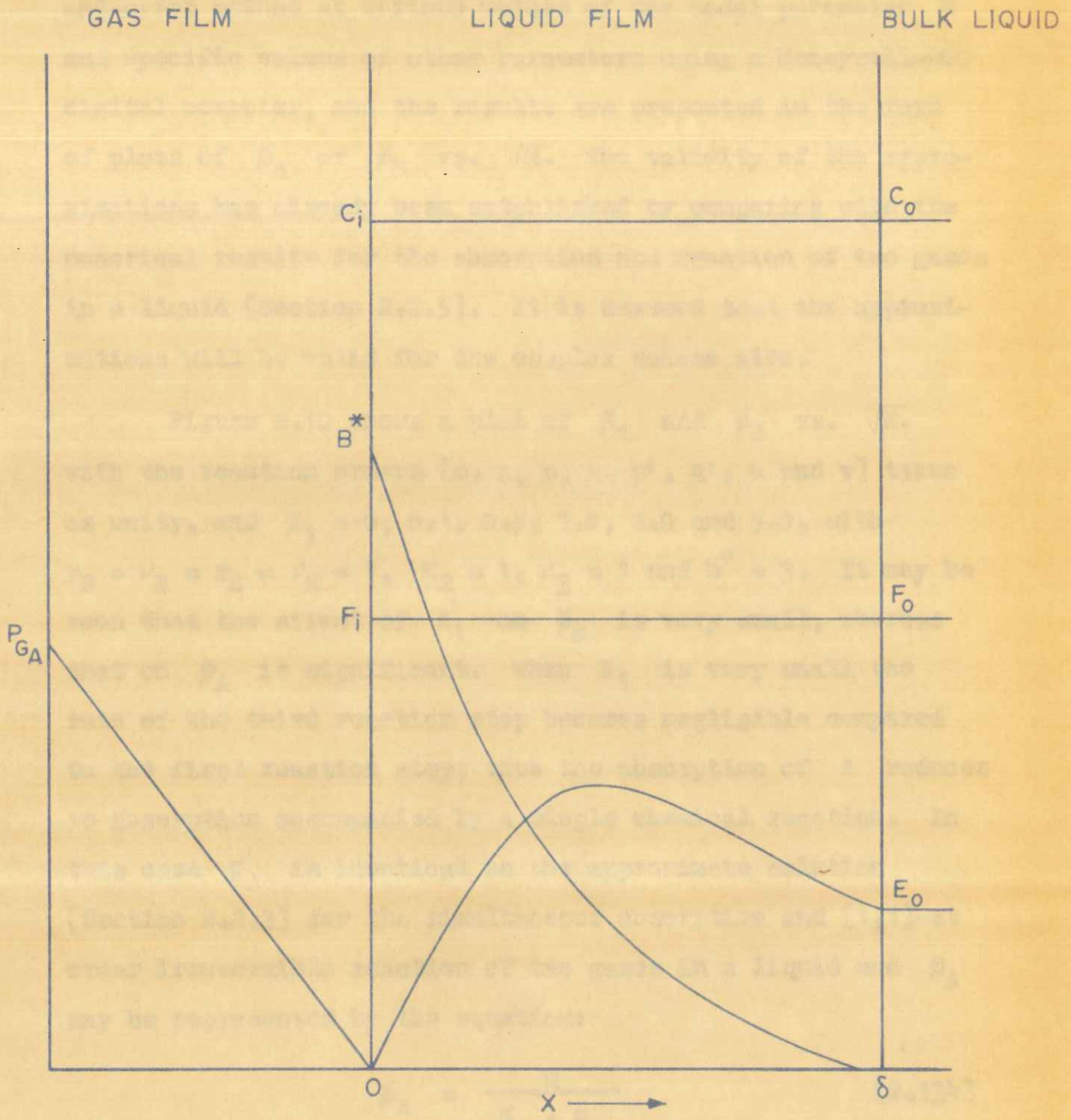


FIG. 2·9: CONCENTRATION PROFILES OF THE REACTING SPECIES FOR CASE (f) and-error method at various values of the model parameter M and specific values of other parameters using a Honeywell-400 digital computer, and the results are presented in the form of plots of ϕ_A or ϕ_B vs. $\sqrt{M}$. The validity of the approximations has already been established by comparing with the numerical results for the absorption and reaction of two gases in a liquid [Section 2.2.5]. It is assumed that the approximations will be valid for the complex scheme also.

Figure 2.10 shows a plot of ϕ_A and ϕ_B vs. $\sqrt{M}$, with the reaction orders [m, n, p, q, p', q', u and v] taken as unity, and K_1 = 0, 0.1, 0.5, 1.0, 2.0 and 5.0, with $r_B = \nu_B = r_E = \nu_E = 1$, $K_2 = 1$, $K_3 = 1$ and $b^* = 3$. It may be seen that the effect of K_1 on ϕ_B is very small, whereas that on ϕ_A is significant. When K_1 is very small the rate of the third reaction step becomes negligible compared to the first reaction step; thus the absorption of A reduces to absorption accompanied by a single chemical reaction. In this case ϕ_A is identical to the approximate solution [Section 2.2.3] for the simultaneous absorption and [1,1]-st order irreversible reaction of two gases in a liquid and ϕ_A may be represented by the equation:

$$\phi_A = \frac{M}{\phi_A + \phi_B} \qquad [2.134]$$

It is also interesting to note that when K_1 is very high the first reaction step becomes negligible compared to the third reaction step and absorption of A reduces to gas absorption accompanied by a single [1,1]-st order irreversible

