A STUDY OF AN ALKYLATION REACTION

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by

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GENERAL INTRODUCTION

In recent years there has been a steady trend towards the production of higher performance automobile engines. This has caused a corresponding need for higher octane motor fuels. Consequently the alkylation process, which combines isoparaffins and light olefins to produce high quality gasoline alkylate, has increased steadily in importance. Because of this increase it has become economically attractive to learn more about the process in the hope of improving it.

In 1966, the Department of Chemical Engineering at McMaster University initiated a final year undergraduate simulation project on an alkylation unit in cooperation with Shell of Canada at their Oakville Refinery. A problem soon arose in trying to simulate the Stratco Reactor used by Shell. There were some published articles (I-1, 2, 3) available which described the dependence of one or two variables with respect to some other variable, but there was little information as to how one could predict the complete output given the input streams and the physical parameters of the reactor. Quantitative product distributions for example, were not available. This information was necessary before changes made in plant conditions studied in the model could be expected to result in an improved profit for the unit.

Part I of this study consisted of obtaining as much quantitative data as possible from both the literature and actual plant data. The collection of the plant data was made much more efficient through the cooperation of Shell of Canada and McMaster University who together financed the author's employment at the Oakville Refinery during the summer months of 1967. The results of this study are presented in Part I of this thesis along with the digital computer simulation model of the reactor which was subsequently written by two McMaster final year chemical engineering students as their part of the fourth year project.

Part II of this study was concerned with a more fundamental problem. It was known that the production of alkylate consisted of mass transfer of paraffins and olefins to the hydrocarbon-acid interface and that either at the interface or in the acid itself, chemical reactions took place to produce alkylate. Theories were available for predicting mass transfer with chemical reaction but according to the literature, had not been used to tackle this complex system. In order to study this problem, a bubble reactor was built where varying mixtures of isobutane and 1-butene were bubbled through a column of concentrated sulphuric acid. The flows and compositions of the gases were measured. An attempt was then made to predict the results by using various mass transfer theories, with and without chemical reaction. The results of this study are presented in Part II of this thesis.

PART I

STUDIES OF A PLANT ALKYLATION REACTOR

INTRODUCTION

Since 1964, the Faculty in Chemical Engineering at McMaster University has been interested in the study of simulation. The approach used is to take each unit operation in a chemical plant and describe it mathematically so that given the inputs and the physical parameters of the equipment, the outputs can be predicted. The storage and transfer of information, and the execution of the various mathematical models are handled by an executive program. The PACER (Process Assembly Case Evaluator Routine) executive was written by Professor P.T. Shannon and a graduate student, Mr. H. Mosler, at Purdue University (I-4). The MACSIM (McMaster Simulator System) is a modified version of PACER developed by the Chemical Engineering Department at McMaster. Details of this executive can be found in Chapters 2, 3 and 4 of reference (I-5). A complete simulation is a mathematical model whose solution will predict the performance of an actual plant as a computer output.

In the fall of 1966, the Faculty along with graduate and undergraduate students had already simulated a sulphuric acid plant (I-6) and were now preparing to test this modular approach in the petrochemical industry. Arrangements were made with the personnel at Shell of Canada's Oakville Refinery to study their complete alkylation unit. The work was undertaken as a fourth year project for the undergraduates and the results appear in reference (I-7). From the beginning the Stratco reactor used at

Shell could not be described mathematically because of the lack of technical information concerning its complex nature. Attempts were made to approach the problem theoretically but failed. It was decided that a study should be made from an empirical point of view and that plant data was necessary. This data chould then be used to produce a statistical model describing the reactor.

It was also realized that problems in communication can easily arise when joint university-industry projects are undertaken. A liaison between the two organizations was necessary so that the information required could be more easily obtained.

Therefore, the author was employed jointly by Shell and McMaster to work at the refinery during the summer of 1967 to study the Stratco reactor and to act as the contact between the university and industry for any problems which dealt with any part of the alkylation unit.

Part I of this thesis presents the findings of the work done at the Oakville Refinery and the subsequent use made of the information.

LITERATURE REVIEW

1. Chemistry of Alkylation

The basic overall reaction consists of combining isobutane and light olefins (C_3 and C_4) in the presence of concentrated sulphuric acid to form isoparaffins (C_7 and C_8). This explanation, however, is extremely simplified.

A more accurate description of the reaction was made possible by Whitmore (1-8, 1-9) who proposed the carbonium ion theory. This approach was later used by Birch and Dunstan (1-10), Schmerling (1-11, 1-12, 1-13), and others to arrive at the presently accepted chemistry of the reaction.

(a) Addition of Proton

The first reaction is the formation of carbonium ions. This occurs by two possible methods.

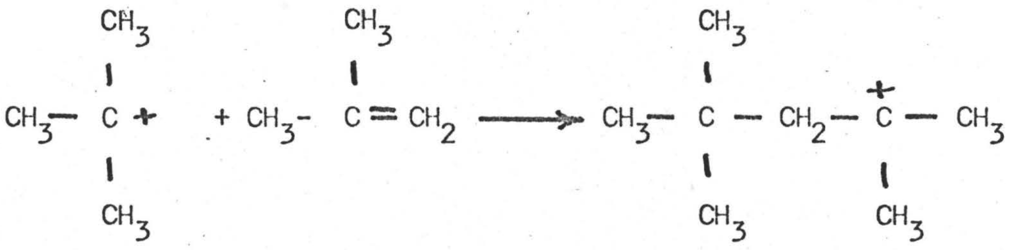
$$(CH_3)_2C{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_3C^{+}OSO_3H^{-} \qquad (1\text{-}1A)$$

$$\begin{aligned}(CH_3)_2CHCH_3 + 2H_2SO_4 \longrightarrow\ & (CH_3)_3C^{+}OSO_3H^{-} \\ & + SO_2 + 2H_2O\end{aligned} \qquad (1\text{-}1B)$$

Reaction (1-1A) is expected to be very fast relative to reaction (1-1B) so that the second is usually ignored. Also, since the anion is of little importance in the chemistry of this reaction it will not be included in the remainder of the description.

(b) Addition of Carbonium Ion to Olefin

The next step consists of the addition of the carbonium ion to an olefin. In the case of isobutene, the product would be a C_8 carbonium ion.

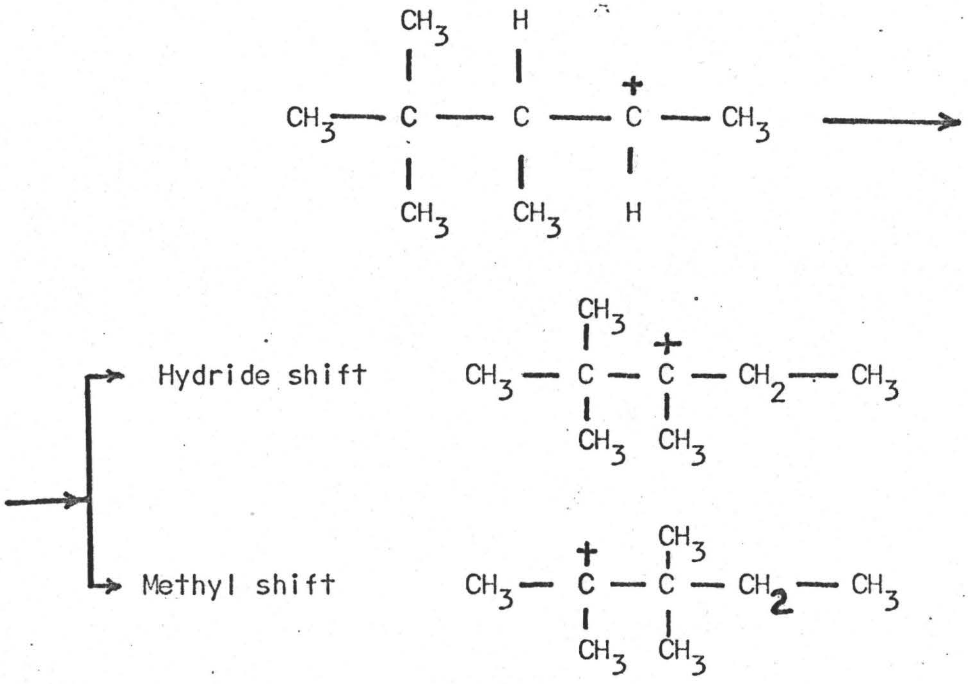


$$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}} + CH_3-\overset{CH_3}{C}=CH_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{\underset{CH_3}{C}}-CH_3 \qquad (1\text{-}2)$$

It should be understood that if different olefins, for example 1 or 2-butene, had been used, then 2,2,3-trimethylpentane (TMP) and 2,2 dimethylhexane (DMH) carbonium ions would have been produced respectively.

(c) Isomerization

The product from reaction (1-2) may now isomerize by either hydride or methyl shifts.



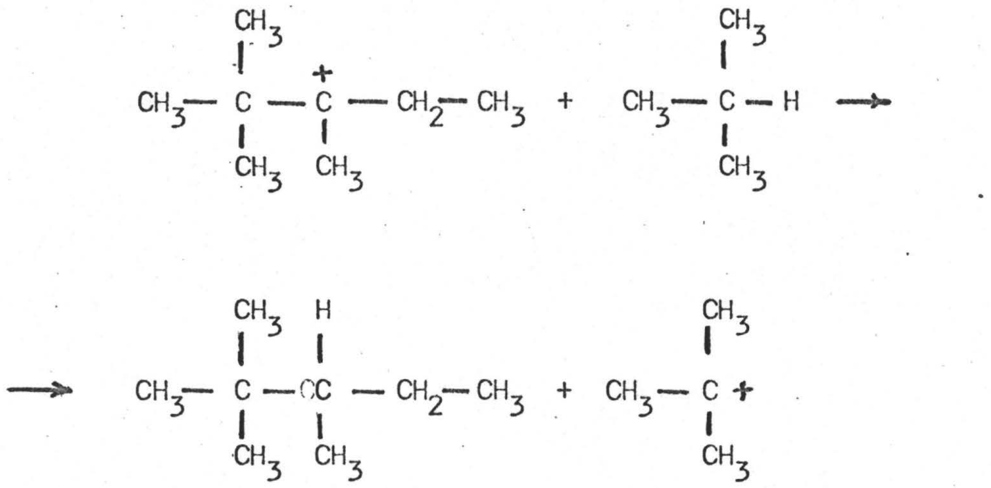
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{+}{\underset{H}{C}}-CH_3 \longrightarrow$$

$$\text{Hydride shift} \quad CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{+}{\underset{CH_3}{C}}-CH_2-CH_3 \qquad (1\text{-}3A)$$

$$\text{Methyl shift} \quad CH_3-\overset{+}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3 \qquad (1\text{-}3B)$$

(d) Hydride Ion Transfer

The fourth reaction (I-4) now occurs between the C_8 carbonium ion and an isobutane molecule to form the desired C_8 product and another C_4 carbonium ion.

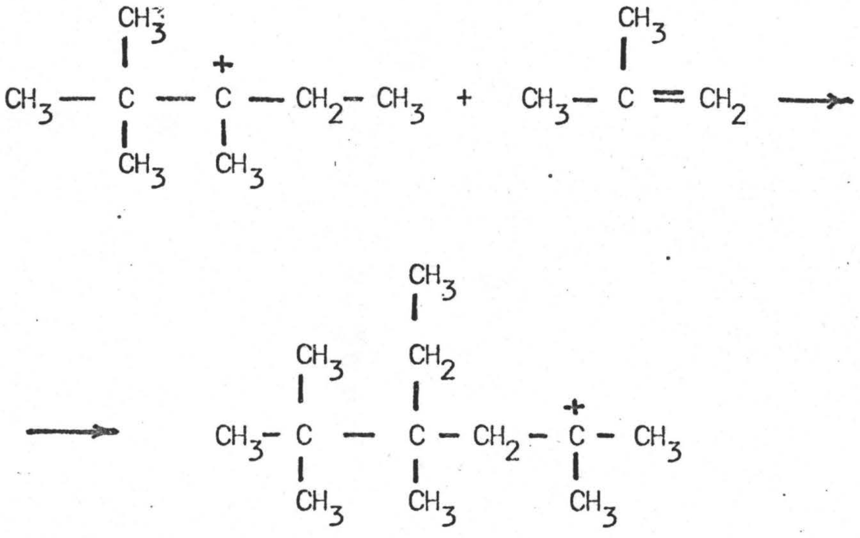


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H \longrightarrow$$

$$\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}\,+ \qquad (I\text{-}4)$$

(e) Polymerization

Instead of reaction (I-4) taking place, an undesirable polymerization can result producing a C_{12} carbonium ion.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3 + CH_3-\overset{CH_3}{C}=CH_2 \longrightarrow$$

$$\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{\overset{CH_3}{CH_2}}{C}}-CH_2-\underset{CH_3}{\overset{+}{C}}-CH_3 \qquad (I\text{-}5)$$

The preceding description indicates qualitatively what products can be expected from the alkylation reactions. The literature, however, does not contain any kinetic rate data which could be used to obtain a quantitative description of the reaction. It has been included so the reader may have a somewhat clearer picture of what goes on in the alkylation reactor.

2. Operating Variables and Their Influence

Although a description of the Stratco reactor is given in the Plant Studies section of this thesis, it is only necessary to present a very simplified description of its operation at this time. This should be sufficient for the reader to understand the effects of the various operating variables.

The reactor is a large Continuous Stirred Tank Reactor into which two immiscible phases are introduced. The one phase is concentrated sulphuric acid and the other a mixture of isobutane, C_3 and C_4 olefins, and normal paraffins. The two phases are emulsified by a large impeller. It is believed that the reaction takes place in the acid phase which acts as a catalyst, and that the olefins transfer into the acid much more quickly than the isobutane. Once the two reactants, isobutane and olefins, are in the acid, the reactions discussed in the previous section are free to take place. After a residence time of about 15 to 20 minutes, the emulsion is sent to a settler where the two phases separate. The hydrocarbon, which contains the alkylate product is taken to the refining process and the acid is recycled back to the reactor.

(a) The Isobutane to Olefin Ratio

It was shown in reaction (I-5) that the C_8 carbonium ion can react with another olefin. It was also mentioned in the introduction to this section that the olefin transfers into the acid much more quickly than the isobutane. Therefore, by keeping the "iC_4/olefin ratio" high, the C_8 carbonium ions can be encouraged to react with isobutane to produce the desired branched chain hydrocarbons.

There are two iC_4/olefin ratios commonly used when describing reactor conditions. The first is called the external ratio and is defined by the moles of isobutane fed to the reactor. The second is called the internal ratio and is defined by the ratio of iC_4/olefin at the point in the reactor where the olefin enters the reactor. In reactors of the mechanically circulated type the impeller establishes a large circulating stream of reacting mixture into which the olefin is introduced; this stream of reacting mix contains a large quantity of iC_4. The internal ratio is computed by dividing the volumetric flowrate of iC_4 in the circulating stream by the volumetric flowrate of olefin fed into it.

Generally speaking, a large external ratio indicates a high percent of iC_4 in the reactor effluent and a high internal ratio indicates that the olefin is dispersed in a very large circulating stream which in turn indicates that good mixing is being obtained.

(b) Reaction Temperature

Cupit (I-I) recommends that the reactor temperature should be between 40 and 50°F. Temperatures above this range increase acid consumption and reduce alkylate quality. Temperatures below this range increase the acid viscosity and make intimate contact between reactants and sulphuric acid difficult to achieve.

(c) Acid Strength

Putney (I-2) states that the alkylation reactions are such that a maximum alkylate quality can be reached at an acid strength (titratable acidity)between 95 and 96 wt % sulphuric acid. The four curves shown in Figure I-I were plotted from batch acid depletion runs in pilot scale equipment. For each curve only acid strength was a variable although for different curves other conditions such as isobutane concentration, space velocity, etc. were changed. No further details concerning these curves were given.