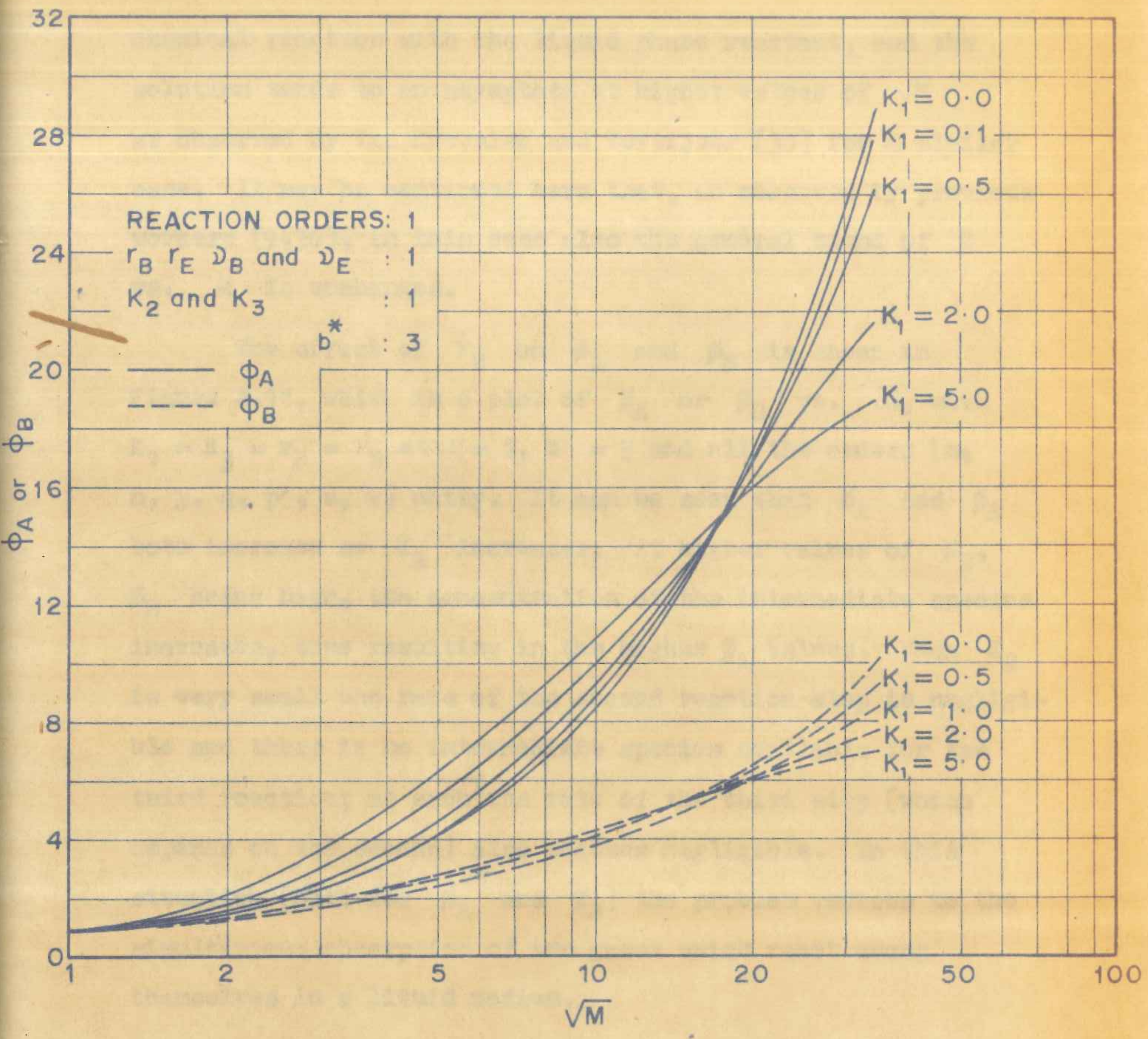


FIG. 2·10: EFFECT OF K_1 ON ϕ vs. $\sqrt{M}$ PLOTS

chemical reaction with the liquid phase reactant, and the solution tends to an asymptote at higher values of $\sqrt{M}$ as observed by Van Krevelen and Hoftijzer [30] for a similar case. It may be mentioned here that, as observed by previous workers [9,30], in this case also the general trend of ϕ vs. M is unchanged.

The effect of K_2 on ϕ_A and ϕ_B is shown in Figure 2.11, which is a plot of ϕ_A or ϕ_B vs. $\sqrt{M}$, with $K_1 = K_3 = r_B = \nu_B = r_E = \nu_E = 1$, $b^* = 3$ and all the orders [m, n, p, q, p', u, v] unity. It can be seen that ϕ_A and ϕ_B both increase as K_2 increases. At higher values of K_2, ϕ_B being high, the concentration of the intermediate species increases, thus resulting in the higher ϕ_A values. When K_2 is very small the rate of the second reaction step is negligible and there is no intermediate species available for the third reaction; as such the rate of the third step [which depends on the second] also becomes negligible. In this situation [both for ϕ_A and ϕ_B] the problem reduces to the simultaneous absorption of two gases which react among themselves in a liquid medium.

Figure 2.12 shows the effect of reversibility of the second reaction step on ϕ_A and ϕ_B. The results are plotted as ϕ_A or ϕ_B vs. $\sqrt{M}$, with $K_1 = K_2 = r_B = r_E = \nu_B = \nu_E = 1$, $b^* = 3$ and all the reaction orders unity, and $K_3 = 5.0, 2.0, 1.0, 0.5, 0.3, 0.1, 0.0$. When $K_3 = 0$ the second reaction step becomes irreversible, and most of the intermediate formed is available for the third step; as such ϕ_A and ϕ_B both