It has also been found by Hughes et al (I-3) that although alkylate yield drops off with decreasing acidity, it can be maintained by an increase in reactor temperature. This is shown in Figure I-2. Yield in this case however, is the total alkylate produced as a wt % of the olefin charged. This yield does not differentiate between C_8 alkylate and undesirable longer chain polymers. 70°F is high enough to cause polymerization of olefins and is not recommended for plant practice.

(d) Acid Consumption

Acid is consumed by a number of different mechanisms. A good part of acid consumption is accounted for by the reaction of various components in the hydrocarbon to form diluents. The formation of propyl sulphates for example, comes under the heading of deleterious reactions. According to Putney (I-2) butadiene can also deplete the acid strength even when present in small amounts. For example one gallon of butadiene depletes 58 pounds of fresh acid from 98 to 90 wt %. Water present in the feed also contributes highly to the reduction of acidity.

FIGURE 1-1

EFFECT OF ACID STRENGTH ON OCTANE NUMBER

PUTNEY 1-2

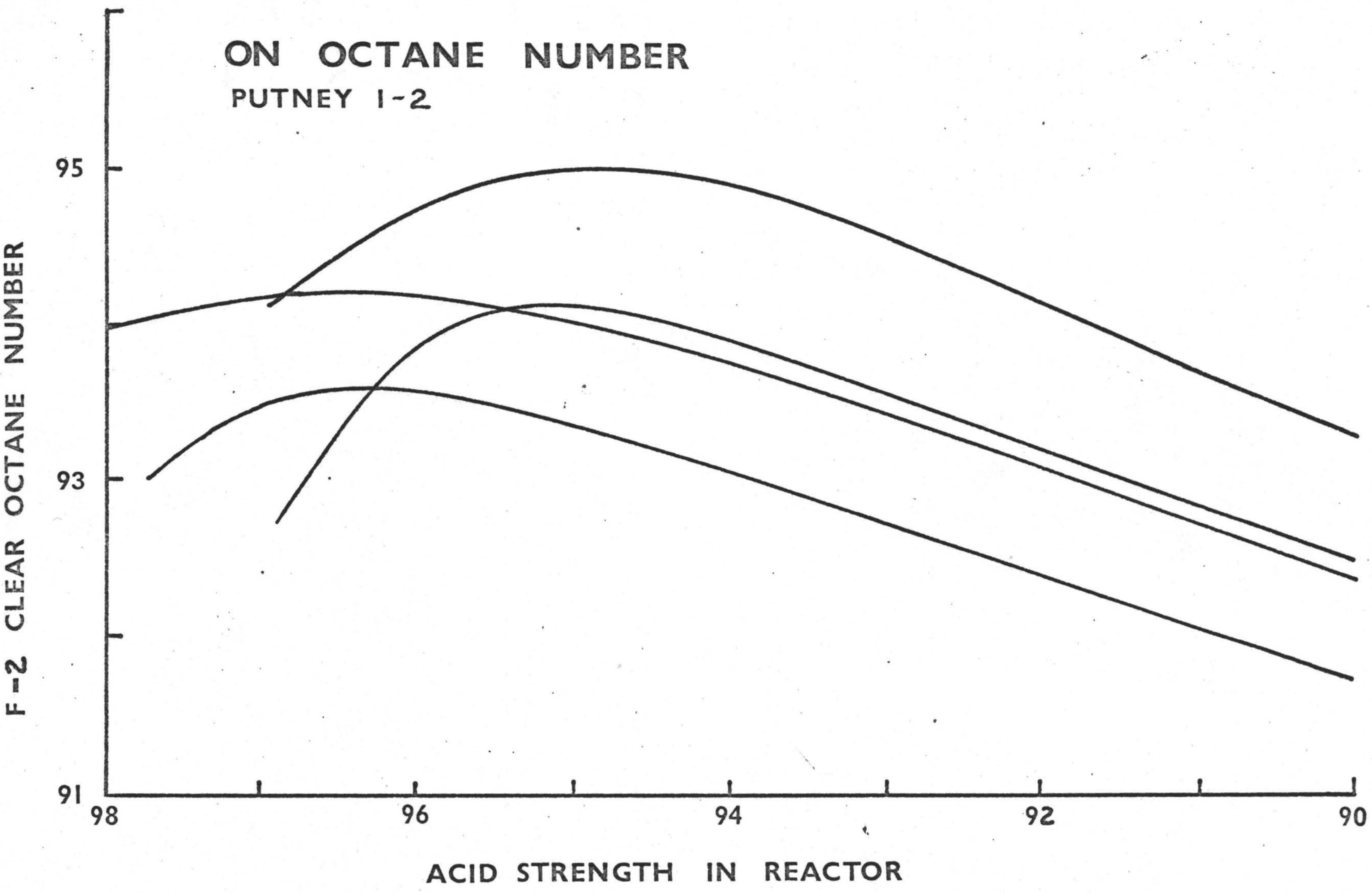
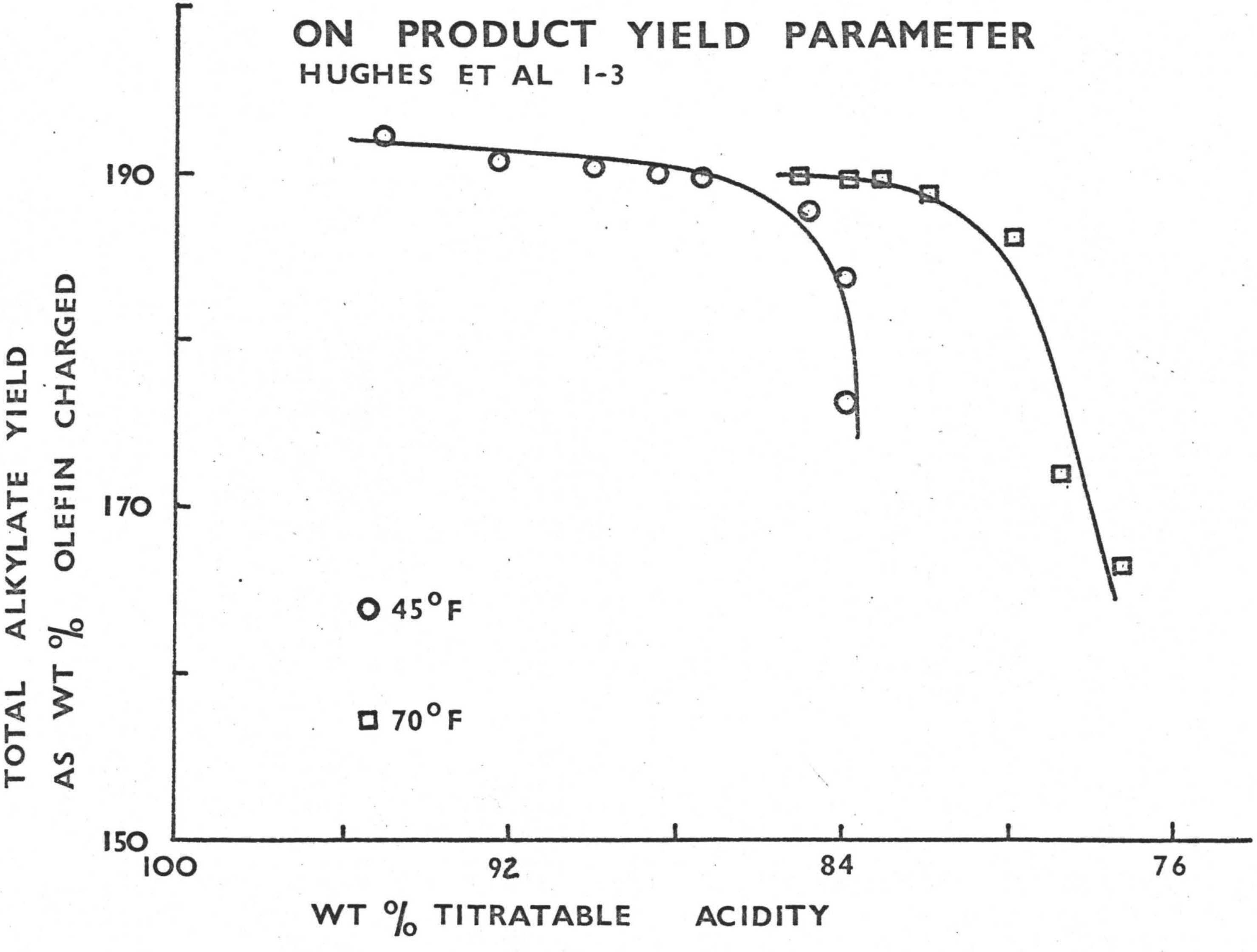


FIGURE 1-2

EFFECT OF TEMPERATURE ON PRODUCT YIELD PARAMETER

HUGHES ET AL 1-3



Although it was shown previously that the optimum alkylate quality is attained by using 95 to 96% acid, this may not be favourable economically. Hughes et al (I-3) show in Figure I-3 that for acids above 82 wt %, the acid consumption rises, increasing acid costs which are a major operating expense. However, as the acid costs become lower as the concentration becomes lower, the quality of alkylate also decreases. Some optimum acid strength based on minimum costs must therefore exist.

(e) Acid to Hydrocarbon Ratio in the Reactor

According to Putney (I-2) this variable is restrained by the physical situation on one side and the economic on the other. If the acid content in the reactor falls below about 40 wt % then phase inversion may occur and heavy losses are incurred. On the other side, a cost versus yield optimum is reached so that a 50:50 volume ratio of acid to hydrocarbon is usually chosen. It is likely that this ratio is somewhat high and that the least acid possible is used.

(f) Degree of Mixing

Available data (I-2) indicates that the change in alkylate quality for a given change in mixing horsepower for butene alkylate is of the order of one F-2 octane number for a reduction of 25% in horsepower when operating at the level of about 0.15 hp input for each barrel of total alkylate per day.

(g) Settler Operation

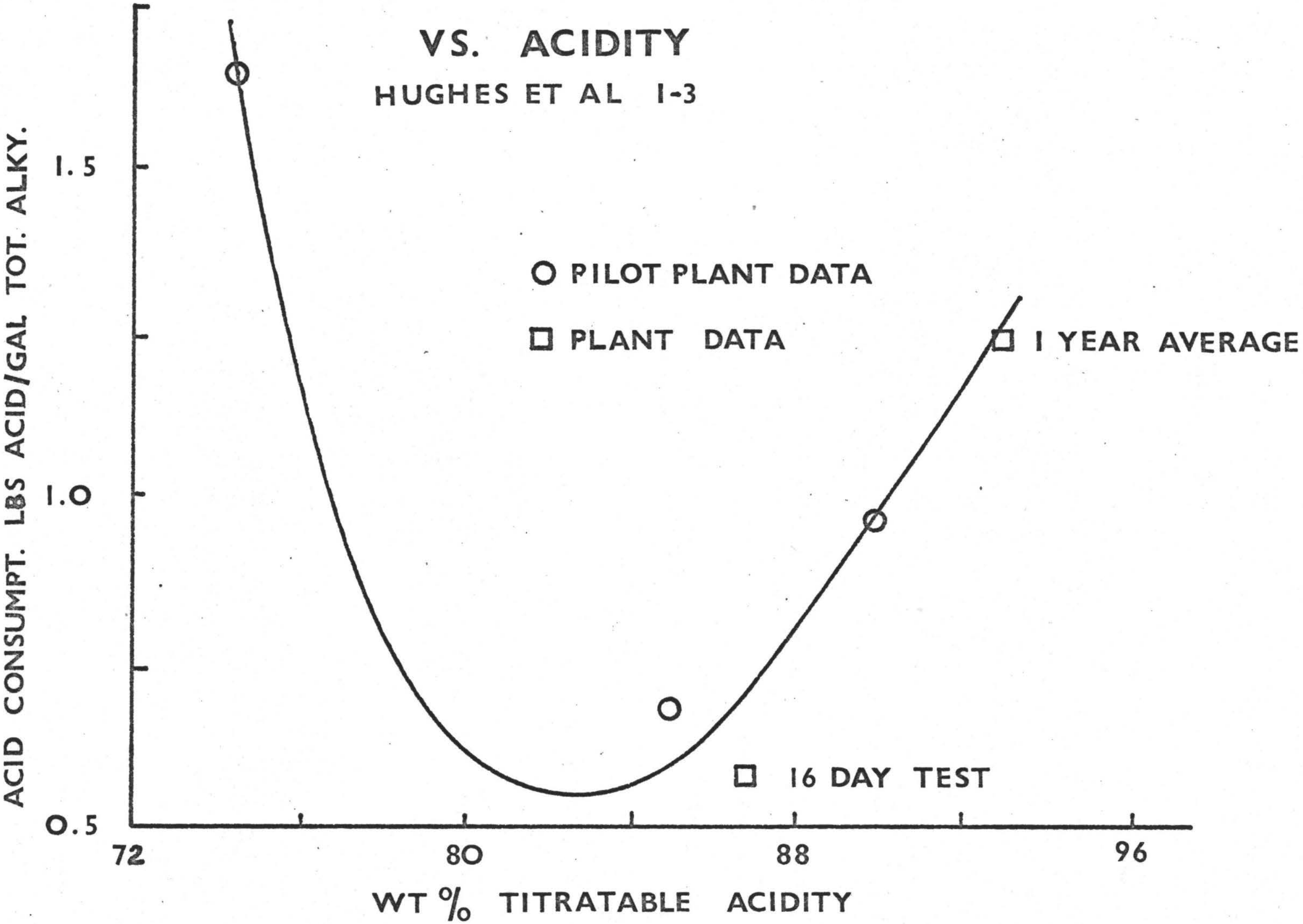
In order to mix the hydrocarbon and acid properly, a temporary emulsion must be formed. The settling time must be long enough to prevent acid carry over into the refining process. If an insufficient length of

FIGURE 1-3

ACID CONSUMPTION FACTOR

VS. ACIDITY

HUGHES ET AL 1-3



time is allowed for settling, the acid returning to the reactor will still contain some hydrocarbon. There it will pick up more and more hydrocarbon until it completely fills the settler and is carried over to the refining process.

PLANT STUDIES

I. Description of the Process

The reactor used by Shell to carry out the alkylation reaction was built by the Stratford Engineering Corporation and is commonly known as the Stratco Reactor shown in Figure I-4. It is basically a horizontal cylindrical vessel containing a heat exchange bundle and a large impeller. The acid and hydrocarbon enter at the eye of the impeller in approximately a 2:3 volume ratio and the resulting emulsion is circulated around the outer shell and back over the exchanger tube bundle. The emulsion is removed at the top of the reactor and passes into the settler, shown in Figure I-5, where the hydrocarbon and acid separate. When the acid concentration drops below about 89 wt %, spent acid is removed and fresh makeup acid is batched to the recycle line to the reactor.

The hydrocarbon product is flashed through a reducing valve and passed through the reactor tube bundle keeping the reactor emulsion at about 50°F. It then goes to the product separator. Here the two phase mixture is further vaporized by the heating coils fed by the depropanizer bottoms. The vapor from the product separator is compressed and distilled in the depropanizer to remove the propane (LPG). The bottoms are returned through the coils of the product separator to the reactor. The liquid phase from the product separator flows to the deisobutanizer where the alkylate is removed from the bottoms. A sidecut takes the n-butane and the tops which contain n- and isobutane, are recycled back to the reactor.