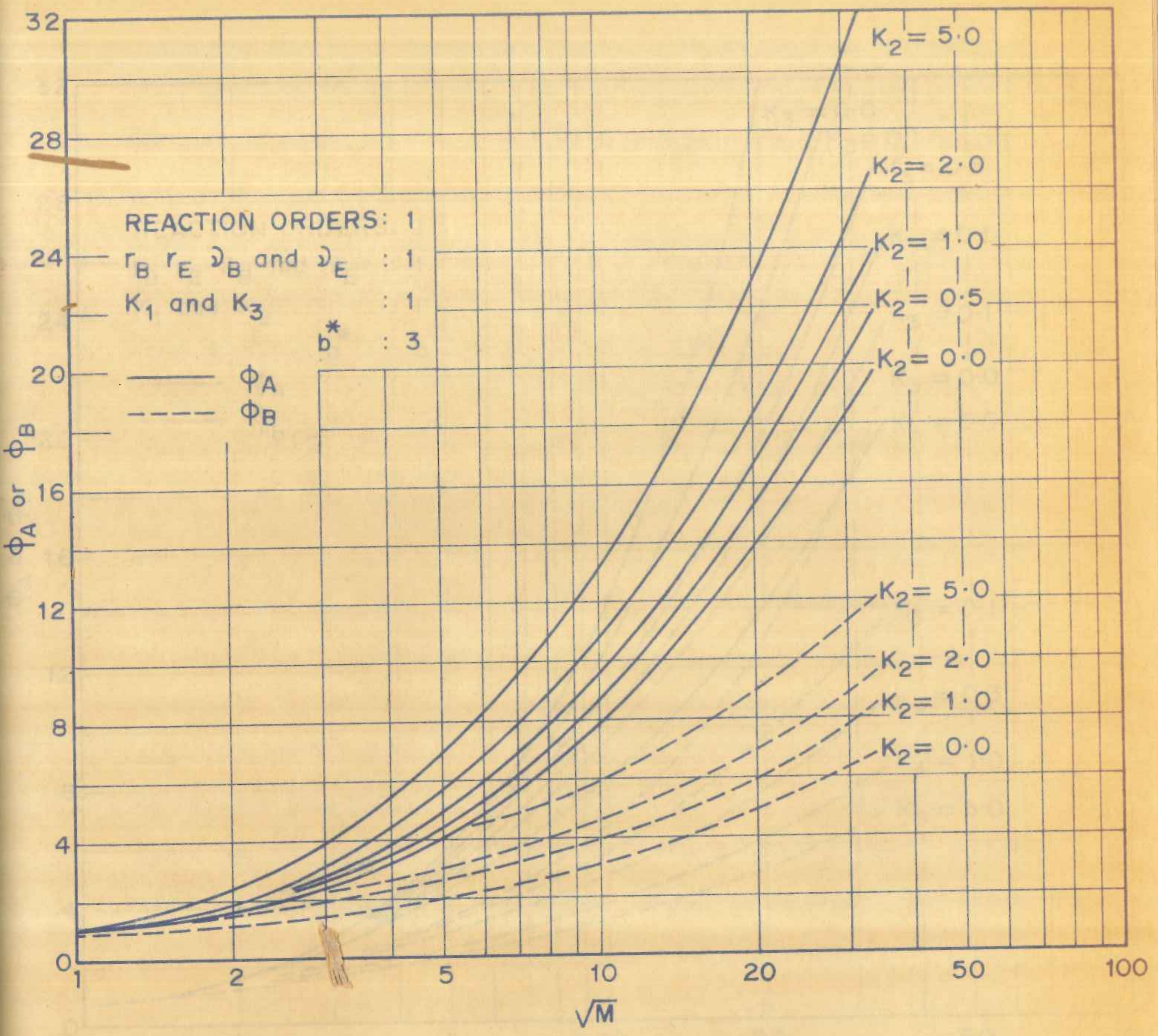


FIG. 2·11: EFFECT OF K_2 ON ϕ vs. $\sqrt{M}$ PLOTS

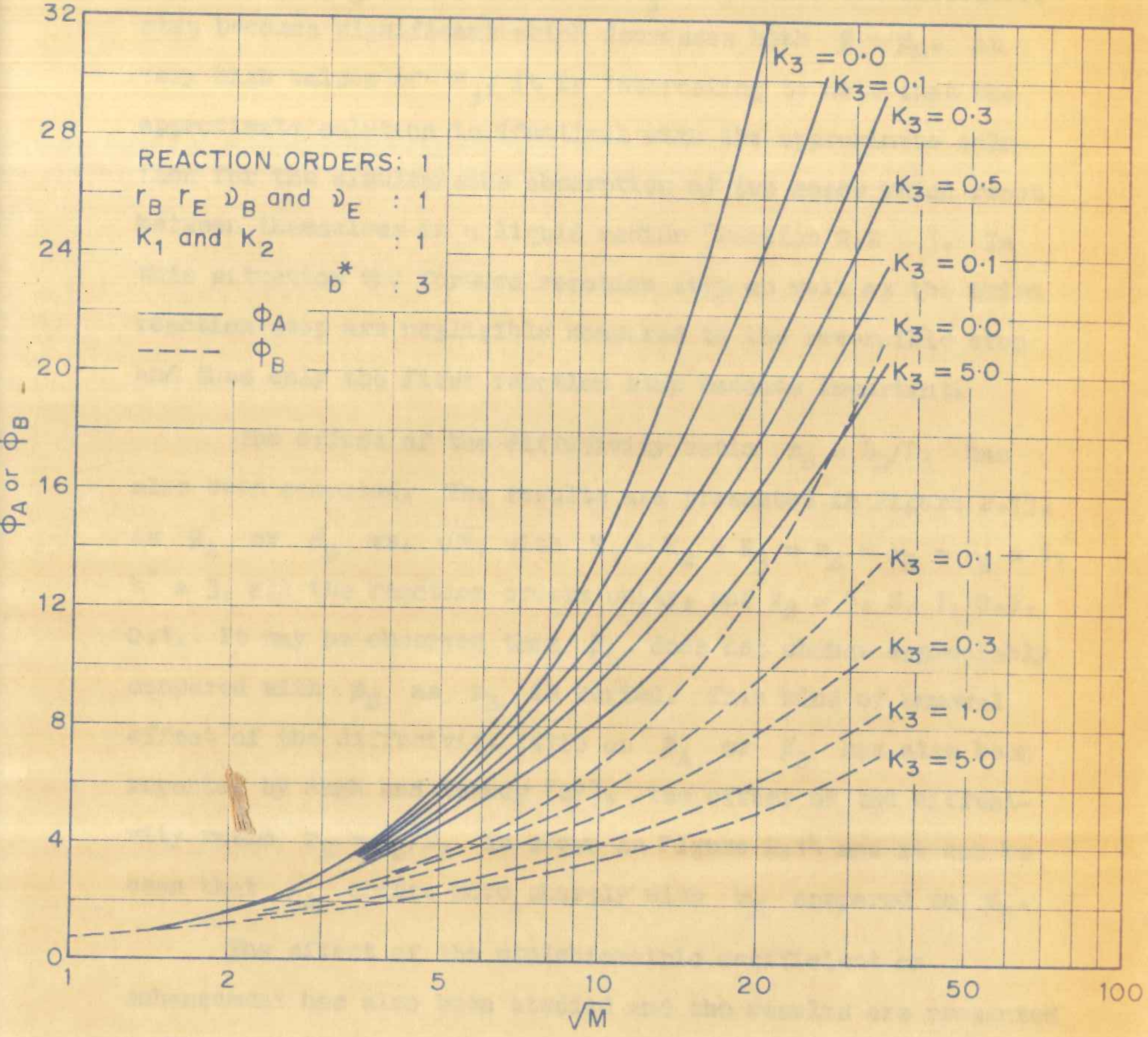


FIG. 2·12: EFFECT OF K_3 ON ϕ vs. $\sqrt{M}$ PLOTS

increase as K_3 decreases. As K_3 increases the reversible step becomes significant which depresses both ϕ_A and ϕ_B. At very high values of K_3, it is interesting to note that the approximate solution is identical with the approximate solution for the simultaneous absorption of two gases which react between themselves in a liquid medium [Section 2.2]. In this situation the forward reaction step as well as the third reaction step are negligible compared to the reversible step and thus only the first reaction step becomes important.

The effect of the diffusivity ratio $r_B = D_B/D_A$ has also been computed. The results are presented in Figure 2.13, as ϕ_A or ϕ_B vs. $\sqrt{M}$, with $K_1 = K_2 = K_3 = r_E = \nu_B = \nu_E = 1$, $b^* = 3$, all the reaction orders unity, and $r_B = 5, 2, 1, 0.5, 0.1$. It may be observed that ϕ_A does not change appreciably compared with ϕ_B as r_B is varied. This kind of unusual effect of the diffusivity ratio on ϕ_A or ϕ_B has also been reported by Shah and Kenney [27]. The effect of the diffusivity ratio $r_E = D_E/D_A$ is shown in Figure 2.14 and it can be seen that ϕ_A change more sharply with r_E compared to ϕ_B.

The effect of the stoichiometric coefficient on enhancement has also been studied and the results are presented in Figure 2.15 and 2.16, as ϕ_A or ϕ_B vs. $\sqrt{M}$, with $K_1 = K_2 = K_3 = r_E = r_B = 1$, $b^* = 3$, the reaction orders unity, and different values of ν_B and ν_E. The effect of ν_B on ϕ_A is negligible whereas ϕ_B changes significantly. ν_E has practically no effect on ϕ_A and ϕ_B at lower values of $\sqrt{M}$, but at higher $\sqrt{M}$ values the effect is quite marked.

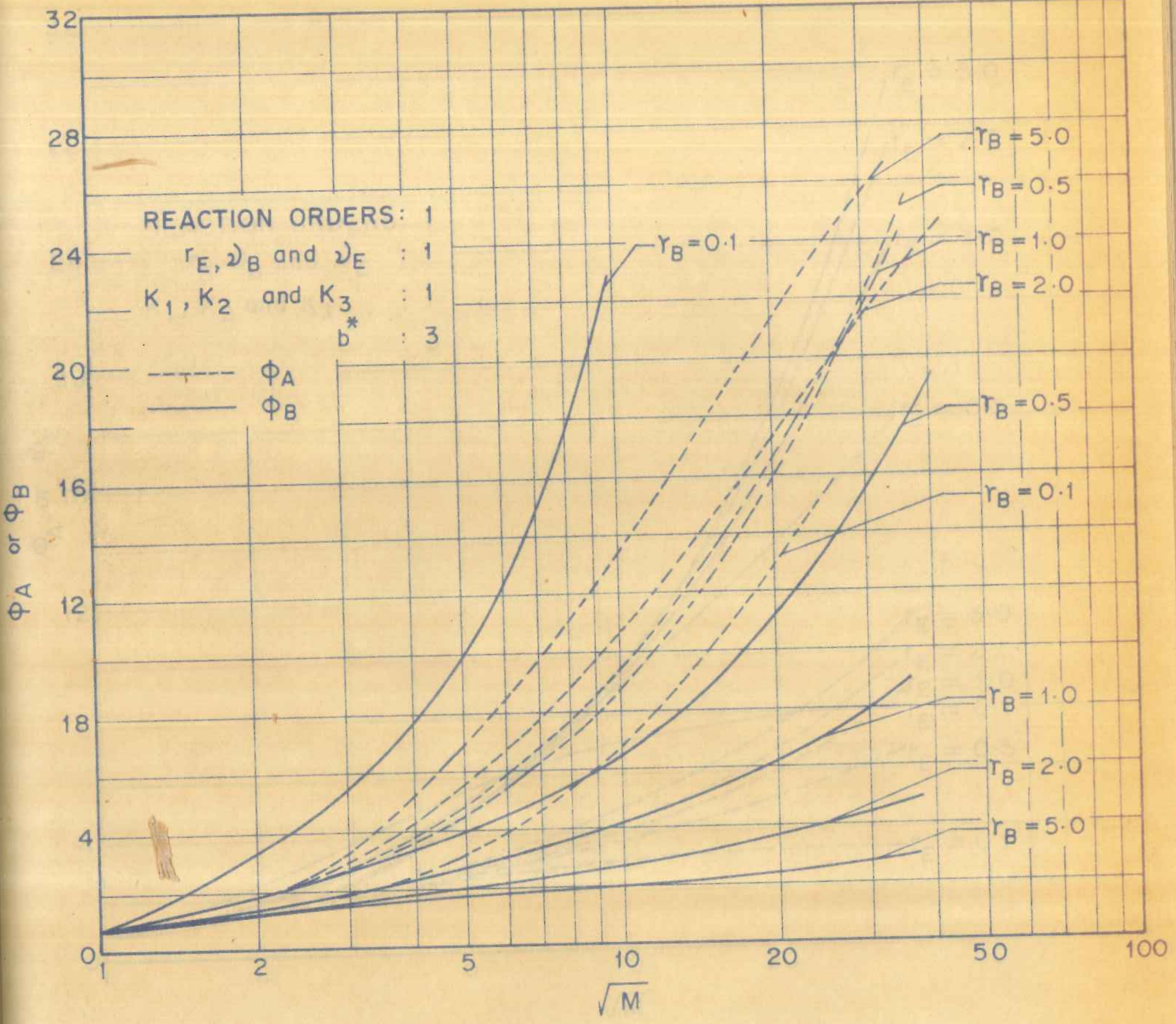


FIG. 2·13: EFFECT OF THE DIFFUSIVITY RATIO γ_B ON ϕ VS. $\sqrt{M}$ PLOTS

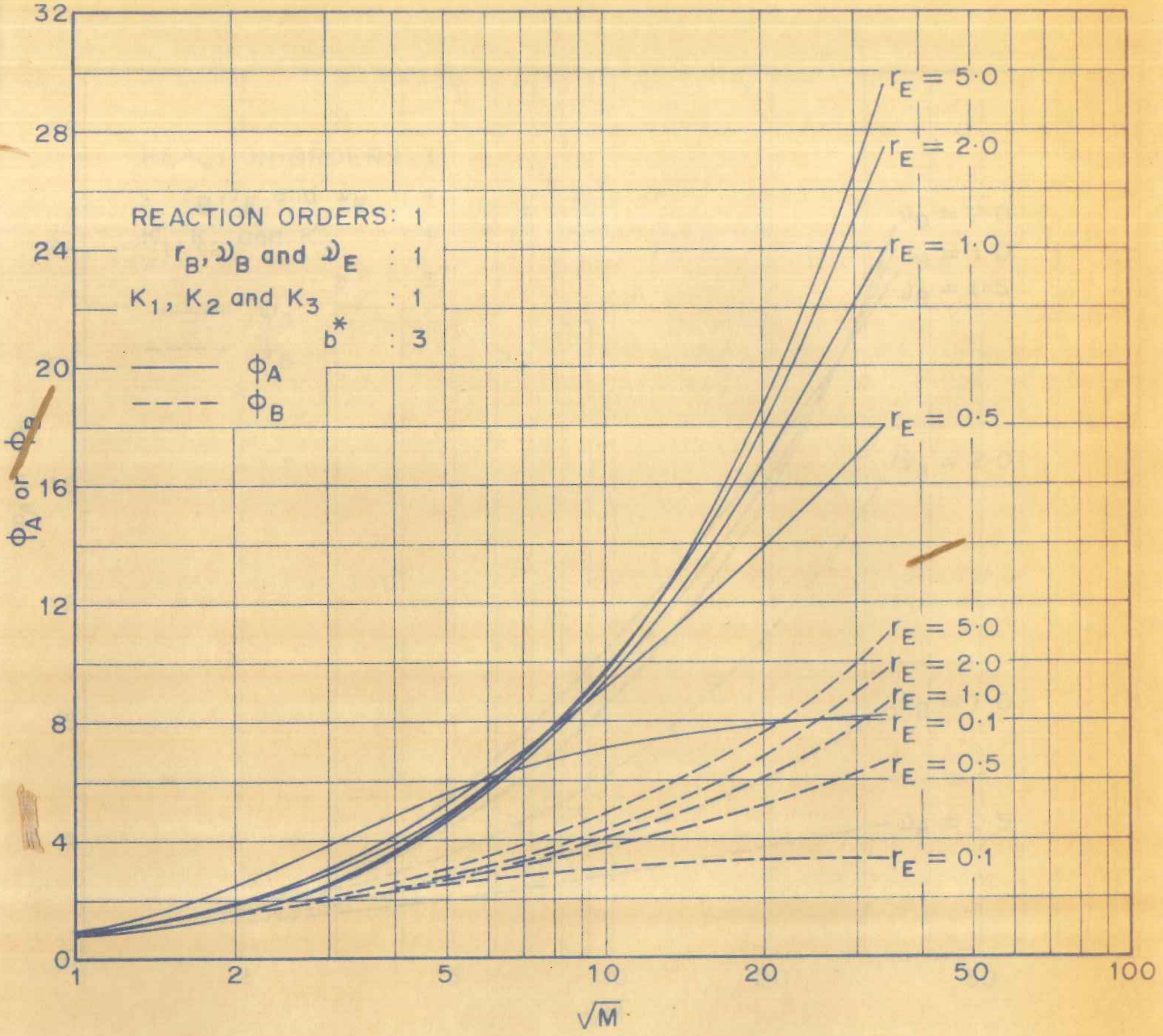


FIG. 2·14: EFFECT OF THE DIFFUSIVITY RATIO r_E ON ϕ vs. $\sqrt{M}$ PLOTS

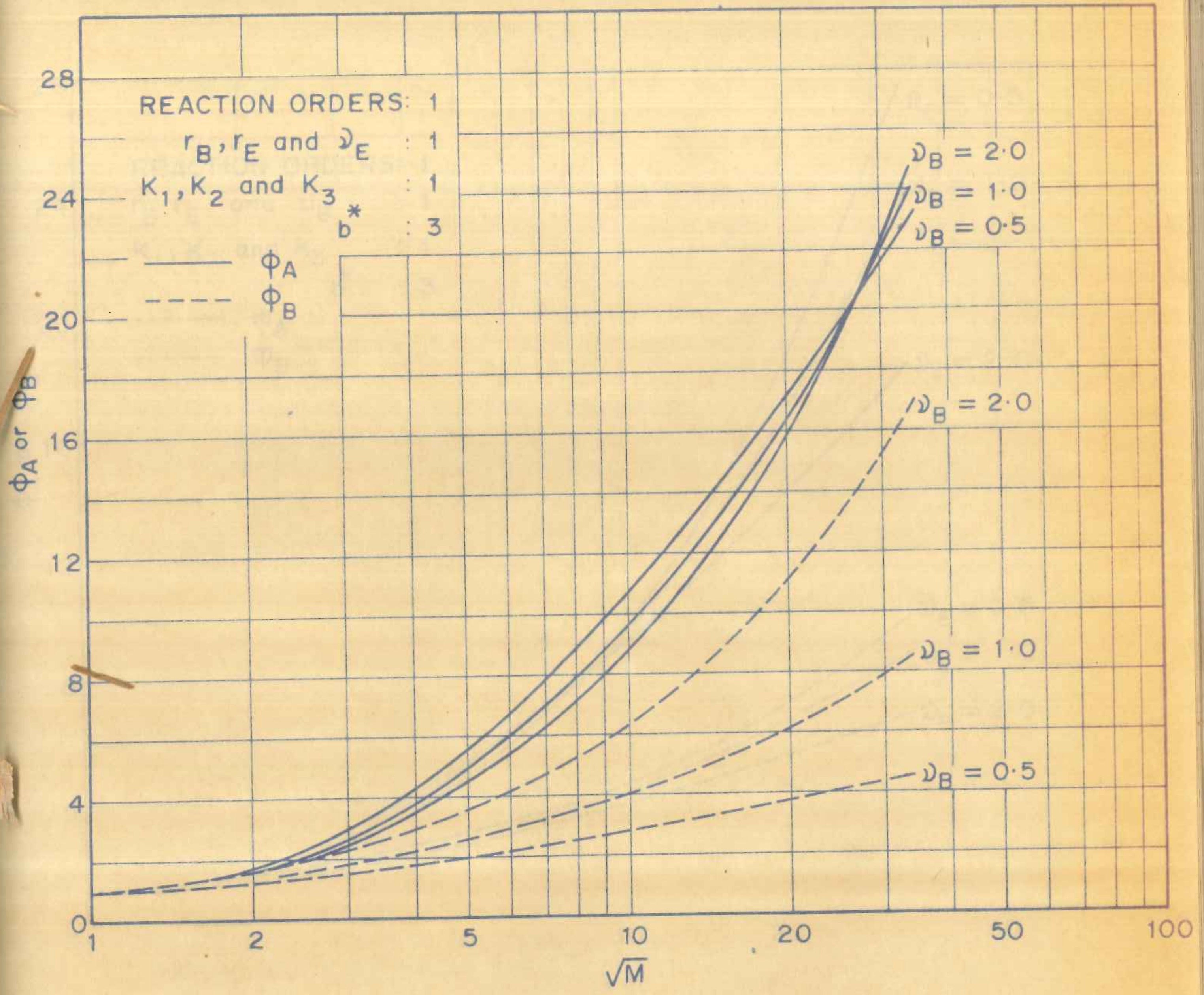


FIG. 2·15: EFFECT OF THE STOICHIOMETRIC RATIO ν_B ON ϕ vs. $\sqrt{M}$ PLOTS

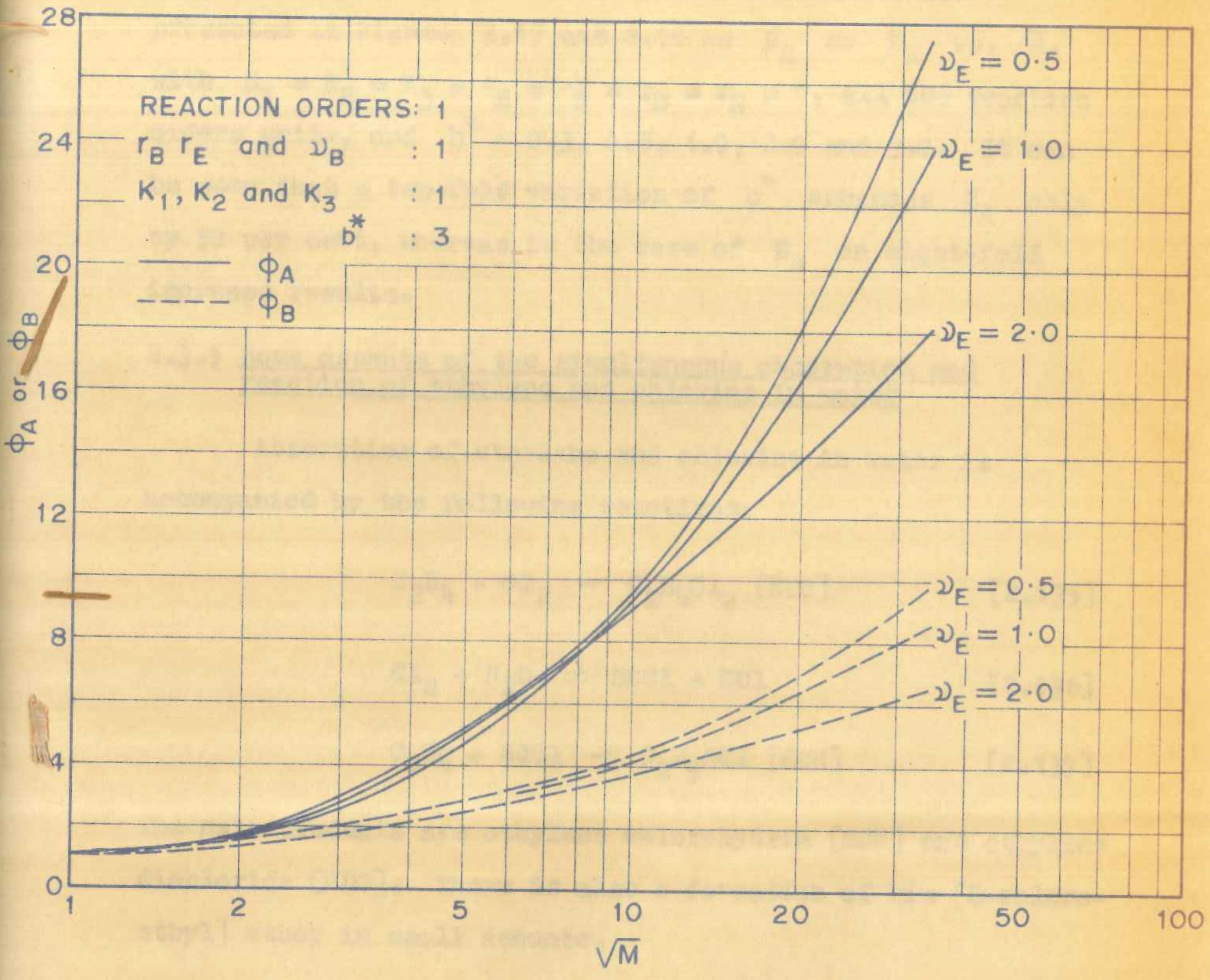


FIG. 2·16: EFFECT OF THE STOICHIOMETRIC RATIO ν_E ON ϕ vs. $\sqrt{M}$ PLOTS

The effect of the solubility ratio b^* of the two gases has also been investigated and the results are presented in Figure 2.17 ~~and 2.18~~ as ϕ_A or ϕ_B vs. $\sqrt{M}$, with $K_1 = K_2 = K_3 = \nu_B = \nu_E = r_B = r_E = 1$, all the reaction orders unity, and $b^* = 0.3, 0.5, 1.0, 2.0$ and 3.0. It can be seen that a ten-fold variation of b^* enhances ϕ_A only by 50 per cent, whereas in the case of ϕ_B an eight-fold increase results.

2.3.5 Some aspects of the simultaneous absorption and reaction of ethylene and chlorine in water

Absorption of ethylene and chlorine in water is accompanied by the following reactions:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 \text{ [EDC]} \qquad [2.135]$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \qquad [2.136]$$

$$C_2H_4 + HOCl \rightarrow C_2H_5OCl \text{ [ECH]} \qquad [2.137]$$

The main products are ethylene chlorohydrin [ECH] and ethylene dichloride [EDC]. There is also a formation of bis [2-chloroethyl] ether in small amounts.

$$C_2H_4 + HOCl + C_2H_5OCl \rightarrow [C_2H_4Cl]_2O + H_2O \qquad [2.138]$$

At lower concentrations of ECH, which represents the practical situation, formation of ether is almost negligible and need not be considered, and the important reactions involved are the three steps mentioned above.