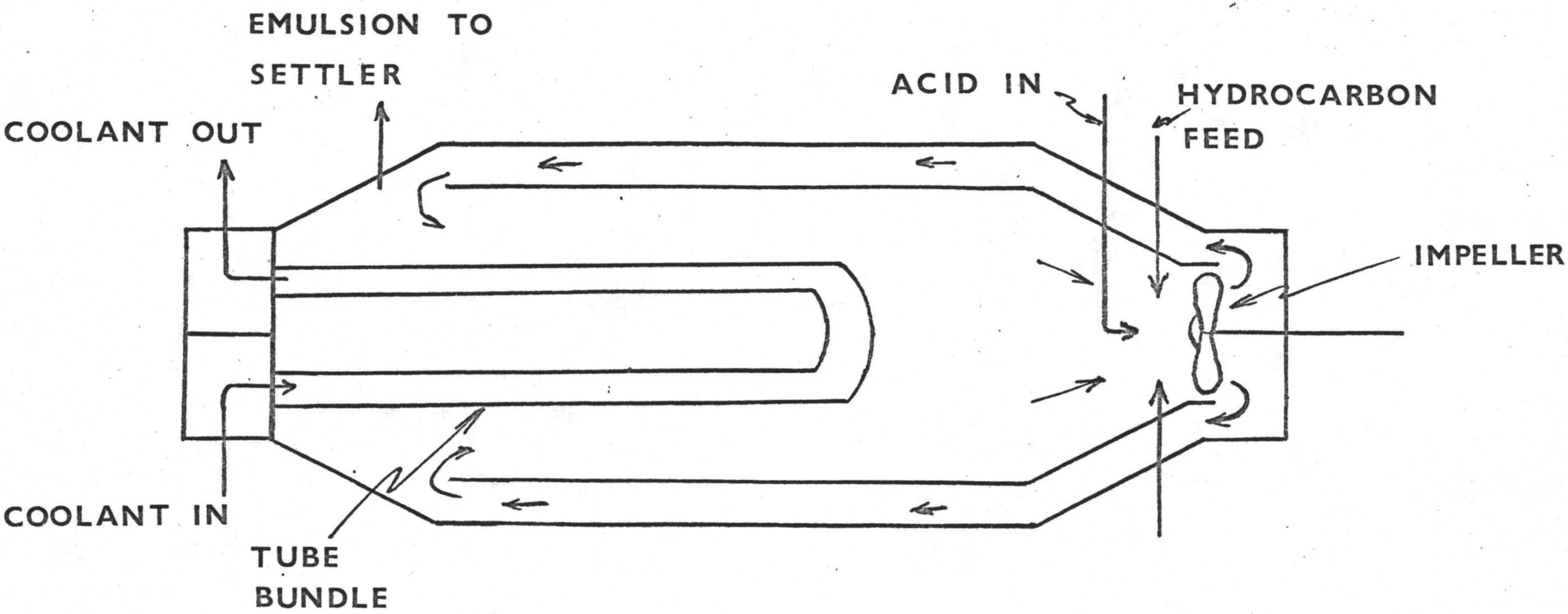


FIGURE 1-4

SIMPLIFIED DIAGRAM OF STRATCO REACTOR

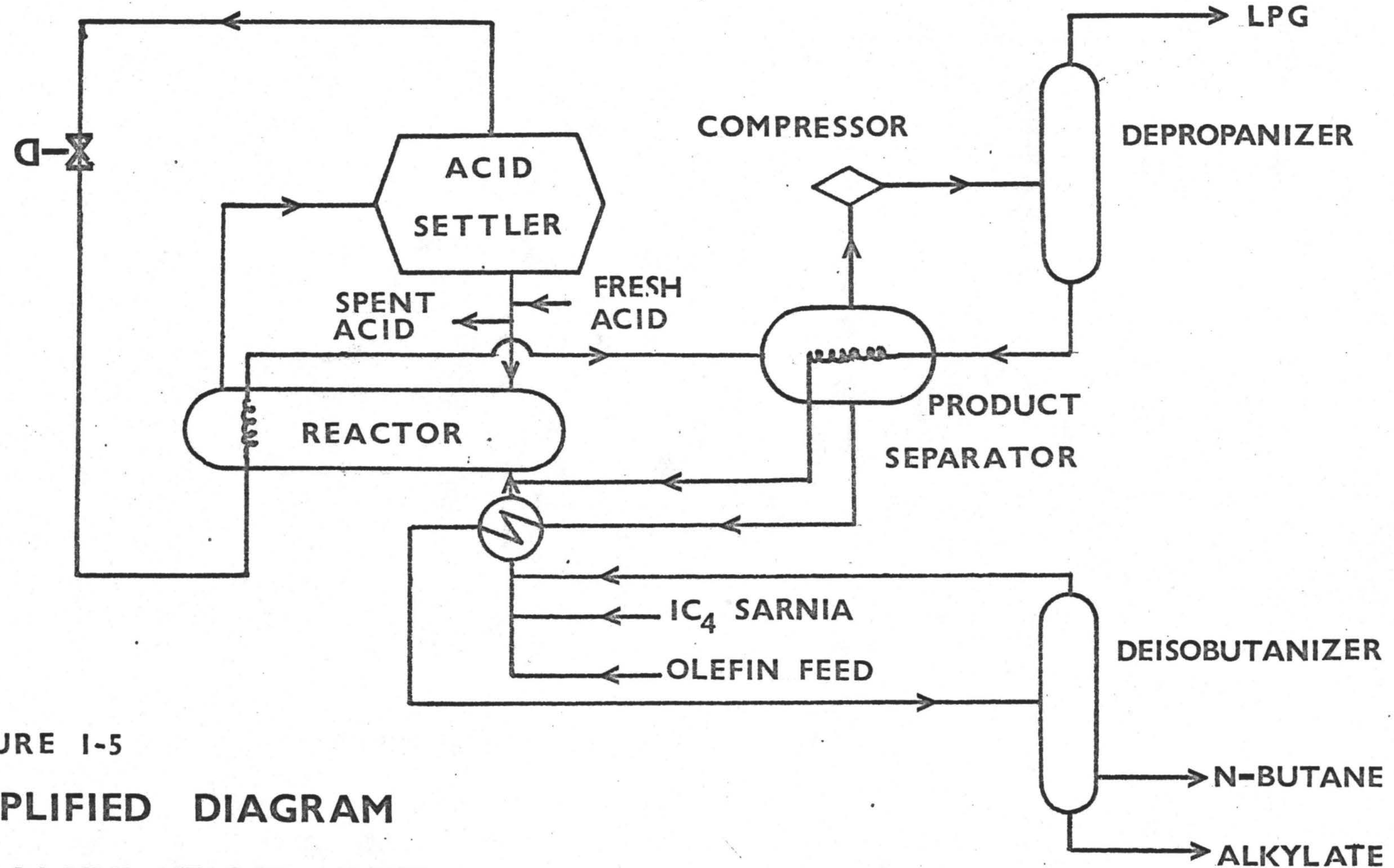


FIGURE I-5

SIMPLIFIED DIAGRAM OF ALKYLATION UNIT

A much fuller description of the process has been made by Shaw (I-14) in his Master's thesis which uses the alkylation process as a case study in simulation. More information is also included in the Final Year Project Report (I-7) which will be referred to again later in this thesis.

2. Results for Prediction of Dependent Variables

(a) Volume of Alkylate Produced

The two major input variables which affect the volume of alkylate produced are the volumes of propene and butene entering the reactor. Since no olefins leave the reactor it is assumed that they all react to form alkylate in some manner similar to that discussed in Section I. of the Literature Review. Therefore, there should be some relationship between the volumes of the two olefins entering and the volume of alkylate produced.

The following equation was used:

$$V_a = k_{PA} V_P + k_{BA} V_B \qquad (I-6)$$

where V_a - volume alkylate out of reactor bbl/day

V_p - volume propene into reactor bbl/day

V_B - volume butene into reactor bbl/day

k_{PA} - propene to alkylate factor $\frac{\text{bbl prop. alkylate}}{\text{bbl propene in}}$

k_{BA} - butene to alkylate factor $\frac{\text{bbl but. alkylate}}{\text{bbl butene in}}$

By knowing V_P, V_B, and V_A for the five runs shown in Appendix I(a), the equations could be plotted as shown in Figure I-6 on a two dimensional graph with the highest density of intersections representing the best solution. This method however, does not work very well because the C_4 olefin/C_3 olefin ratio changes very little and yields ill conditioned equations. Therefore, more information was needed.

If the assumption could be made that all propene and butene react to form C_7 and C_8 alkylate respectively and that they each react stoichiometrically with isobutane then the following can be calculated.

1 bbl propene reacts to form 1.77 bbl C_7 alkylate

1 bbl butene reacts to form 1.77 bbl C_8 alkylate

These two factors are plotted along the X and Y axes in Figure 1-6 and the resulting point lies on the lines produced from the plant data.

Cupit, Gwyn and Jernigan (1-1) state the 1.75 - 1.78 as a resonable reasonable range for a propene to alkylate factor and 1.70 - 1.72 for a butene to alkylate factor. Shell's employees at Oakville use a similar pair of factors, i.e. 1.72 for propene and 1.69 for butene. These points are shown in Figure 1-6.

The three different sets of factors were then used to predict the volume of alkylate which should be produced and this was compared with the actual alkylate produced in the plant. This comparison is shown in Table 1-1. Although there is very little difference among the three, Cupit appears to have the best correlation.

(b) Volume of Acid Consumed

The first attempts to determine acid consumption using the plant data given in Appendix 1(a) gave scattered results. This was explained by the fact that the acid consumed during a day is not necessarily the same as the volume of acid put to the reactor, i.e., the reactor may run on

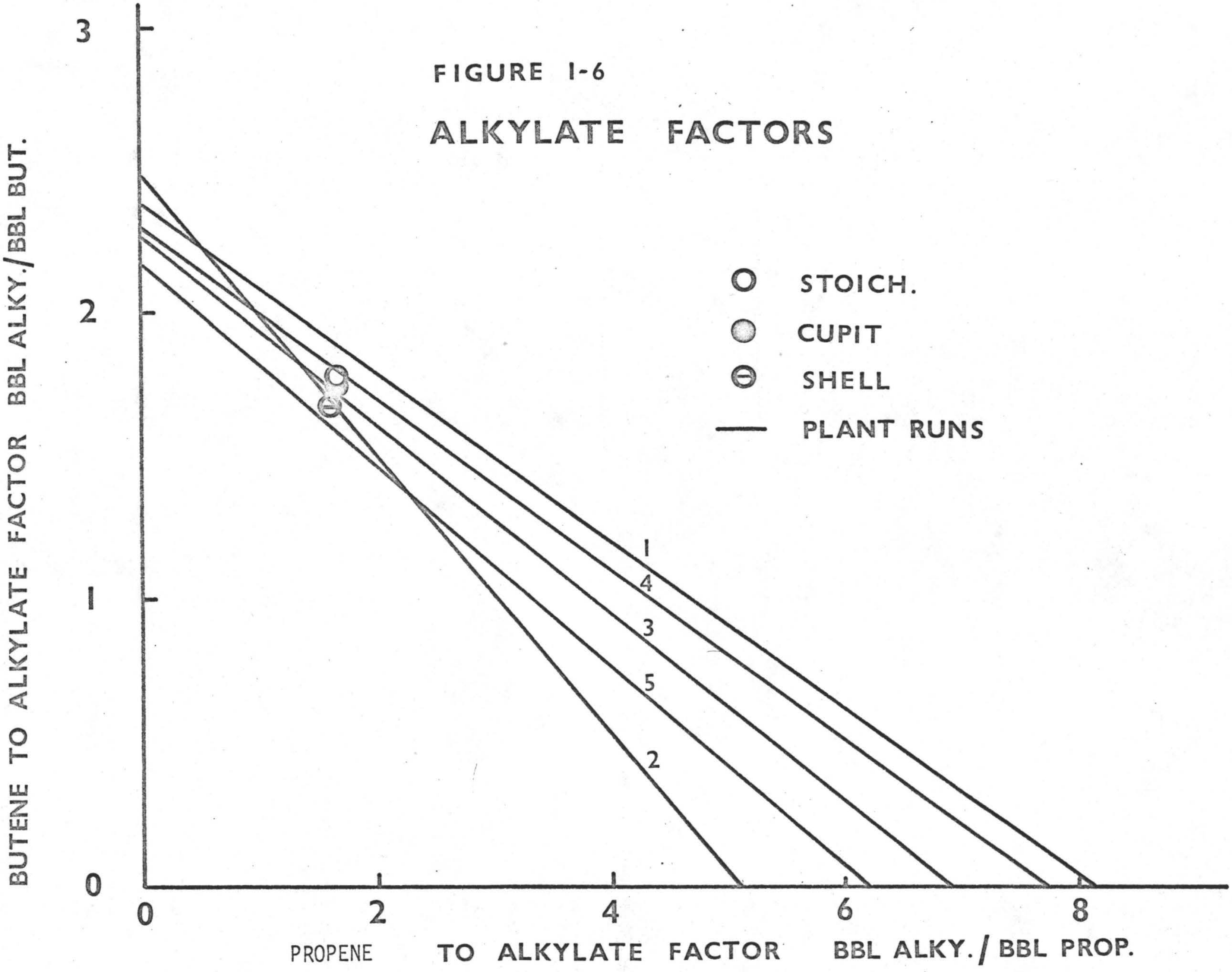


FIGURE I-6

ALKYLATE FACTORS

TABLE I-1

COMPARISON OF PREDICTED VOLUMES OF ALKYLATE

Stoichiometric		Shell		Cupit et al		Plant
Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day
1294.9	-3.8	1241.4	-7.7	1260.2	-6.3	1345.6
1446.8	6.9	1389.5	2.7	1412.5	4.4	1353.2
1778.1	4.4	1705.2	0.1	1731.5	1.7	1702.8
1925.1	-0.1	1845.6	-4.2	1873.6	-2.8	1926.6
2209.5	6.0	2119.6	1.7	2152.9	3.3	2085.1

yesterday's acid at the beginning of the day. Then when acid is batched, it may not be used up until the next day. The length of time between these two events is too short for their effects to cancel. Consequently, only acid consumption data that was taken over long periods of time or short periods with strict observation could be used.

Two variables affecting acid consumption were the volumes of propene and butene entering the reactor. It is common however to base acid consumption on the volume of propene and butene alkylate produced. This presents no difficulty since there is a linear relationship between olefin fed to the reactor and alkylate produced. Two more variables which affect acid consumption were iC_4/olefin ratio and temperature. The following equation was chosen assuming a linear relationship for all four variables:

$$V_a = k_{Pa} V_{PA} + k_{Ba} V_{BA} + k_{Ra} (R_b - R_r) + k_{Ta} (T_b - T_r) \qquad (1\text{-}7)$$

where	V_a	- volume acid consumed	bbl/day
	V_{PA}	- volume propene alkylate	bbl/day
	V_{BA}	- volume butene alkylate	bbl/day
	R_b	- base iC_4/olefin ratio = 5.5	moles iC_4/moles olefin
	R_r	- test run iC_4/olefin ratio	moles iC_4/moles olefin
	T_b	- base temperature = 50°F	°F
	T_r	- test run temperature	°F
	k_{Pa}	- propene acid consumption factor	$\frac{\text{bbl acid}}{\text{bbl propene alkylate}}$
	k_{Ba}	- butene acid consumption factor	$\frac{\text{bbl acid}}{\text{bbl butene alkylate}}$
	k_{Ra}	- iC_4/olefin ratio correction	$\frac{\text{bbl acid}}{iC_4\text{/olefin ratio}}$
	k_{Ta}	- temperature correction	bbl acid/°F

In order to solve this equation, data from longer runs was used. The propene acid consumption factor k_{Pa}, was 0.0511 and the butene factor k_{Ba}, was 0.0359. The iC_4/olefin correction k_{Ra}, was 9.14 when operating at 1800 bbl/day debutanized alkylate and the temperature correction k_{Ta}, was 0.0145. These equations, however, were ill conditioned and need some confirmation from another source.