An analysis of this system would be useful in the

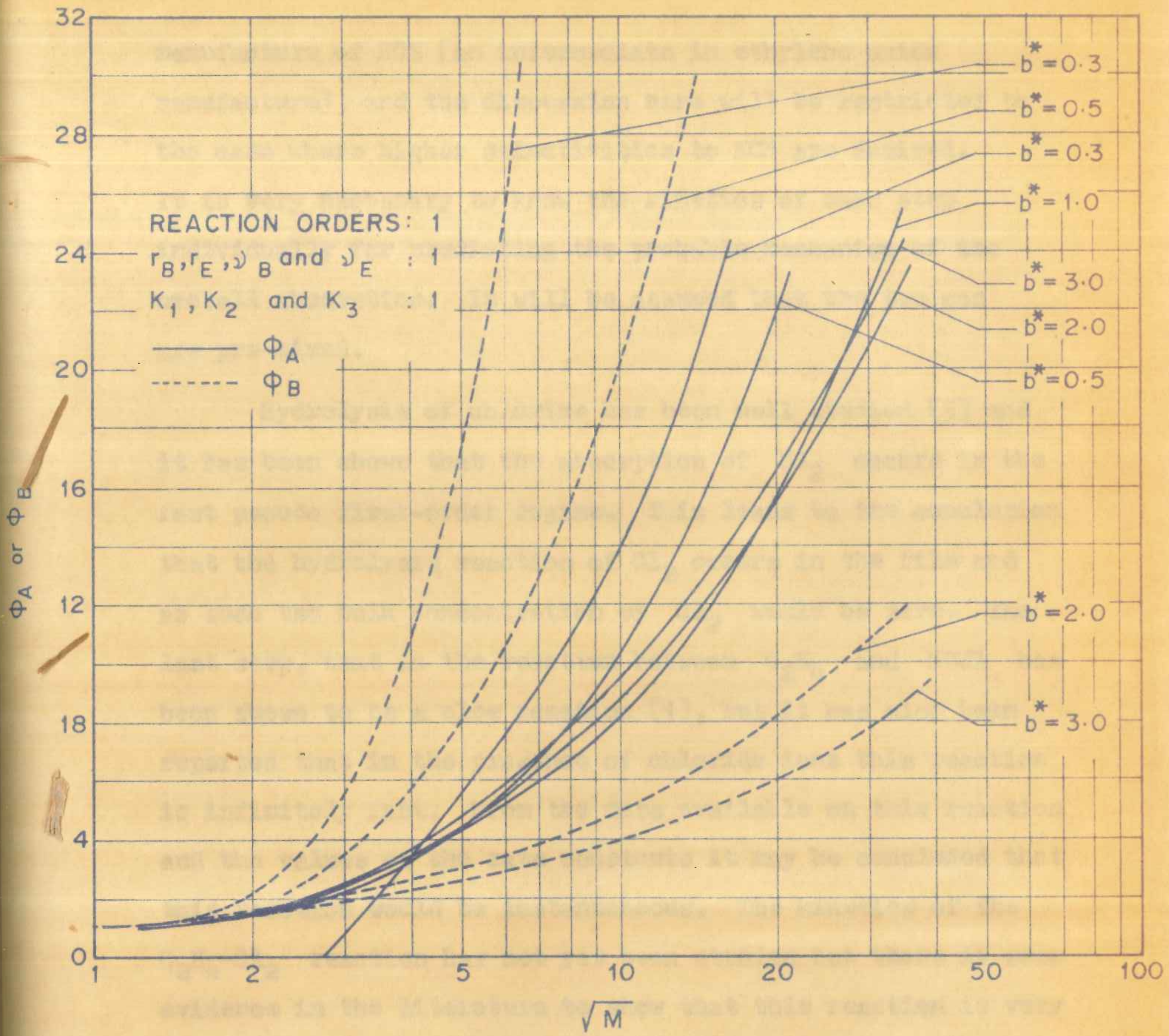


FIG. 2.17 : EFFECT OF THE SOLUBILITY RATIO b^* ON ϕ

VS. $\sqrt{M}$ PLOTS

manufacture of ECH [an intermediate in ethylene oxide manufacture], and the discussion here will be restricted to the case where higher selectivities to ECH are desired. It is very necessary to know the kinetics of each step individually for predicting the probable mechanism of the overall absorption. It will be assumed that the two gas are pre-mixed.

Hydrolysis of chlorine has been well studied [5] and it has been shown that the absorption of Cl_2 occurs in the fast pseudo first-order regime. This leads to the conclusion that the hydrolysis reaction of Cl_2 occurs in the film and as such the bulk concentration of Cl_2 would be zero. The last step, that is the reaction between C_2H_4 and HOCl has been shown to be a slow reaction [1], but it has also been reported that in the presence of chloride ions this reaction is infinitely fast. From the data available on this reaction and the values of the rate constants it may be concluded that this reaction would be instantaneous. The kinetics of the C_2H_4-Cl_2 reaction has not yet been studied but there is some evidence in the literature to show that this reaction is very slow in comparison to the C_2H_4-HOCl reaction the presence of chloride ions. From this it may be concluded that the absorption of C_2H_4 and Cl_2 conforms to case [f] discussed in Section 2.3.3.

2.4 SUMMARY AND CONCLUSIONS

The problem of simultaneous absorption of two gases followed by complex chemical reactions has been analysed in two parts as discussed in Section 2.1: [a] absorption and reaction of two gases among themselves; and [b] analysis of the complex scheme represented by the following reactions:

$$Z_A\ A[g] + Z_B\ B[g] \xrightarrow{k_1} Z_X\ X \qquad [2.139]$$

$$Z_B\ B[g] + Z_c\ C[l] \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Z_E\ E[l]\ Z_F\ F[l] \qquad [2.140]$$

$$Z_A\ A[g] + Z_E\ E[l] \xrightarrow{k_4} Z_Y\ Y \qquad [2.141]$$

There are many important reactions involving absorption and reaction of two gases among themselves, viz. NH_3 and CO_2 in water, C_2H_4 and Cl_2 in HCl solution. As these reactions give industrially important products, it is necessary to know the mechanism of absorption for the design of plants for these products. Roper et al [25] have given numerical solutions to the differential equations characterising this problem based on the penetration theory, while Ramachandran and Sharma [19] have analysed the problem based on the film theory to obtain an analytical solution. The latter workers assumed linear concentration profiles for the gaseous species in the film which is unrealistic. Hence in the present work an exponential profile has been assumed to obtain an analytical solution. This has been discussed in Section 2.2. It may be concluded that the solution [based on a nonlinear profile] given in the present work is superior to Ramachandran and Sharma's solution and also that the proposed exponential profiles may be used to solve some problems involving complex reactions. This has been clearly brought out by comparison for a pseudo m^{th} order reaction and the numerical solution [Section 2.2].

Using the above exponential profiles, an analysis of the complex scheme was worked out based on the film theory for a fast reaction regime. The reaction terms in the differential equations representing the material balances of the species are nonlinear and analytical solutions for such equations have not been possible so far. Hence the concentration terms of the gaseous species were linearised in terms of the distance from the interface, the film thickness and the enhancement during absorption. The concentrations of the nonvolatile reactants were assumed to be constant near the interface in the analysis for the gas A. In the analysis for the gas B, the reversible reaction 2.140 must be considered and the substitution of $E = E_i$ may not be correct since E and F are present throughout the film. Hence a rigorous relationship [Equation 2.56] was substituted for E in solving the differential equation for the gas B.

Solutions were obtained for the enhancement factors [viz. ϕ_A and ϕ_B] which represent the magnitudes by which the rates of absorption are increased due to the chemical reactions involved. The expressions for ϕ_A and ϕ_B were obtained in terms of various diffusion and reaction parameters and the results have been presented as ϕ_A or ϕ_B vs. $\sqrt{M}$ at different values of the parameters [where M is the dimensionless model parameter]. From these results, the following conclusions have been drawn.

1. The ratio of the rate constants of reaction 2.141 and 2.139 [K_1] has a negligible effect on the enhancement of B, but as K_1 increases enhancement in A increases up to values of $\sqrt{M} = 10$, while at higher values of $\sqrt{M}$ it decreased. It is interesting to note that when K_1 is high, reaction 2.139 becomes negligible compared to reaction 2.141 and absorption of A reduces to gas absorption accompanied by irreversible chemical reaction with the liquid phase reactant, in which ϕ_A approaches an asymptote at higher values of $\sqrt{M}$. This is why ϕ_A decreases at higher values of $\sqrt{M}$.

2. ϕ_A and ϕ_B both increase as the value of K_2 [k_2/k_1] increases in the entire range of $\sqrt{M}$. At lower values of K_2 there is no E available for reaction 2.141 to occur; as such reactions 2.140 and 2.141 are almost negligible. In this situation the problem reduces to the simultaneous absorption of two gases which react among themselves in a liquid medium.

3. ϕ_A and ϕ_B increase as K_3 decreases. A 50-fold decrease in K_3 causes an increase in ϕ_A by a factor of 1.75 and in ϕ_B by 2.33, at a value of $\sqrt{M} = 10$.