Cupit et al (1-1) state that the propene acid consumption factor is about 0.125 bbl acid/bbl propene alkylate and 0.032 bbl acid/bbl butene alkylate. He does not state however, whether or not acid consumption is also a function of iC_4/olefin ratio and temperature. It is unfortunate that so little seems to be known about acid consumption although it is the highest operating cost in alkylation. When 100 bbl/day of acid are used, it amounts to approximately 900 dollars per day. This would be the consumption when producing about 2000 bbl/day alkylate.

In the final analysis a hybrid model was chosen which appears to work satisfactorily. The only major difference between it and the results from solving the four equations was with the propene acid consumption factor. It was found that Cupit's values were more reasonable. This resulted in the following relationship.

$$V_a = 0.125\ V_{PA} + 0.032\ V_{BA} + 9.14\ (R_b - R_r) - 0.0145\ (T_b - T_r) \tag{1-8}$$

(c) Volume of Isobutane Consumed

Once again it is expected that the volumes of propene and butene entering the reactor would be the two independent variables affecting the iC_4 consumption. As before, a linear relationship was assumed and the following equation used.

$$V_i = k_{Pi} V_P + k_{Bi} V_B \tag{1-9}$$

where	V_i	- volume isobutane consumed	bbl/day
	V_P	- volume propene into reactor	bbl/day
	V_B	- volume butene into reactor	bbl/day
	k_{Pi}	- propene iC_4 consumption factor	$\frac{\text{bbl } iC_4 \text{ consumed}}{\text{bbl propene in}}$
	k_{Bi}	- butene iC_4 consumption factor	$\frac{\text{bbl } iC_4 \text{ consumed}}{\text{bbl butene in}}$

The plant data shown in Appendix I(a) were then substituted into this equation and the results plotted in Figure I-7. These lines represented however, a whole family of solutions and more information was needed to arrive at two separate and distinct factors.

If the assumption could be made that all the propene and butene react stoichiometrically with the isobutane then the following factors would be obtained. One barrel of propene would react with 1.28 barrels of isobutane to produce C_7 alkylate and one barrel of butene would react with 1.11 barrels of isobutane to produce C_8 alkylate. This assumes that no polymerization occurs.

Cupit et al (I-1) state that the propene factor is 1.27 - 1.32 and the butene factor is 1.10 - 1.16. Shell at Oakville reports 1.105 for the propene factor and 1.13 for the butene factor. All these values are shown in Figure I-7.

Table I-2 shows how each pair of factors would predict the iC_4 consumption along with the actual plant consumption. It is seen that Run 5 is predicted quite high in all three cases. This could be due to the fact that a particular run had the lowest iC_4/olefin ratio and hence some

FIGURE 1-7

IC_4 CONSUMPTION FACTORS

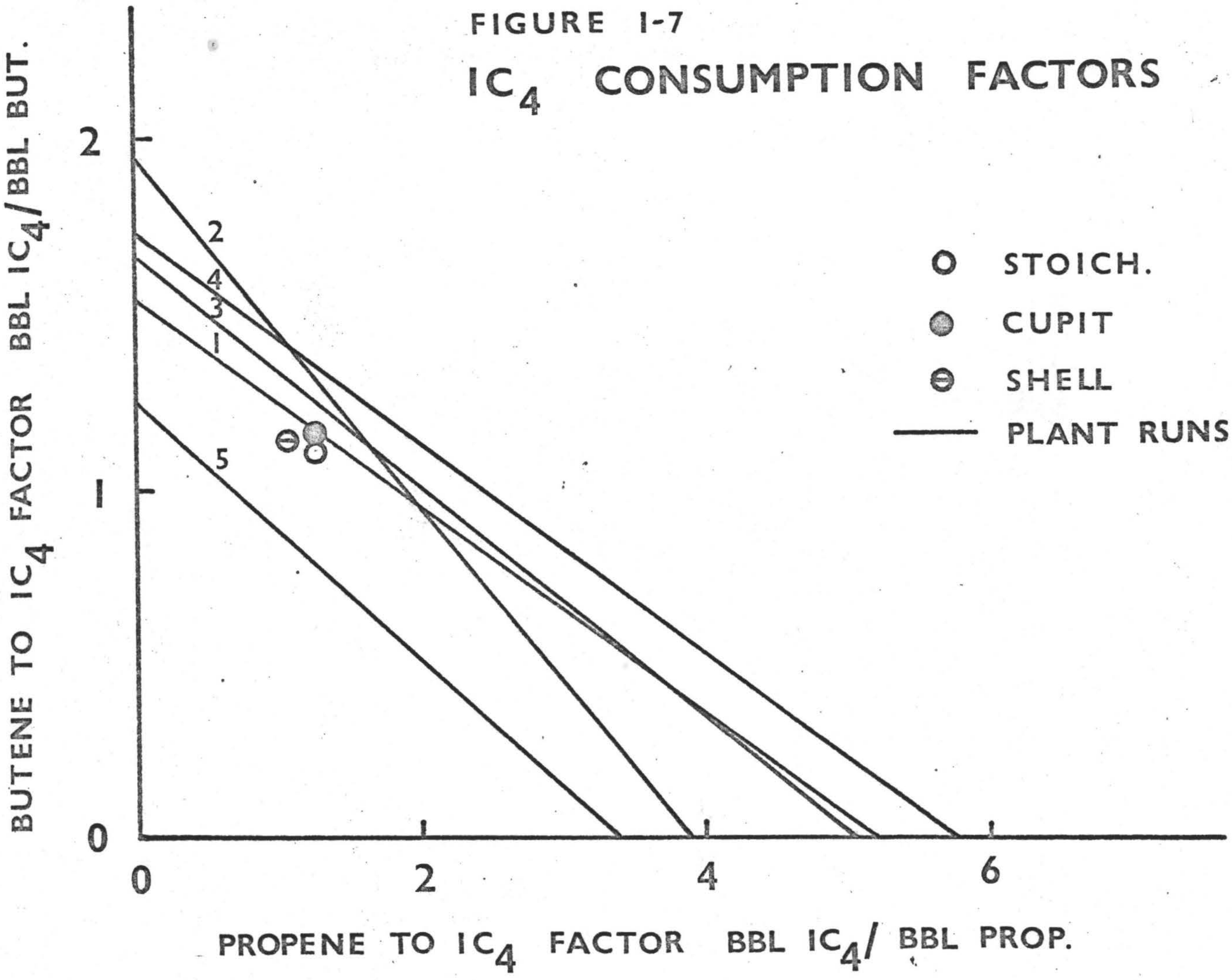


TABLE I-2

COMPARISON OF PREDICTED VOLUMES OF iC_4 CONSUMPTION

Stoichiometric		Shell		Cupit et al		Plant
Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day	% dev	Volume Alkylate bbl/day
840.4	-2.8	822.5	-4.9	957.4	10.7	864.6
952.7	-7.2	916.7	-10.7	1065.3	3.7	1027.1
1157.1	-8.1	1129.0	-10.3	1313.7	4.4	1258.8
1249.8	-12.7	1222.7	-14.6	1423.1	-0.6	1431.1
1442.1	28.1	1402.3	24.5	1631.1	44.8	1126.2

polymerization reduced the iC_4 consumption.

(d) Product Distribution

It has been shown in the literature review that the chemistry of alkylation is very complex. Consequently a statistical approach for describing the product distribution was necessary. Unfortunately Shell at Oakville does not ordinarily analyze the alkylate produced to the extent which would be required. They report the alkylate as C_6^+, i.e. C_6 molecules and heavier. They did however, perform some tests in the fall of 1966 which produced 21 sets of more complete data and these are shown in Appendix I(b). These data were subsequently taken by two fourth year students, H. Canning and J. Gates, and regressed. The complete results of their work can be found in reference (1-7).

By using an IBM 7040 computer and an IBM library routine called MLTREG it was possible for them to perform a multiple variable regression analysis on the plant data. Since all regression equations were to use lb mole/hr units, all the data was changed accordingly.

The known inputs to the reactor were the temperature, the analysis of the combined organic feed, and the volumetric flow of organic feed. The independent variables calculated from this data were temperature and molar flows of nC_3, $C_3^=$, nC_4, $iC_4^=$, iC_4, nC_5, and iC_5. The known outputs from the reactor were the analysis of the deisobutanizer (DIB) bottoms and its flow. The dependent variables calculated from this data were molar flows of iC_5, 2,3-DMB, 2,4-DMP, 2,3-DMP, 2,2,4-TMP, Group I (which consisted of 2,4-DMH, 2,5-DMH, and 2,2,3-TMP), Group II (which consisted of 2,3,4-TMP, 2,3,3-TMP, and 2,3-DMH) and C_9 and heavier.

The development of regression equations occurred in two steps. First, linear regression of all the independent variables versus each dependent variable was done. These equations were of the form:

$$y = a_o + a_1x_1 + a_2x_2 \; .... \; a_nx_n$$

The equations contained one constant and at most nine coefficients. Since the program entered the independent variables in their relative order of importance and printed statistical tests after each entry, the less significant variables were readily identified and deleted.

The second step taken by them was to try to improve on the linear fit by including powers and ratios of the independent variables. In all the equations tried the residuals increased i.e. became worse, although in some instances the fraction of variability removed increased slightly. The final regression equations selected contained only first power variables and no interaction terms.

Table I-3 indicates the fit they obtained with the regression. The fraction of variability removed may be defined as the sum of squares due to regression, i.e. the actual y-value minus the mean value, divided by the sum of squares about regression, i.e. the actual y-value minus the predicted value. If the fit were perfect then the fraction of variability removed would be equal to unity. The values in Table I-3 however, are for the most part about 20 to 35% below unity. This is not a particularly good fit. Figure I-8 gives a fair indication of what the best fit looks like when graphed.

Table I-4 indicates the range over which the correlations are applicable.

TABLE I-3

FRACTION OF VARIABILITY REMOVED BY REGRESSION

Dependent Variable	Fraction of Variability Removed
C6=2,3-DMB	0.656
C7=2,4-DMP	0.662
C7=2,3-DMP	0.810
C8=2,2,4-TMP	0.799
C8=Group I	0.686
C8=Group II	0.721
C9+	0.249

FIGURE 1-8

PREDICTED VS. ACTUAL 23 DMP

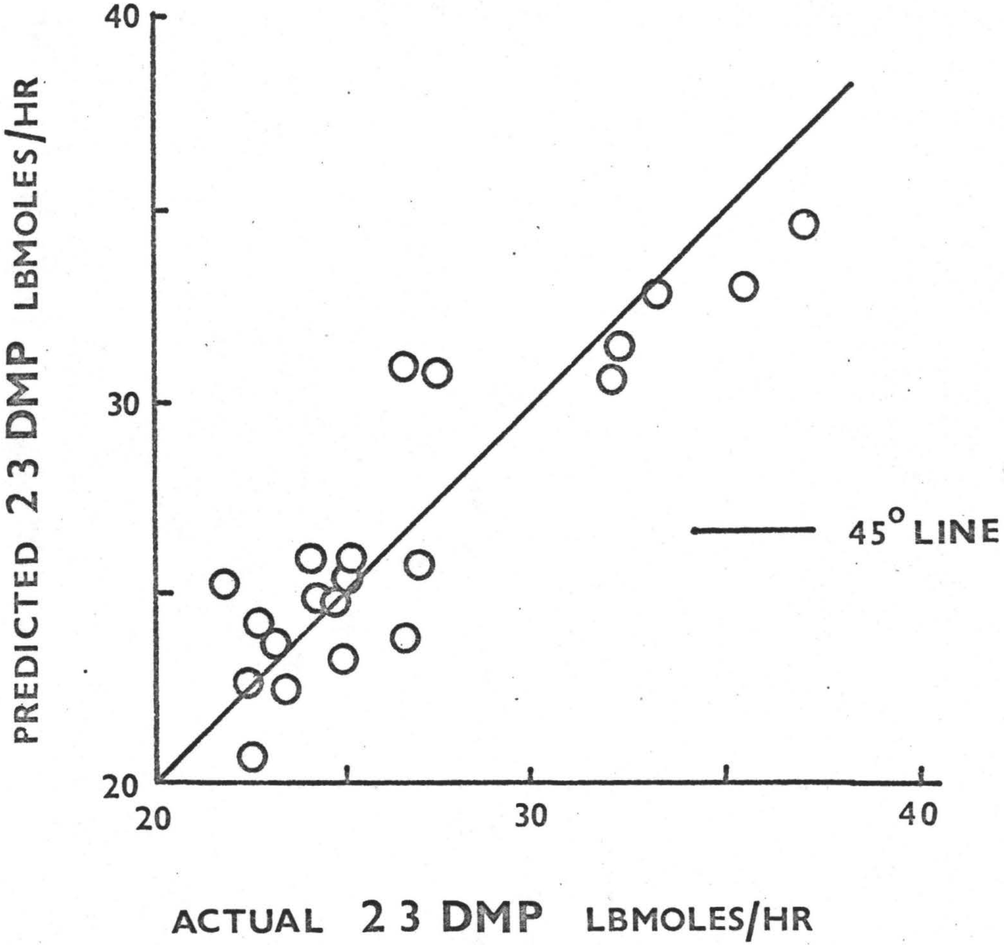


TABLE I-4

RANGES OF INDEPENDENT VARIABLES

Component	Maximum (lb mole/hr)	Minimum (lb mole/hr)
$C3$	245.6	92.6
$C3^{=}$	91.4	59.6
$n\text{-}C4$	609.1	190.6
$i\text{-}C4$	989.0	634.2
$n\text{-}C4^{=}$	52.5	28.1
$i\text{-}C4^{=}$	62.9	39.1
$i\text{-}C5$	25.1	6.7

(e) Heat of Reaction

Cupit et al (I-I) state that 840 Btu are released for every pound of propene alkylated and 615 Btu for every pound of butene. These values along with a number of other ones depending on the choice of products, can be calculated using the heats of formation. None of these calculations however, yield values as low as required to explain the plant data. The experience of Shell employees has been the same and they use values which are about 85% of those given in the literature, i.e. 710 Btu/lb propene and 520 Btu/lb butene. These values agree with the plant data.

(f) Heat of Mixing

The impeller in the Stratco Reactor is a major source of heat into the system. A measure of the quantity of heat added was obtained by knowing the voltage applied to the motor and the current drawn. The calculation showed that 1.24×10^6 Btu/hr should be produced on the average. This value compares reasonably with the one used by Shell employees which is a constant 1.0×10^6 Btu.

REACTOR MODEL

I. Description of Reactor Computer Model

Some explanation is necessary concerning some of the terms used in the computer subroutine. To begin with the program needs as its input, all the flows in lb. mole/hr of each component coming into the reactor along with the total flow, temperature and pressure. This information is carried in the stream list. This list numbers each of the inputs and refers to them by number only throughout the whole simulation. The flow components in the stream list are shown in Table I-5.

An input to the model is defined as STRMI(I,J) where STRMI represents Stream In, I represents the organic feed to the reactor when I=I or the acid recycle to the reactor when I=2, and J represents any one of the entries in the stream list from I to 3I. The output from the model is catalogued in exactly the same way except that STRMO refers to Stream Out.

The major section of this program which was not elaborated on before is the prediction of the product distribution using the regression equations. These correlations are found for STRMO(I,J) where J = I8, 3I in the program listing. The values for the coefficients which are represented by a subscripted letter are found under the DATA section of the same letter. The coefficients are listed there in numerical order.

The rest of the program is self explanatory with the possible exception of the normalization section. After all the output streams have been predicted, it is necessary to make sure that there is a mass balance around the reactor. Consequently the program checks to see whether the outputs do equal the inputs, and if they do not then it forces a balance.

TABLE I-5

STREAM LIST FOR ALKYLATION PLANT

Stream Element Number	Component	Stream Element Number	Component
1	stream number	17	isobutene
2	stream flag	18	n-pentane
3	total flow, lb mole/hr	19	isopentane
4	temperature, °F	20	isopentene
5	pressure, psia	21	C6
6	water	22	2,3-DMB
7	sulphuric acid	23	C7
8	sodium hydroxide	24	2,4-DMP
9	sodium sulphate	25	2,3-DMP
10	alkyl sulphate	26	C8
11	C2's and less	27	2,2,4-TMP
12	n-propane	28	Group I 2,4-DMH 2,5-DMH 2,2,3-TMP
13	propene	29	Group II 2,3,4-TMP 2,3,3-TMP 2,3-DMH
14	n-butane	30	C9
15	isobutane	31	C9+
16	n-butene		

CONCLUSIONS

1. Tests were made to determine whether or not the Shell Oakville reactor performed as the literature indicated.

   (a) The volume of alkylate produced in the plant correlated well with the volume predicted in the literature.

   (b) The volume of acid consumed did not correlate well with the literature prediction because of the omission of two correction factors (i.e. the dependence of acid consumption on the iC_4/olefin ratio and temperature in the reactor were ignored). The final correlation consisted of the literature values plus the two correction factors. This result worked reasonably.

   (c) The volume of isobutane consumed correlated well with the volume predicted in the literature.

   (d) The heat of reaction in the plant appeared to be about 15% lower than that predicted by the literature.

2. Work was done to predict product distribution as a function of the input streams to the reactor and the temperature in the reactor. Since the correlations were based on the small number of data sets available it was not possible to make a proper evaluation of the results. Obviously, more data sets are needed to test and improve the present correlations and these data might best be obtained through a program of planned plant runs.

3. A computer model was written by two undergraduate students employing all the previous correlations to produce a quantitative description of the Shell Oakville alkylation reactor.

NOMENCLATURE FOR PART I

k_{Ba} - butene acid consumption factor, bbl acid/bbl butene alkylate

k_{BA} - butene to alkylate factor, bbl butene alkylate/bbl butene in

k_{Bi} - butene iC_4 consumption factor, bbl iC_4 consumed/bbl butene in

k_{Pa} - propene acid consumption factor, bbl acid/bbl propene alkylate

k_{PA} - propene to alkylate factor, bbl propene alkylate/bbl propene in

k_{Pi} - propene iC_4 consumption factor, bbl iC_4 consumed/bbl propene in

k_{Ra} - iC_4/olefin ratio correction, bbl acid/(iC_4/olefin ratio)

k_{Ta} - temperature correction, bbl acid/°F

R_b - base iC_4/olefin ratio = 5.5, moles iC_4/moles olefin

R_r - test run iC_4/olefin ratio, moles iC_4/moles olefin

T_b - base temperature = 50°F, °F

T_r - test run temperature, °F.

V_a - volume acid consumed, bbl/day

V_A - volume alkylate out of reactor, bbl/day

V_B - volume butene into reactor, bbl/day

V_{BA} - volume butene alkylate, bbl/day

V_i - volume isobutane consumed, bbl/day

V_P - volume propene into reactor, bbl/day

V_{PA} - volume propene alkylate, bbl/day

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PART II

A LABORATORY STUDY OF MASS TRANSFER OF HYDROCARBON GASES INTO SULPHURIC ACID

INTRODUCTION

While working on Part I of this thesis during the summer months of 1967, it became increasingly obvious that very little fundamental knowledge was available on the alkylation reactions. It was known that there must be mass transfer of isobutane and C_3 and C_4 olefins from the hydrocarbon phase up to the hydrocarbon-acid interface and probably into the acid phase itself. Then some chemical reactions similar to those shown in Part I of this thesis took place with the result that C_8 alkylate was produced.

It was realized that this system consisting of mass transfer with chemical reaction could provide an interesting study. It was not the usual type of chemical reaction where A transfers into B and reacts to produce C. This system consisted of A and B in one phase transferring into a liquid catalyst (sulphuric acid) and reacting to produce a great number of products.

In order to study this system a contactor was needed where an input of hydrocarbon could be introduced, contacted with the acid and removed. When steady state was achieved, the difference would represent the amount transferred into the acid. In order to amplify this difference as much as possible, it was decided to work with the hydrocarbons as gases. For this reason a bubble reactor was built.

Theoretical studies were made using the pentration theory and diffusion with chemical reaction to predict the experimental results. Part II of this thesis presents the findings of this study.

LITERATURE REVIEW

I. Bubble Shape and Size

The fundamentals of bubble motion as found in the literature have been reviewed by Yau (II-1). Since the prediction of bubble surface area is greatly simplified when the bubble is spherical, it is of interest to study the conditions under which spherical bubbles will be produced. Yau refers to three articles which deal with the classification of bubbles. Each of them use a different criterion for predicting whether the bubble will be spherical or not. Siemes and Gunther (II-2) state that the volume of the bubble must be less than 0.05 cc, Datta et al (II-3) require that the diameter be less than 0.4 cm, while Rosenberg (II-4) reports that the Reynolds Number must be less than 400.

2. Mass Transfer

(a) Film Theory

In 1923, Whitman (II-5) put forward a theory for analyzing mass transfer rates by assuming the existence of two stagnant films on either side of the interface. For steady state transfer, all solute diffusing from the gas phase to the interface must do so at the same rate as from the interface to the bulk of the liquid. This resulted in the following relationships.

$$N_A = k_G (p - p_i) = k_L (C_i - C_o) \tag{II-1}$$

where N_A - rate of mass transfer, gmole/(cm^2)(sec)

k_G - gas-film coefficient, gmole/(cm^2)(sec)(atm)

k_L - liquid-film coefficient, gmole/(cm^2)(sec)(gmole/cm^3)

p - partial pressure of diffusing gas in main stream, atm

p_i - partial pressure of diffusing gas at phase boundary, atm

C_i - concentration at phase boundary, gmole/cm^3

C_o - concentration of bulk liquid, gmole/cm^3

This two-film theory assumed that there was no hold-up of solute in the film and that steady-state was reached instantaneously.

(b) Penetration Theory

In 1935, Higbie (II-6) presented the penetration theory. He studied the situation where a bubble rises through a liquid, and in particular, the mass transfer into an element of fluid moving around the gas bubble. Since this element was assumed to be stagnant, unsteady diffusion took place during the time which the element was in contact with the bubble. By solving the equation for Fick's Second Law for transfer into a semi-infinite medium, he produced an equation (II-2) for evaluating physical mass-transfer coefficients.

$$k_L = 2\sqrt{\frac{D}{\pi t_e}} \qquad \text{(II-2)}$$

where D - diffusivity of gas in the liquid, cm^2/sec

π - constant = 3.14, dimensionless

t_e - life of the fluid element, sec

Since equation (II-2) is the general expression, t_e can be evaluated for many different situations. In the case of a bubble of gas rising through a liquid, the following simple relationship holds shown in equation (II-3).

$$t_e = d/u_b \tag{II-3}$$

where d - vertical length of the bubble, cm

u_b - velocity of the bubble, cm/sec

(c) Chemical Reaction

The film theory and the penetration theory as they have been shown in sections 2(a) and (b) have dealt with physical mass transfer only. If, however, chemical reaction is involved, appropriate changes can be made.

One example is shown by Sherwood and Pigford (II-7) using the theory of the stagnant film of finite thickness for a slow first-order reaction. The method used is to perform a mass balance over a differential element of volume within the liquid film. The result of this analysis is the same as Fick's Second Law without the time dependence of concentration. For the first order reaction the following equation can be written.

$$D_A \frac{d^2 C_A}{dx^2} = kC_A \tag{II-4}$$

where D_A - diffusivity of A, cm^2/sec

C_A - concentration of A in liquid, gmole/cm^3

x - distance from the interface, cm

k - reaction rate constant for first order reaction in the liquid phase, sec^{-1}

By solving this equation it is possible to obtain a relationship for C_A vs. x. It is also possible to obtain the mass transferred across the interface by the following relationship.

$$N_A = - D_A \frac{dC_A}{dx} \tag{II-5}$$

If the value of k is very large causing the reaction to be very fast, then $-dC_A/dx$ will become a constant causing the concentration to drop to zero at some finite distance x_R from the gas-liquid interface. If this is the case, then $-dC_A/dx$ can be replaced by C_{Ai}/x_R and the new form of equation (II-5) becomes equation (II-6).

$$N_A = -D_A C_{Ai}/x_R \tag{II-6}$$

where C_{Ai} - concentration of A in the liquid at the gas-liquid interface, gmole/cm^3

x_R - effective thickness of the liquid film from the gas-liquid interface to the position where the concentration of A becomes zero, cm.

This assumption is based on a very similar one made by Sherwood and Pigford (II-7) for the theory of the stagnant film of finite thickness for rapid second order irreversible reaction.

3. Physical Aspects of Alkylation Reactions

(a) Reaction Rate Constants

Although there is some knowledge of the mechanism by which isobutane and olefins react, very little is known about the reaction rate constants. Albright (II-8) states "..the chemical reactions are fast; how fast .. is not yet known."

(b) Equilibrium Concentrations

The solubility of isobutane in different concentrations of sulphuric acid at 56°F was reported by Cupit, Gwyn, and Jernigan (II-9). They presented solubilities at three acid concentrations between 96.5 and 99.5 wt % using water as the diluent. These solubilities however, were for isobutane at 2.2 atm and had to be modified to be applicable in this work.

In the case of the solubilities of olefins in sulphuric acid, Albright (II-8) makes the following statement. "Although reliable solubility data for olefins in sulfuric acid are not available, it is certain that relatively high solubilities exist for these compounds."

(c) Diffusion Coefficients

Two similar methods were found in the literature for calculating diffusion coefficients: the Wilke (II-10) equation based on the Stokes-Einstein equation and a modified version by Reddy and Doraiswamy (II-11)

(d) Absorption Rates of 1-Butene

In 1930, H.S. Davis and R. Schuler published a paper entitled "The Relative Rates of Absorption of the Gaseous Olefins into Sulphuric Acid at 25°C" (II-12). Their experimental results showed that the quantity of 1-butene absorbed in unit time was proportional to the partial pressure of the olefin. A complete account of their work is shown in Appendix 3(c).

THEORETICAL PRINCIPLES

I. Simulation of a Bubble Reactor

In order to simulate a bubble reactor it is probably best to look at one single bubble and describe it mathematically. Some simplifying assumptions must be included in this analysis and they will be stated as they are made.

As a bubble of a gaseous solution of 1-butene in isobutane leaves the nozzle and begins to rise, its volume changes because of two main factors. Isobutane and 1-butene both leave the bubble by mass transfer tending to reduce its volume, and pressure decreases with height tending to increase its volume.

(a) Volume Change due to Transfer of Isobutane

As an initial attempt to describe the transfer of isobutane across the interface, assume that there is no chemical reaction and that the absorption can be described by Higbie's Penetration Theory, i.e. using equations (II-1, 2, 3). In order to use this theory it is necessary to know D_{AB}, the diffusivity of isobutane in sulphuric acid, d, the vertical length of the bubble, u_b, the velocity of the bubble, C_i, the concentration of isobutane at the phase boundary, and C_o, the concentration of isobutane in the bulk of the liquid.

The diffusion coefficient of isobutane in 93 wt % sulphuric acid has been calculated using two methods and the calculations shown in

Appendix 3(a). The two predictions are within 25% and the value used is 7.97×10^{-7} cm^2/sec.

The vertical length of the bubble was calculated assuming that the bubble was spherical. This was possible since the physical conditions were well within the limits reported by the authors (II-2, 3, 4) mentioned in the literature review.

Because the bubble velocity was small, it could be measured using a stopwatch and was found to be 15 cm/sec. Measurements were based on the rise from the nozzle to the surface, and hence the initial velocity of the bubble to its terminal velocity was neglected.

The equilibrium concentration of isobutane in 93 wt % sulphuric acid was determined to be 0.01 wt % or 3.18 gmole/cc of acid from the data given by Cupit et al (II-9). The calculations are shown in Appendix 3(b).

The concentration of isobutane in the bulk of the acid will be discussed later in this section.

The change in volume of the bubble due to the loss of isobutane can then be described by the following equation.

$$\frac{dV}{dt} = \frac{RTA}{P} \times F_{iC_4} \times (C_i - C_o) \times 2\sqrt{\frac{D}{\pi t_e}} \qquad \text{(II-7)}$$

where V - volume of bubble, cm^3

t, t_e - time, sec.

R - universal gas law constant, (cm Hg)(cc)/gmole)($^\circ$K)

T - temperature, °K

A - area of bubble, cm^2

P - pressure, cm Hg

F_{iC_4} - volume fraction of isobutane in bubble

(b) Volume Change due to Transfer of 1-Butene

Davis and Schuler (II-12) have reported a relationship between the concentration of sulphuric acid and the rate at which 1-butene will absorb into it. Their results are shown in Appendix 3(c). They obtain a constant called the specific absorption coefficients which measures the (volume of 1-butene transferred)/(square cm of surface area)/(second). The volume is measured at the pressure of the system. Their results can be used to produce the following equation.

$$\frac{dV}{dt} = C \times A \times F_{1C_4^{=}} \qquad (II\text{-}8)$$

where V - volume of bubble, cm^3

t - time, sec

C - specific absorption coefficient, $cm^3/cm^2/sec$

A - area of bubble, cm^2

$F_{1C_4^{=}}$ volume fraction of 1-butene in bubble

(c) Importance of Steady-State Assumption

It was mentioned in Part I(a) of this section that the concentration of isobutane in the bulk of the acid would be discussed later. This is because this value was not measured experimentally. It is possible however, to calculate it if the acid is continuously being taken out of the reactor and replaced by fesh acid.

When this is the case, there must be a mass balance maintained at steady-state where the amount of isobutane entering the acid by mass transfer must equal the amount leaving in the bulk of the acid. This was taken into account in the simulation of the bubble reactor.

EXPERIMENTAL DETAILS

I. Mass Transfer Apparatus

A diagramatic sketch of the apparatus is shown in Figure II-1. A detailed description of the bubble column and a photograph of the complete apparatus are given in Appendix 4.