4. A 50-fold increase in the diffusivity ratio r_B [viz. D_B/D_A] enhances ϕ_A by a factor of 2.0 and ϕ_B by 11.2 at $\sqrt{M} = 10$. This unusual effect has also been reported by Shah and Kenney [27].

5. At $\sqrt{M} = 10$, a fifty-fold increase in r_E [viz. D_E/D_A] results in an increase in ϕ_A by a factor of 1.3, but at $\sqrt{M} = 30$ ϕ_A changes by a factor of 3.3. The enhancement in B also increases by the same order as r_E increases.

6. The effect of the stoichiometric coefficient ν_B [viz. Z_B/Z_A] on the enhancement in A is negligible, but a four-fold increase in ν_B increases the enhancement in B by a factor of 2.0 at $\sqrt{M}$ = 10 and 3.6 at $\sqrt{M}$ = 30. The ratio of the stoichiometric coefficient ν_E [viz. Z_E/Z_A] has a negligible effect on the enhancement of A and B.

7. A ten-fold decrease in the solubility ratio causes an increase in the enhancement in A by a factor 1.7, but that of B by a factor of 8.0, at $\sqrt{M}$ = 6.

In addition to the above general analysis, the following special cases have also been considered:

1. Solubility of one of the gases is very high [i.e. $B^* >> A^*$].
2. A and B both react in the bulk liquid.
3. Reactions 2.139 and 2.140 occur in the bulk and reaction 2.141 in the fast reaction regime [i.e. in the film].
4. Reactions 2.139 and 2.141 occur in the bulk reaction 2.140 in the fast reaction regime [i.e. in the film].
5. Reaction 2.140 is instantaneous and reaction 2.139 and 2.141 [viz. those involving A] are in the fast reaction regime.
6. Reaction of 2.141 is instantaneous and reactions 2.139 2.140 [viz. those involving B] are in the fast reaction regime.

These cases include practically all the situations that may be encountered in industrially important systems. Thus the corresponding model can be used for design purposes. Some aspects of one such system, viz. simultaneous absorption of

C_2H_4 and Cl_2 in water, have been discussed, which should provide a theoretical basis for adjusting the reaction conditions to obtain maximum selectivity for the desired product, viz. ethylene chlorohydrin [which is subsequently converted to ethylene oxide, a product of commerce].

NOTATION

A	gaseous species A or concentration of A at any point in the liquid film g mole/cm^3
a	effective gas-liquid interfacial area, cm^2/cm^3
B	gaseous species B or concentration of B at any point in the liquid film, g mole/cm^3
b^*	B^*/A^*
C	reactant species C or concentration of C at any point in the liquid film, g mole/cm^3
c	C/A^*
D	diffusion coefficient, subscript indicating the species, cm^2/sec
E	reactant species E or concentration of E at any point in the liquid film, g mole/cm^3
e	E/A^*
F	reactant species F or concentration of F at any point in the liquid film, g mole/cm^3
f	F/A^*
H	Henry's law solubility coefficient, g mole/cm^3 atm
K	equilibrium constant
K_1	$\frac{k_4}{k_1} {A^*}^{u+v-m-n}$
K_1'	$\frac{k_4}{k_1'} {A^*}^{u+v-m}$
K_2	$\frac{k_2}{k_1} {A^*}^{p+q-m-n}$
K_2^*	$\frac{k_3}{k_1} {A^*}^{u+v-m-n}$
K_3	$\frac{k_3}{k_1} {A^*}^{p'+q'-m-n}$
k, k_1, k_2, k_3, k_4	general order reaction rate constants

k', k'', k_1'	pseudo m^{th} order reaction rate constants
k_L	liquid side mass transfer coefficient in the absence of chemical reaction, cm/sec
k_G	gas side mass transfer coefficient, g mole/cm^2 sec atm
$\underline{l}$	fractional hold-up of the liquid phase
$m, n, p, q, p', q', u, v, w$	orders of reactions with respect to various species
M	$\frac{2}{m+1} \frac{Z_A k_1 A^{*m-1} B^{*n} \delta^2}{D_A}$
	$\frac{4}{[m+1][n+1]} \frac{Z_A k A^{*m-1} B^{*n} \delta^2}{D_A}$ in Section 2.2
	$\frac{2}{m+1} \frac{Z_A k_1 A^{*m-1} E_o^n \delta^2}{D_A}$ in Table 1.1
	$\frac{2}{m+1} \frac{Z_A k_1' A^{*m-1} \delta^2}{D_A}$ for a pseudo m^{th} order case
M_1	$M \left[1 + \frac{[m+1]}{[u+1]} K_1' e_i^v \right]$
M_2	$M \left[\left(\frac{e_i}{q_E} \right)^n + \frac{[m+1]}{[p+1]} K_2 q_E^{q-n-1} c_i \right]$
M_3	$M \left(\frac{e_i}{q_E} \right)^q \left[\frac{m+1}{p+1} \frac{\nu_B}{r_B} q_E^{q-n} b^{*p-1} K_2 \right]$
M_4	$M \left(\frac{e_i}{q_E} \right)^n \left[1 + \frac{[m+1]}{[p+1]} K_2 \frac{c_i^q}{e_1^n} \right]$

M'	$k_1 \left[\frac{c_i}{D_A} + \frac{1}{KD_E} \right] \delta^2$
M''	$M \left(\frac{c_i}{q_E} \right)^n \left[1 + \frac{[m+1]}{[p+1]} \frac{\nu_E}{r_E} T \right]$
M_1'	$M K_2 \frac{m+1}{p+1} \frac{\nu_B}{r_B} q_E^{q-n} b^{*p-1} \left[\frac{q_C}{q_E} + \frac{\nu_C}{\nu_E} \frac{r_E}{r_C} \left(1 - \frac{e_i}{q_E} \right) \right]^q$
$\overline{M}$	$M (e_i/q_E)^n \left[1 + \frac{\nu_C}{r_C} T_1 \right]$
$\overline{M}_1$	$M \left[1 + \frac{1}{r_E K} \right]$
$\overline{M}_2$	$M K_2^* \frac{m+1}{u+1} \frac{\nu_B}{r_B} q_E^{v-n} b^{*u-1} \left[\frac{q_F}{q_E} + 1 - \frac{e_i}{q_E} \right]^v$
P	partial pressure of the solute gas, atm
$q_A, q_B,$ $q_C, q_E,$ q_F	A_o/A^*, B_o/A^*, C_o/A^*, E_o/A^*, F_o/A^*
R	rate of absorption of the gaseous component at the interface, g mole/cm^2 sec
R'	rate of absorption of the gaseous component per unit volume of the liquid, g mole/cm^3 sec
r	rate of chemical reaction, g mole/cm^3 sec
$r_B, r_C,$ r_E, r_F	defined by D_B/D_A, D_C/D_A, D_E/D_A, D_F/D_A
S	any reacting species S or concentration of S at any point in the film

T	$\frac{K e_i^{p-1} f_i^{q}}{c_i^{n}}$
T_1	$K_2 e_i^{p-1} q_E^{q-n} \frac{[q_p/q_E] + 1 - [e_i/q_E]^{q}}{[e_i/q_E]^{n}}$
t	time of contact, sec
U	velocity in the direction of diffusion, cm/sec
x	distance in the direction of diffusion, cm
X	product species X
y	product species y
Z	stoichiometric coefficient, subscript indicating the species

Greek symbols

α_1, α_2	constants in Equations 2.59 and 2.68
δ	film thickness, cm
B' C' E' F	defined by Z_B/Z_A, Z_C/Z_A, Z_E/Z_A, Z_F/Z_A
λ	the depth of penetration of A, cm
ϕ	enhancement factor, subscript indicating the species

Subscripts

*	denotes the value of the concentration of a species when the solution attains equilibrium with the gas
i	gas-liquid interface
o	liquid bulk
G	gas phase