Initially the gas mixing reservoir was evacuated through the check valve G by a vacuum pump. Then 1-butene and isobutane were introduced separately into the gas mixing reservoir at A to prepare a desired mixture. The relative amounts of each gas were known approximately by the reading on the pressure gauge F. When the gases were thoroughly mixed, a sample was taken and analyzed using a gas liquid chromatograph. The check valve Q was then opened, the pressure regulator B was set, and the fine metering valve H was adjusted to maintain a desired flowrate. The volumetric flowrate was measured by the soapfilm meter D, and the flowrate at standard conditions could be calculated by knowing the pressure reading on the manometer C. The capillary flowmeter E was used to make sure that the flowrate was steady at all times. The gas was then passed through another fine metering valve I and then through the nozzle in the bubble column. The column was kept at 25 + .2°C by a temperature controlled water bath. The exit gas flow was measured by a similar arrangement to the inlet by a capillary flowmeter J, a soap film meter K, and a manometer L. The gas was analyzed by a gas liquid

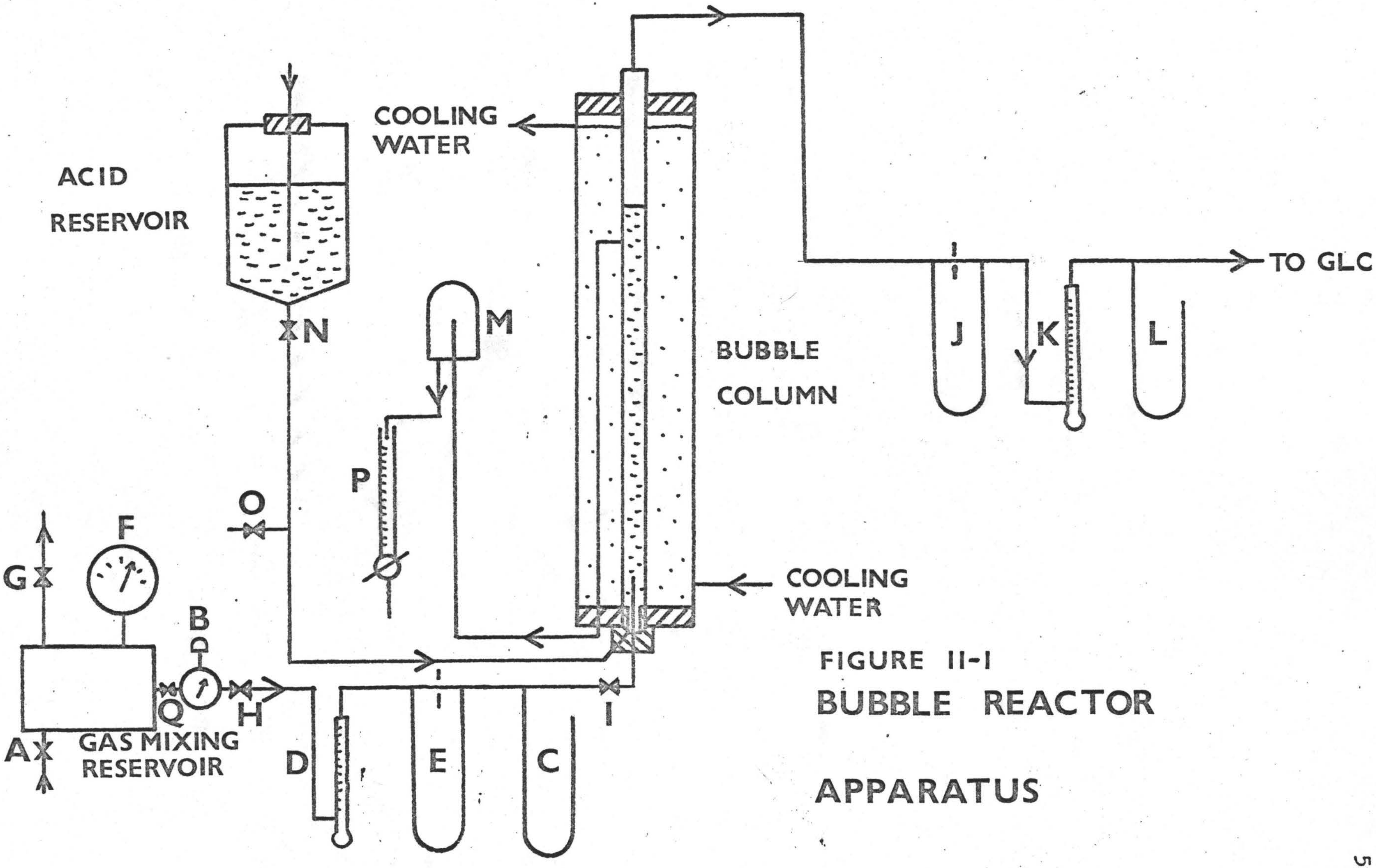


FIGURE II-1
BUBBLE REACTOR
APPARATUS

chromatograph.

The acid concentration in the bubble column was kept constant by a continuous addition and removal of fresh and spend acid respectively. The fresh acid was contained in the acid reservoir equipped with a constant head device. This consisted of a capillary tube immersed in the acid and open to the atmosphere. The check valve N was opened and the acid flowed into the base of the bubble column. The acid was removed through a port at the top of the column and passed through a constant level device M. The flowrate was measured using a burette P and a stop watch. Acid samples from both the reservoir and the column were taken for each experiment from valve O and the concentrations analyzed.

RESULTS AND ANALYSIS

The results obtained in this study are presented graphically in Figures II-2, II-3, II-4 and II-5. The raw data in tabular form may be found in Appendix 5.

Figure II-2 shows a plot of the observed isobutane transferred as well as the amount predicted by the penetration theory without chemical reaction, vs. the iC_4/olefin ratio in the feed. The experimental results disagree entirely with the penetration theory predictions at low iC_4/olefin ratios but approach one another as the iC_4/olefin ratio increases. It appears that at low iC_4/olefin ratios, the I-butene affects the transfer of isobutane by chemical reaction but at high iC_4/olefin ratios, the small amount of I-butene has little effect and the isobutane transferred by physical absorption alone.

Consequently a different theory for predicting the mass transfer of isobutane across the interface was needed. The approach taken was the same as shown in section 2(c) of the literature survey. A simple reaction mechanism was chosen as follows:

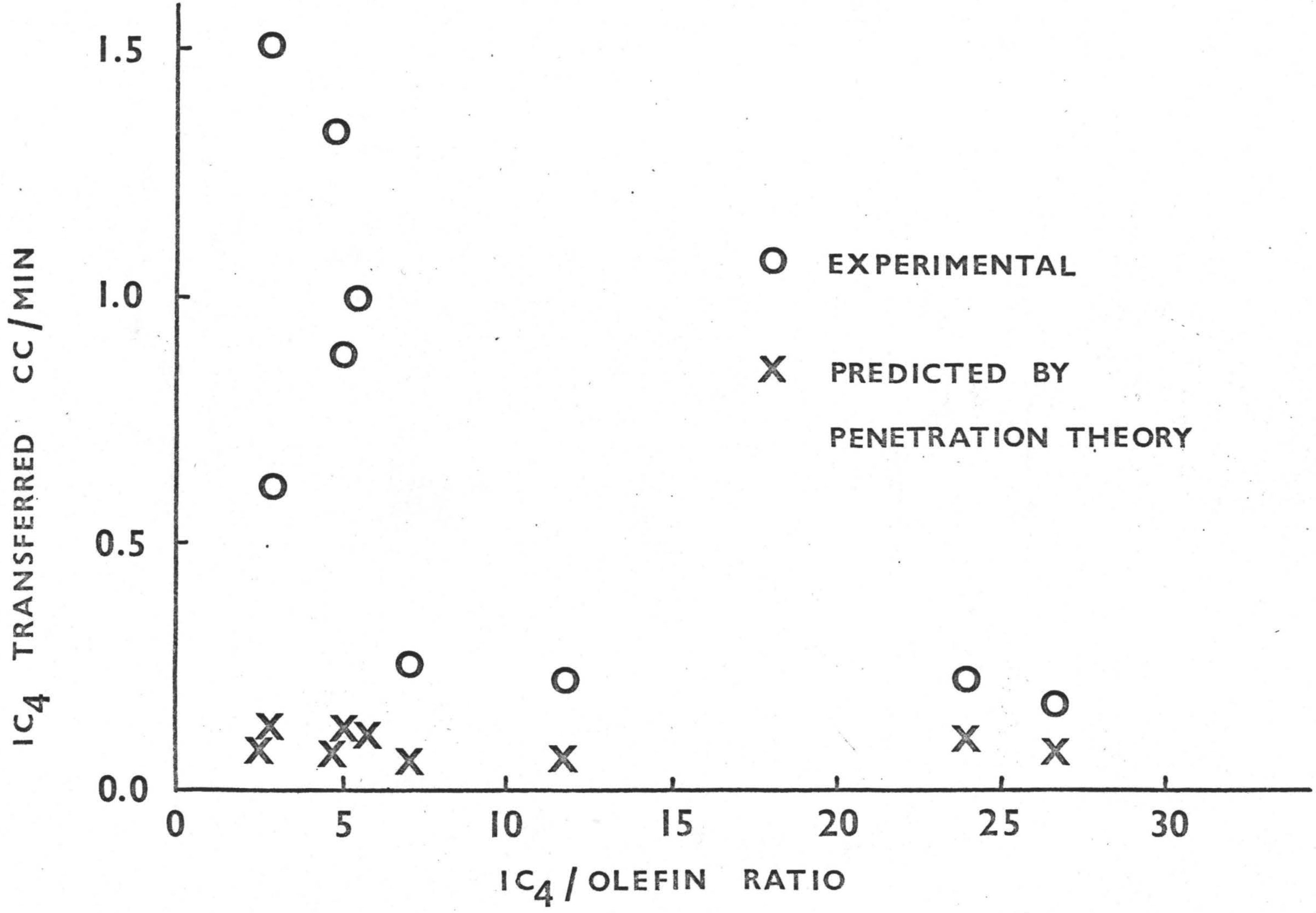
$$A + B \xrightarrow{k_1} \text{Products}$$

$$B + B \xrightarrow{k_2} \text{Products}$$

where A represents isobutane and B represents I-butene and k_1 and k_2 are second order reaction rate constants in $(\text{sec})^{-1} \times (\text{gmole/cm}^3)^{-1}$.

FIGURE II-2

COMPARISON OF PENETRATION THEORY WITH EXPERIMENTAL



The mass balance was then performed over a small differential element of volume and the following second order differential equations resulted:

$$D_A \frac{d^2C_A}{dx^2} = k_1 C_A C_B \qquad (II-9)$$

$$D_B \frac{d^2C_B}{dx^2} = k_1 C_A C_B + k_2 C_B^2 \qquad (II-10)$$

In order to solve these equations, it was necessary to know D_A, D_B, k_1, k_2 and four boundary conditions. It was reasonable to choose $D_A = D_B = 7.97 \times 10^{-7}$ cm^2/sec since both molecules were of similar size. The reaction rate constants however, were not known at all. One possible alternative was to substitute reasonable values for boundary conditions into the equations and solve for the k's. This analysis was begun using an analog computer to find an approximate solution and then completed using the Euler Predictor-Corrector Method for solving ordinary differential equations on a CDC 6400 digital computer.

The substitution of reasonable values into the equations was not a simple matter. In the case of 1-butene, no solubility in acid was known. It was expected according to Albright (II-8) that it should be higher than isobutane. With this small bit of information it was arbitrarily guessed to be 2.0×10^{-5} gmole/cm^3 when the pressure was 1 atm of pure gas. A good estimate of the initial gradient was obtained from Davis (II-12), and because the butene was able to react with itself, it was expected that its concentration and its gradient would drop to zero at some distance from the interface. In the case of isobutane, the interfacial concentration was known and a reasonable gradient at the interface was chosen as well as a starting value for k_1.

The program was set up so that if the k_1 was poorly chosen to give negative concentrations then it would be adjusted accordingly. It was then a matter of adjusting k_2 until the concentration of 1-butene and its slope equalled zero at some distance from the interface. The result of $k_2 = 2.45 \times 10^{12}$ (sec)$^{-1}$ (gmole/cm^3)$^{-1}$ was so large that it caused the concentration of 1-butene to drop linearly to zero at a distance of 9.50×10^{-6} cm from the interface. Because of the rapid rate of reaction by 1-butene with itself, it was expected and found that various values of k_1 had little effect on the value of k_2. This result was extremely helpful in that the solution to equation (II-10) could be replaced by:

$$C_B = C_{Bi} \quad (1 - \ x/x_R) \tag{II-11}$$

for x less than or equal to x_R and

$$C_B = 0 \tag{II-12}$$

for x greater than x_R

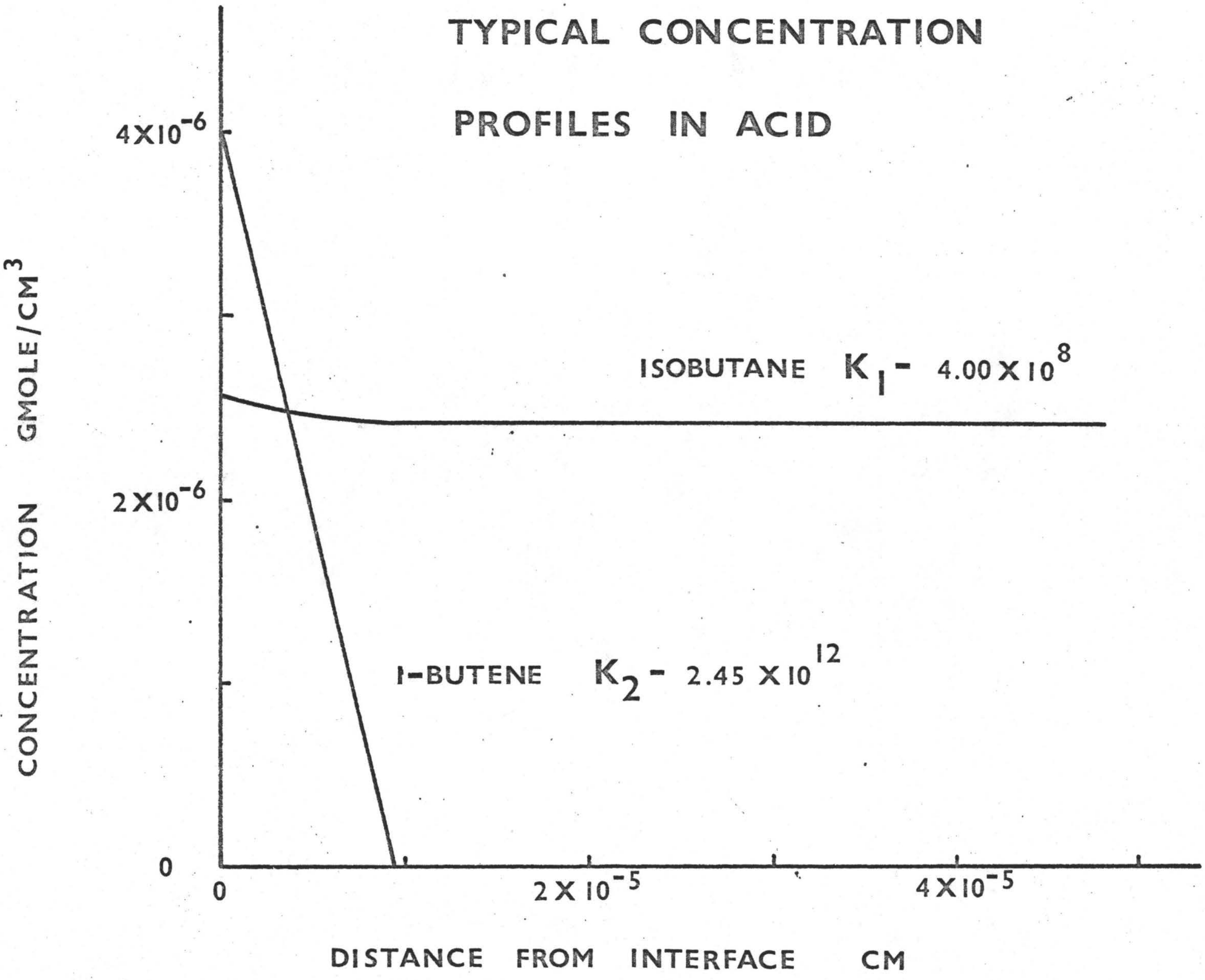
where x_R - effective thickness of the liquid film from the gas-liquid interface to the position where the concentration of B becomes zero, cm.

x - distance from interface, cm

A plot of typical concentration profiles found in this study are shown in Figure II-3.

The next step was to test the reaction mechanism with the experimental data. This was done by setting k_1 and predicting the amounts

FIGURE II-3



TYPICAL CONCENTRATION PROFILES IN ACID

of isobutane which should be transferred. A value for $k_1 = 1.4 \times 10^9$ $(sec^{-1})(gmole/cm^3)^{-1}$ produced the predicted results shown in Figure II-4. Table II-I shows the results leading up to the final choice for k_1.

The next step was to test this mechanism with some information from plant experience to confirm its consistency. It was stated in Part I of this study that a high iC_4/olefin ratio in the feed tended to reduce polymerization of the olefins causing the consumption of isobutane and olefin to react in the stoichiometric ratio of one to one. Therefore, the predicted isobutane transferred divided by the I-butene transferred was plotted against the iC_4/olefin ratio and is shown in Figure II-5. The plot shows a definite trend of the ratio of isobutane to I-butene transferred increasing toward unity as the iC_4/olefin ratio increases. The fact that the values are so far from unity is probably because the temperature at which these experiments were performed was 77°F as opposed to the 32°F recommended in plant practice. It is well understood that higher temperatures do increase the amount of polymer produced.

The present work has been an exploratory investigation on an aspect of the alkylation reactions. Admittedly the experimental data was not as good as had been expected and contains considerable scatter. None of the runs included, however, gave reason for doubting their accuracy. Runs I and 2 were preliminary experiments where some of the measurements were not taken. Runs 6, 9, 10, and II were discarded because of experimental problems during the runs. All other runs were included because in all cases conditions appeared to be normal.

FIGURE II-4

COMPARISON OF FILM THEORY WITH EXPERIMENTAL

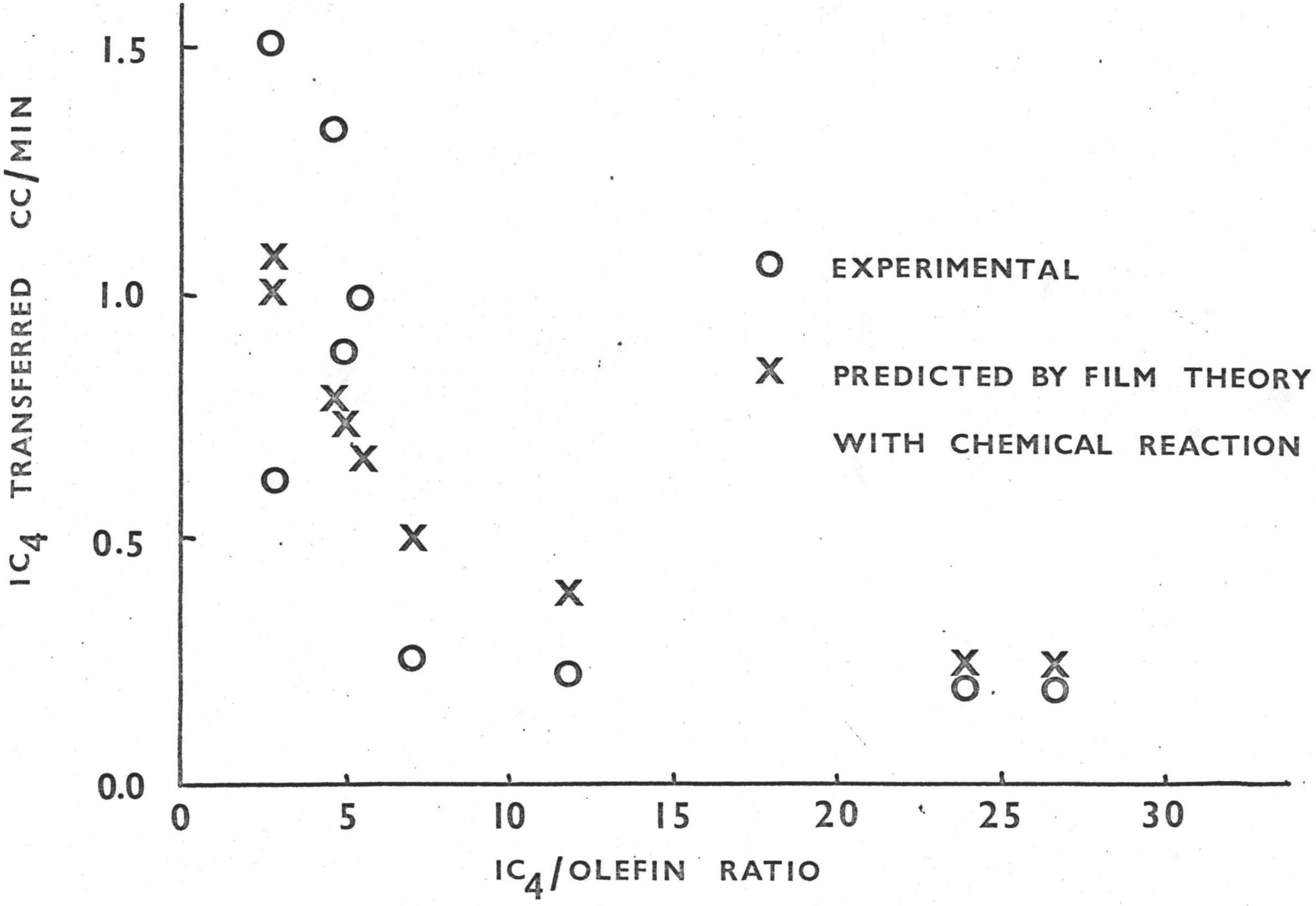


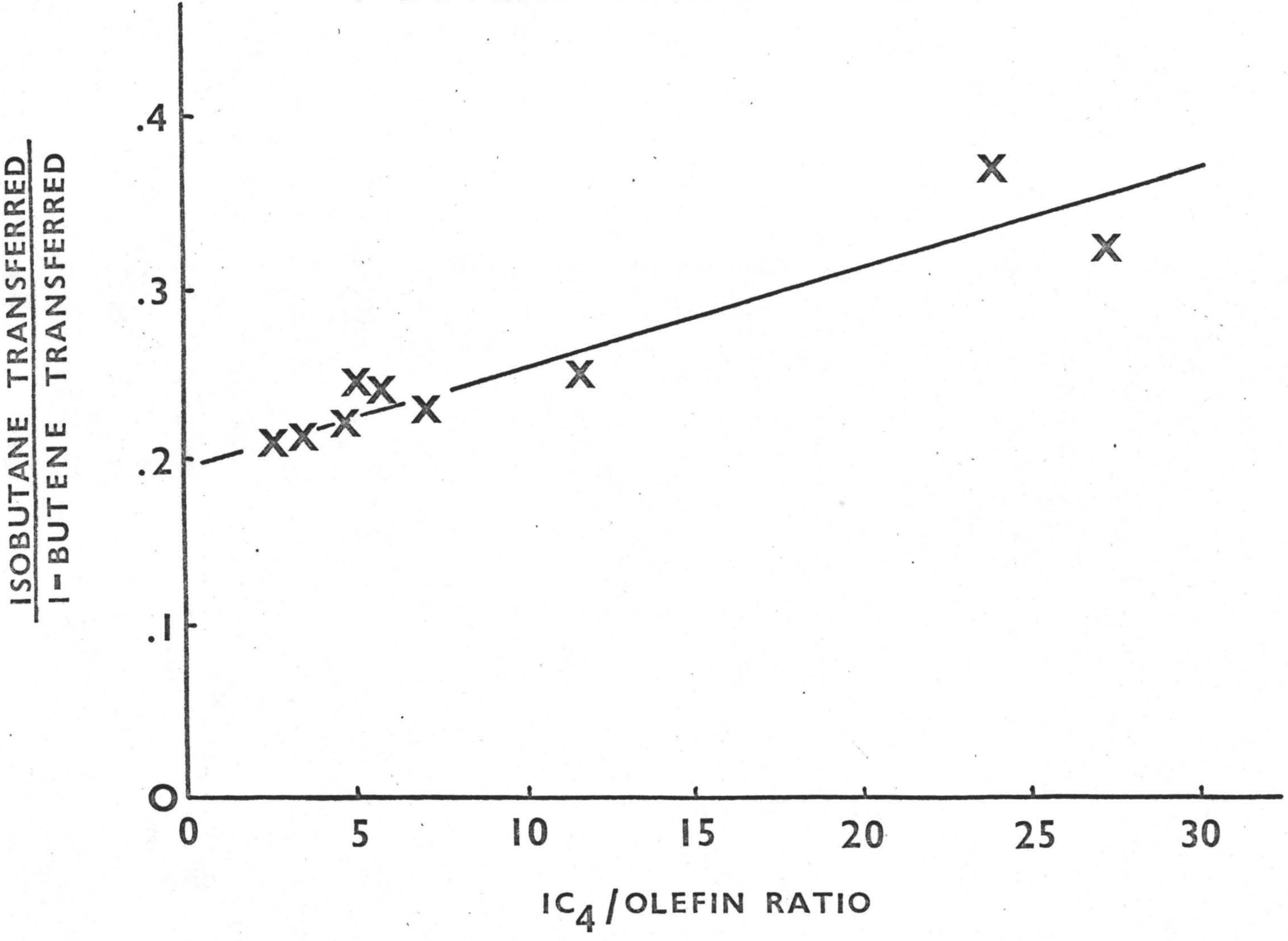
TABLE II-I

PREDICTED RATES OF ISOBUTANE TRANSFER

Run Number	Isobutane Transferred, cm^3/min				
	Predicted				Experimental
	$k_1=4\times10^8$	$k_1=8\times10^8$	$k_1=1\times10^9$	$k_1=1.4\times10^9$	
3	0.29	0.44	0.56	0.74	0.88
4	0.14	0.18	0.20	0.26	0.22
5	-	-	0.57	0.76	1.34
7	-	-	0.16	0.21	0.17
8	-	-	0.25	0.36	0.22
12	-	-	0.81	1.07	1.51
13	-	-	0.74	0.98	0.66
14	-	-	0.47	0.66	1.00
15	-	-	0.37	0.49	0.25

FIGURE II-5

RATIO OF ISOBUTANE TO
1-BUTENE TRANSFERRED



Because of the large differences in amounts of isobutane transferred at different iC_4/olefin ratios, it was possible to detect a definite trend in the data in spite of the experimental scatter. It was obvious that the Penetration Theory could not be used to interpret the results. This was expected and confirmed to be true. The second order reaction mechanism however, worked quite well. Added confidence in this mechanism was gained when it predicted the increase of isobutane to l-butene transfer at the higher iC_4/olefin ratios. The mechanism had been consistent with plant experience.

It is reasonable to point out that future experiments should probably be carried out in a different apparatus. A possible design would consist of a laminar jet of sulphuric acid surrounded by a mixture of the gases. This method would afford a more accurate measurement of the interfacial area and would also remove the inherent errors in the flow measurement of the gases. The time for an experimental run might also be considerably reduced.

CONCLUSIONS

1. Experimental work was done to measure the amounts of isobutane and 1-butene which would transfer into sulphuric acid in a bubble reactor. Although the data contained considerable scatter, it was evident that the amount of isobutane transferred increased rapidly as the iC_4/olefin ratio decreased.
2. The Penetration Theory was not able to predict the experimental results at low iC_4/olefin ratios although agreement between experimental and predicted increased as the iC_4/olefin ratio increased.
3. A second order chemical reaction mechanism was found to explain the experimental data.
4. The reaction mechanism also predicted that the amount of isobutane transferred relative to the 1-butene transferred, increases with increasing iC_4/olefin ratio. This agreed with plant experience.

NOMENCLATURE FOR PART II

A - area, cm^2

C - specific absorption coefficient, cm^3/(cm^2)(sec)

C_A - concentration of A in liquid, gmole/cm^3

C_{Ai} - concentration of A at phase boundary, gmole/cm^3

C_B - concentration of B in liquid, gmole/cm^3

C_{Bi} - concentration of B at phase boundary, gmole/cm^3

C_i - concentration at phase boundary, gmole/cm^3

C_o - concentration of bulk liquid, gmole/cm^3

d - vertical length of bubble, cm

D - diffusivity of gas in liquid, cm^2/sec

D_A - diffusivity of A in liquid, cm^2/sec

D_B - diffusivity of B in liquid, cm^2/sec.

$F\ IC_4$ - volume fraction of isobutane in bubble

$F\ IC_4$ - volume fraction of l-butene in bubble

k - reaction rate constant for first order reaction in liquid phase (Sec $^{-1}$)

k_1, k_2 - reaction rate constants for second order reactions, (sec^{-1})(gmole/cm^3)$^{-1}$

k_G - gas-film coefficient, gmole/(cm^2)(sec)(atm)

k_L - liquid-film coefficient, gmole/(cm^2)(sec)(gmole/cm^3)

N_A - rate of mass transfer, gmole/(cm^2)(sec)

p - partial pressure of diffusing gas at phase in main stream, atm

p_i - partial pressure of diffusing gas at phase boundary, atm

P - total pressure, cm Hg

R - universal gas law constant, (cm Hg)(cm^3)/(gmole)(°K)

t - time, sec

t_e - life of fluid element, sec

T - temperature, °K

u_b - velocity of bubble, cm/sec

V - volume of bubble, cm^3

x - distance from the interface, cm

x_R - effective thickness of the liquid film from the gas liquid interface to the position where the concentration of the reactant becomes zero, cm.

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APPENDICES

APPENDIX I

I. Raw Data from Actual Plant Studies

(a) Raw Data from Five Plant Runs

TABLE A-I

TEMPERATURE ACID CONCENTRATION AND ALKYLATE YIELD FROM FIVE PLANT RUNS

Run No.	Day Ending	Temp. °F	Acid Concn. wt %	Alkylate - C5's & greater bbl/day
1	July 29, 1966	45.	91.1	1345.6
2	Nov., 11, 1966	46.	90.6	1353.2
3	March, 23, 1967	50.	90.5	1702.8
4.	April 28, 1967	50.	90.5	1926.6
5	July 7, 1967	52.	90.8	2085.1

TABLE A-2

FLOWS FROM FIVE-PLANT RUNS

	Flow	Volume Percent								
	bbl/day	C3	C3$^{=}$	iC4	nC4	iC4$^{=}$	tC4$^{=}$	cC4$^{=}$	iC5	nC5
Run 1										
Olef. Fd.	2587	16.5	6.2	19.6	36.3	8.4	7.8	4.9	0.2	0.0
iC4 Sarnia	1012	10.4	0.6	43.4	42.9	1.3	0.4	0.2	0.2	0.1
DIB Tops	4293	8.2	0.0	72.1	19.6	0.0	0.0	0.0	0.0	0.0
DeC3 Btms	4874	4.0	0.0	67.1	28.4	0.0	0.0	0.0	0.5	0.0
Run 2										
Olef. Fd.	1840	23.0	13.6	15.2	17.5	14.4	7.3	6.0	3.1	0.0
iC4 Sarnia	1977	8.2	0.9	53.3	34.6	1.5	0.3	0.2	0.8	0.3
DIB Tops	3438	6.3	0.3	83.2	10.0	0.2	0.0	0.0	0.0	0.0
DeC3 Btms	4871	1.1	0.0	78.2	19.8	0.0	0.0	0.0	0.9	0.0
Run 3										
Olef. Fd.	3030	14.1	7.6	21.6	33.4	10.4	5.5	4.2	3.0	0.0
iC4 Sarnia	1531	7.8	1.1	40.1	39.5	5.9	2.3	1.5	1.6	0.2
DIB Tops	3481	6.0	0.0	67.5	25.7	0.5	0.4	0.0	0.0	0.0
DeC3 Btms	5517	2.1	0.0	54.2	42.0	0.1	0.0	0.0	1.6	0.0
Run 4										
Olef. Fd.	3189	11.9	7.6	25.1	29.4	10.9	6.8	5.5	2.9	0.0
iC4 Sarnia	1318	6.4	0.6	52.8	32.2	3.0	2.9	1.5	0.6	0.0
DIB Tops	3234	4.6	0.0	66.8	26.7	1.9	0.0	0.0	0.0	0.0
DeC3 Btms	5698	3.1	0.0	56.0	38.7	0.0	0.0	0.0	2.2	0.0
Run 5										
Olef. Fd.	3557	14.7	9.1	19.8	31.3	13.4	6.5	4.9	0.2	0.0
iC4 Sarnia	1064	7.5	0.8	46.9	40.5	1.3	1.2	0.7	1.0	0.1
DIB Tops	3656	7.3	0.0	69.1	23.6	0.0	0.0	0.0	0.0	0.0
DeC3 Btms.	4413	2.4	0.0	49.0	45.0	0.0	0.0	0.0	2.6	0.0