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APPENDIX - 1

EXPERIMENTAL RESULTS: DIFFUSIVITY

RUN NO.1

System: Hydrogen chloride-nitrobenzene
Temperature: 26°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	3.8	140	23.90
20	6.85	150	24.70
30	9.30	160	25.35
40	11.40	170	26.00
50	13.25	180	26.60
60	14.90	190	27.10
70	16.40	200	27.60
80	17.70	210	28.05
90	19.00	220	28.45
100	20.15	230	28.85
110	21.30	240	29.20
120	22.20	270	29.95
130	23.10	300	30.55

RUN NO.2

System: Hydrogen chloride-nitrobenzene
Temperature: 40°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement sec
10	3.95	150	25.70
20	7.10	160	26.25
30	10.00	170	26.75
40	12.55	180	27.30
50	14.60	190	27.80
60	16.30	200	28.25
70	18.10	210	28.70
80	19.70	220	29.10
90	20.90	230	29.50
100	21.90	240	29.90
110	22.80	250	30.25
120	23.70	260	30.60
130	24.50	270	30.90
140	25.10	280	31.75

RUN NO.3

System: Hydrogen chloride-nitrobenzene
Temperature: 50°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	3.8	150	20.25
20	6.4	160	20.80
30	8.65	170	21.30
40	10.65	180	21.75
50	12.20	190	22.15
60	13.40	200	22.55
70	14.50	210	22.95
80	15.45	220	23.35
90	16.30	230	23.65
100	17.10	240	24.00
110	17.80	250	24.30
120	18.50	260	24.60
130	19.15	270	24.85
140	19.70		

RUN NO.4

System: Hydrogen chloride-nitrobenzene
Temperature: 58.5°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	4.6	155	18.70
20	7.3	165	19.15
30	9.1	175	19.50
40	10.5	185	19.85
50	11.7	195	20.20
65	13.2	205	20.55
75	14.05	215	20.80
85	14.75	225	21.15
95	15.45	235	21.45
105	16.10	245	21.75
115	16.75	255	22.05
125	17.30	265	22.35
135	17.80	275	22.55
145	18.30	305	23.30

RUN NO.5

System: Ethylene-nitrobenzene
Temperature: 30°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	0.55	180	5.15
20	1.05	190	5.30
30	1.50	200	5.45
40	1.95	210	5.55
50	2.35	220	5.65
60	2.70	230	5.75
70	3.05	240	5.85
80	3.30	250	5.95
90	3.55	260	-
100	3.80	270	6.10
110	4.05	280	6.20
120	4.25	290	6.30
130	4.45	300	6.40
140	4.65	320	6.55
150	4.75	340	6.70
160	4.85	360	6.85
170	5.00		

RUN NO.6

System: Ethylene-nitrobenzene
Temperature: 40°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	0.55	180	5.15
20	1.00	190	5.30
30	1.45	200	5.40
40	1.90	210	5.50
50	2.30	220	5.60
60	2.65	230	5.70
70	3.00	240	5.80
80	3.30	250	5.87
90	3.55	260	5.95
100	3.75	270	6.05
110	3.95	280	6.10
120	4.15	290	6.20
130	4.35	300	6.27
140	4.55	320	6.35
150	4.70	340	6.45
160	4.85	360	6.55
170	5.00		

RUN NO.7

System: Ethylene-nitrobenzene
Temperature: 50°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	0.65	180	5.10
20	1.10	190	5.20
30	1.55	200	5.30
40	2.00	210	5.40
50	2.40	220	5.50
60	2.75	230	5.575
70	3.05	240	5.650
80	3.35	250	5.725
90	3.60	260	5.800
100	3.80	270	5.875
110	4.00	280	5.950
120	4.20	290	6.000
130	4.40	300	6.05
140	4.55	330	6.15
150	4.70	340	6.25
160	4.85	360	6.35
170	5.00		

RUN NO.8

System: Ethylene-nitrobenzene
Temperature: 60°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
10	0.75	180	5.20
20	1.25	190	5.30
30	1.70	200	5.40
40	2.10	210	5.50
50	2.50	220	5.575
60	2.85	230	5.650
70	3.20	240	5.725
80	3.50	250	5.800
90	3.80	260	-
100	4.05	270	5.9
110	4.25	280	-
120	4.45	290	6.00
130	4.60	300	6.10
140	4.75	320	6.25
150	4.90	340	6.35
160	5.00	360	6.45
170	5.10		

RUN NO.9

System: Ethylene-ethylene dichloride
Temperature: 15°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	1.1	100	5.70
10	1.95	110	5.90
15	2.50	120	6.05
20	2.9	140	6.35
25	3.25	160	6.60
30	3.50	180	6.80
40	4.00	200	7.00
50	4.4	220	7.20
60	4.75	240	7.40
70	5.00	260	7.55
80	5.25	280	7.70
90	5.50	300	7.85

RUN NO.10

System: Ethylene-ethylene dichloride
Temperature: 19°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	1.0	110	7.25
10	1.8	120	7.50
15	2.5	130	7.70
20	3.0	140	7.95
30	3.9	160	8.40
40	4.6	180	8.75
50	5.15	200	9.05
60	5.60	220	9.30
70	6.10	240	9.50
80	6.40	260	9.75
90	6.70	280	10.00
100	7.00	300	10.20

RUN NO.11

System: Ethylene-ethylene dichloride
Temperature: 25°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	0.9	100	5.00
10	1.6	110	5.15
15	2.1	130	5.45
20	2.5	150	5.70
25	2.8	170	6.00
30	3.05	180	6.15
40	3.45	200	6.40
50	3.80	220	6.60
60	4.10	240	6.85
70	4.35	260	7.05
80	4.60	280	7.25
90	4.80	300	7.45

RUN NO.12

System: Ethylene-ethylene dichloride
Temperature: 30°C
Area of the absorbing interface: 0.0687 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	0.7	125	3.15
15	1.65	155	3.40
25	2.05	185	3.55
35	2.25	215	3.70
45	2.40	245	3.85
55	2.50	275	4.00
65	2.65	305	4.10
85	2.80	335	4.20
105	2.95	365	4.30

RUN NO.13

System: Hydrogen chloride-ethylene dichloride
Temperature: 15°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	5.9	150	24.80
10	9.4	160	25.65
15	11.1	170	26.50
20	11.8	180	27.20
25	12.35	190	27.70
30	12.85	200	28.20
40	13.90	210	28.75
50	14.95	220	29.25
60	16.10	230	29.75
70	17.20	240	30.30
80	18.30	250	30.85
90	19.35	260	31.40
100	20.40	270	31.95
110	21.35	280	32.40
120	22.30	290	32.75
130	23.20	300	33.15
140	24.00		

RUN NO.14

System: Hydrogen chloride-ethylene dichloride
Temperature: 25.5°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	4.2	130	16.30
10	5.55	140	17.05
15	6.35	150	17.75
20	6.85	160	18.35
25	7.30	170	18.90
30	8.00	180	19.40
35	8.70	190	19.95
40	9.35	200	20.40
45	9.90	210	20.85
50	10.30	220	21.25
55	10.60	230	21.70
60	10.90	240	22.10
70	11.60	250	22.40
80	12.50	260	22.75
90	13.30	270	23.05
100	14.15	280	23.35
110	14.90	290	23.60
120	15.60	300	23.85

RUN NO.15

System: Hydrogen chloride-ethylene dichloride
Temperature: 30°C
Area of the absorbing interface: 0.0341 cm^2

Time min	Displacement cm	Time min	Displacement cm
5	3.5	180	18.00
10	5.35	190	18.50
15	5.80	200	19.00
20	6.00	210	19.45
25	6.20	220	19.90
30	6.40	230	20.30
40	7.05	240	20.70
50	7.85	250	21.1
60	8.70	260	21.45
70	9.60	270	21.80
80	10.60	280	22.15
90	11.65	290	22.50
100	12.60	300	22.80
110	13.40	310	23.10
120	14.20	320	23.35
130	14.95	330	23.60
140	15.65	340	23.85
150	16.30	350	
160	16.90	360	
170	17.40		

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