(b) Raw Data from Twenty-one Plant Runs

TABLE A-3

COMBINED FEED AND ANALYSIS OF TWENTY-ONE PLANT RUNS

Run No.	Comb. Feed	Volume Percent								
	bbl/day	C3	C3$^{=}$	iC4	nC4	iC4$^{=}$	tC4$^{=}$	cC4$^{=}$	iC5	nC5
1A	10240	12.34	3.20	45.53	33.32	2.66	1.14	0.76	1.06	0.00
2A	10500	13.83	3.12	49.91	27.65	2.37	1.04	0.66	1.41	0.00
3A	11090	12.72	3.78	42.16	35.42	2.38	1.14	0.86	1.53	0.00
4A	11610	11.19	3.77	40.38	37.35	2.66	1.23	0.95	2.46	0.00
5A	11920	8.03	3.90	55.09	25.82	2.73	1.41	1.03	1.98	0.00
6A	11600	9.20	4.32	53.29	26.20	2.74	1.23	1.04	1.98	0.00
7A	11520	9.37	4.16	55.01	24.37	2.73	1.23	1.04	2.10	0.00
8A	11770	8.58	4.24	56.26	24.97	2.64	1.23	1.04	1.05	0.00
9A	12200	8.48	3.58	56.38	25.33	2.73	1.41	1.04	1.05	0.00
10A	9030	6.07	2.90	64.88	19.66	2.80	1.40	1.03	1.27	0.00
11A	10480	8.00	3.24	66.47	16.34	2.81	1.41	1.03	0.70	0.00
12A	11410	9.16	3.01	55.69	24.90	2.82	1.41	1.03	1.98	0.00
13A	11010	10.25	3.43	54.66	25.00	2.93	1.42	1.04	1.28	0.00
14A	11630	10.51	3.18	55.76	24.18	2.83	1.23	1.04	1.28	0.00
15A	10080	13.29	3.93	61.38	12.81	3.98	1.90	1.42	1.29	0.00
16A	10700	11.52	3.44	48.58	29.13	3.03	1.52	1.14	1.64	0.00
17A	11645	10.44	3.19	48.45	31.16	2.74	1.32	0.94	1.75	0.00
18A	11570	11.15	3.11	50.03	28.86	2.74	1.32	1.04	1.75	0.00
19A	11130	12.60	3.53	51.60	25.85	2.94	1.52	1.14	0.82	0.00
20A	11640	11.96	3.28	49.11	29.13	2.84	1.33	0.95	1.41	0.00
21A	11630	10.98	3.11	48.01	30.91	2.93	1.51	1.14	1.40	0.00

TABLE A-4

DEISOBUTANIZED ALKYLATE OUTPUT AND ANALYSIS OF TWENTY-ONE PLANT RUNS

Run No.	Alky Flow	Volume Percent								
	bbl/day	iC5	2,3 DMB	2,4 DMP	2,3 DMP	224 TMP	GROUP I	GROUP II	C9	C9+
1A	1597	16.5	9.4	8.6	15.3	13.5	6.3	17.1	5.0	8.3
2A	1494	12.7	8.1	9.1	17.8	16.8	5.7	18.5	3.2	8.2
3A	1707	16.5	8.6	8.5	13.9	11.9	6.5	15.8	6.2	12.0
4A	1740	15.6	8.9	8.5	14.2	12.6	6.3	15.7	6.2	12.2
5A	1690	15.6	7.1	9.7	15.5	15.0	5.7	17.5	8.8	5.0
6A	2130	15.7	7.5	9.1	16.4	14.9	5.4	13.3	13.9	3.9
7A	1980	16.7	7.1	8.3	16.4	15.0	5.6	17.8	4.2	8.8
8A	2020	10.9	8.1	10.3	18.0	16.1	5.5	18.8	3.6	8.8
9A	1990	13.1	7.9	10.3	15.8	17.2	6.2	16.8	3.9	8.9
10A	1975	16.6	6.9	9.7	16.0	17.2	5.5	17.4	3.6	7.0
11A	1625	10.9	6.7	8.9	16.6	19.9	5.8	20.9	2.7	7.7
12A	1750	15.2	7.3	8.9	14.9	17.8	5.9	18.3	3.9	7.9
13A	1740	13.9	7.4	8.9	14.2	18.0	6.2	18.5	4.1	8.8
14A	1760	15.7	7.6	8.7	13.5	17.3	6.4	17.4	4.7	8.7
15A	1757	16.5	7.8	8.7	12.6	16.5	6.5	16.5	5.2	9.6
16A	1642	12.5	8.4	9.6	13.9	17.3	6.9	17.3	4.6	9.6
17A	1777	17.3	7.9	9.0	12.6	16.1	6.7	15.7	5.3	9.4
18A	1856	17.0	7.8	8.7	12.4	17.0	6.4	17.0	4.8	9.0
19A	1772	14.0	7.9	9.1	14.2	17.8	6.3	17.8	4.1	7.8
20A	1750	14.6	7.6	8.8	12.3	16.8	6.6	16.8	3.4	13.2
21A	1788	16.0	8.1	8.6	12.4	16.4	6.7	16.4	5.2	10.2

```
$IBFTC REAC25
      SUBROUTINE REAC25
C     WRITTEN BY H. CANNING AND J. GATES
C     REVISED BY I. SHAW    MAY 1968
C     THIS MODEL PERFORMS A MASS AND HEAT BALANCE ON THE STRATCO
C     REACTOR AT SHELL OAKVILLE
C
C     EN VECTOR
C     1. EQUIPMENT NUMBER
C     2. SET TO 0.0 TO SUPRESS MASS BALANCE PRINTOUT
C     3. SET AT 0.0 TO SUPRESS HEAT BALANCE PRINTOUT
C     4. SET TO 1.0 TO SUPRESS LIMIT OF CORRELATION CHECK AND PRINTOUT
C     5. EQUIPMENT NUMBER OF PRODUCT SEPARATOR
C     6. LOCATION OF MOLECULAR WEIGHT IN PHYSICAL PROPERTIES
C     7. LOCATION OF LIQUID SPECIFIC HEATS IN PHYSICAL PROPERTY PACKAGE
C     8. IMPELLER POWER IN KW WHICH IS A CONSTANT
C
C     ******************************************************************
C    -MODEL USES CORRELATION EQUATIONS TO PREDICT OUTPUTS FROM INPUTS
C    -ACID DILUTUON IS CAUSED BY WATER IN THE FEED AND BY THE PRODUCTION
C     OF ALKYL SULPHATES
C    -PRODUCTION OF ALKYL SUPHATES CALCULATED BY EQUATIONS BASED ON
C     MASS BALANCES AND FACTORS BELIEVED TO EFFECT ACID CONSUMPTION
C    -ANY NAOH ASSUMED TO GO TO NA2SO4
C    -N-C3 AND N-C4 ARE ASSUMED INERT AND UNCHANGED ACROSS THE REACTOR
C    -I-C4 USAGE IS CALCULATED FROM I-C4 TO OLEFIN USAGE FACTORS
C    -OLEFINS ASSUMED COMPLETELY REACTED
C    -ALL OTHER OUTPUTS CALCULATED BY REGRESSION EQUATIONS
C
C     STRMI(1,J) IS THE ORGANIC FEED TO THE REACTOR
C     STRMI(2,J) IS THE ACID RECYCLE TO THE REACTOR
C
C     ******* MACSIM COMMON DECK, FOR ALKYLATION.  T.T. APR.29,1968.****
      COMMON  NOCOMP,KSETS,NIN,NOUT,NE,STRMI(5,31),STRMO(5,31),EN(50,20)
      COMMON AEN(4,102),ENC(50,20),NOPP,X,XMOLE(26),PPSC(17,26),PPMX(17)
      DIMENSION B(9), C(9), D(9), E(9), F(9), G(9), H(9), R(9)
      DIMENSION HIHLMT(9), BTMLMT(9)
C
C     ******************************************************************
C     DEFINE CONSTANTS AND CORRELATION COEFFICIENTS
      DATA B /33.0341, -0.0671101, 0.0, -0.02202443, 0.0, 0.668633,
     1        -0.328644, -0.927387, 0.104107 /
      DATA C /15.1189, -0.0292867, 0.0830969, -0.0109155, 0.00763949,
     1        0.300093, -0.177285, -0.130126, 0.0133338 /
      DATA D /4.99554, -0.0351862, 0.0445619, 0.119407E-03, 0.00323341,
     1        0.139254, -0.168913, -0.102607, 0.294273 /
      DATA E /28.2760, -0.0483364, 0.251499, 0.00487267, -0.0116686,
     1        -0.182781, -0.341756, -0.0546192, 0.286463 /
      DATA F /-8.44706, 0.00144286, -0.140933, 0.0223955, -0.00217905,
     1        -0.0724850, -0.0237373, -0.0965011, 0.617014 /
      DATA G /2.45950, -0.0105513, -0.00913172, -0.00276322, 0.00446859,
     1        0.176672, -0.0644604, -0.0462004, 0.0956723 /
```

```
      DATA H /18.9267, -0.0175973, 0.0270972, 0.0133159, -0.739504E-03,
     1       -0.214328, 0.0827224, -0.119848, 0.150898 /
      DATA R /7.17834, -0.0146893, -0.0345164, -0.0144946, 0.00835222,
     1       0.337128, -0.205448, -0.150647, 0.263569 /
      DATA HIHLMT / 245.6, 91.4, 609.1, 989.0, 52.5, 62.9, 100.0, 25.1,
     1            100.0 /
      DATA BTMLMT / 92.6, 59.6, 190.6, 634.2, 28.1, 39.1, 0.0, 6.7, 0.0/
C
C     ***********************************************************
C     THIS CHECKS FOR INPUTS OUT OF CORRELATION LIMITS
      IF(EN(NE,4).GT.0.5)  GO TO 15
      DO 10 J=12,20
      LL = J-11
      IF(STRMI(1,J).LT.BTMLMT(LL)) WRITE(6,4446) BTMLMT(LL),J,STRMI(1,J)
   10 IF(STRMI(1,J).GT.HIHLMT(LL)) WRITE(6,4446) HIHLMT(LL),J,STRMI(1,J)
C
C     ***********************************************************
C     USE REGRESSION EQUATIONS TO CALCULATE FLOWS IN ORGANIC PHASE
   15 STRMO(1,4) = STRMI(1,4) + 8.0
      STRMO(1,5) = 85.0
      STRMO(1,6) = STRMI(1,6) + STRMI(2,6)
      STRMO(1,8) = 0.0
      STRMO(1,9) = STRMI(1,9) + STRMI(2,9) + 0.5*STRMI(1,8)
      NOPP = EN(NE,6)
      WEIGHT = 0.0
      DO 20 J=1,26
   20 WEIGHT = WEIGHT + STRMI(2,J+5)*PPSC(NOPP,J)
      ACID = STRMI(2,7)*PPSC(NOPP,2)/WEIGHT
      ACDOIL = ((STRMI(1,13)*2.0)*(1.0 + 2.5*(0.90-ACID)) +
     1       ((STRMI(1,16)+STRMI(1,17))*0.6)*(1.0 + 2.5*(0.90-ACID)) +
     2          STRMI(1,20)*1.0)*0.0035
      RATIO = STRMI(1,15)/(STRMI(1,13)+STRMI(1,16)+STRMI(1,17)+
     1                                                STRMI(1,20))
      ACDOIL = ACDOIL*(1.0 + (5.5-RATIO)*0.114)
      ACDOIL = ACDOIL*(1.0 - (50.0-STRMO(1,4))*0.0145)
      STRMO(1,10) = STRMI(1,10) + STRMI(2,10) + ACDOIL
      STRMO(1,7) = STRMI(2,7) - STRMI(1,8)*0.5 - (STRMO(1,10) -
     1                             (STRMI(1,10)+STRMI(2,10)))
      STRMO(1,11)= STRMI(1,11)
      STRMO(1,12) = STRMI(1,12)
      STRMO(1,13) = 0.0
      STRMO(1,14) = STRMI(1,14)
      STRMO(1,15)= STRMI(1,15) - (0.8760*STRMI(1,13)+1.030*STRMI(1,16)
     1             +1.001*STRMI(1,17)+ 0.9411*STRMI(1,20))*0.926
      STRMO(1,16) = 0.0
      STRMO(1,17) = 0.0
      C5PROD   =   B(1) + B(2)*STRMI(1,12) + B(3)*STRMI(1,13) + B(4)*
     1 STRMI(1,15) + B(5)*STRMI(1,14) + B(6)*STRMI(1,17) + B(7)*
     2 STRMI(1,16) + B(8)*STRMI(1,19) + B(9)*STRMO(1,4)
      STRMO(1,18) = STRMI(1,18) + 0.10*C5PROD
      STRMO(1,19) = STRMI(1,19) + 0.90*C5PROD
      STRMO(1,20) = 0.0
      STRMO(1,21) = STRMI(1,21)
```

```
      STRMO(1,22) = C(1) + C(2)*STRMI(1,12) + C(3)*STRMI(1,13) + C(4)*
     1 STRMI(1,15) + C(5)*STRMI(1,14) + C(6)*STRMI(1,17) + C(7)*
     2 STRMI(1,16) + C(8)*STRMI(1,19) + C(9)*STRMO(1,4)
      STRMO(1,22)=STRMO(1,22)    +   STRMI(1,22)
      STRMO(1,23) = STRMI(1,23)
      STRMO(1,24) = D(1) + D(2)*STRMI(1,12) + D(3)*STRMI(1,13) + D(4)*
     1 STRMI(1,15) + D(5)*STRMI(1,14) + D(6)*STRMI(1,17) + D(7)*
     2 STRMI(1,16) + D(8)*STRMI(1,19) + D(9)*STRMO(1,4)
      STRMO(1,24)=STRMO(1,24)    +   STRMI(1,24)
      STRMO(1,25) = E(1) + E(2)*STRMI(1,12) + E(3)*STRMI(1,13) + E(4)*
     1 STRMI(1,15) + E(5)*STRMI(1,14) + E(6)*STRMI(1,17) + E(7)*
     2 STRMI(1,16) + E(8)*STRMI(1,19) + E(9)*STRMO(1,4)
      STRMO(1,25)=STRMO(1,25)    +   STRMI(1,25)
      STRMO(1,26) = STRMI(1,26)
      STRMO(1,27) = F(1) + F(2)*STRMI(1,12) + F(3)*STRMI(1,13) + F(4)*
     1 STRMI(1,15) + F(5)*STRMI(1,14) + F(6)*STRMI(1,17) + F(7)*
     2 STRMI(1,16) + F(8)*STRMI(1,19) + F(9)*STRMO(1,4)
      STRMO(1,27)=STRMO(1,27)    +   STRMI(1,27)
      STRMO(1,28) = G(1) + G(2)*STRMI(1,12) + G(3)*STRMI(1,13) + G(4)*
     1 STRMI(1,15) + G(5)*STRMI(1,14) + G(6)*STRMI(1,17) + G(7)*
     2 STRMI(1,16) + G(8)*STRMI(1,19) + G(9)*STRMO(1,4)
      STRMO(1,28)=STRMO(1,28)    +   STRMI(1,28)
      STRMO(1,29) = H(1) + H(2)*STRMI(1,12) + H(3)*STRMI(1,13) + H(4)*
     1 STRMI(1,15) + H(5)*STRMI(1,14) + H(6)*STRMI(1,17) + H(7)*
     2 STRMI(1,16) + H(8)*STRMI(1,19) + H(9)*STRMO(1,4)
      STRMO(1,29)=STRMO(1,29)    +   STRMI(1,29)
      AA     =      R(1) + R(2)*STRMI(1,12) + R(3)*STRMI(1,13) + R(4)*
     1 STRMI(1,15) + R(5)*STRMI(1,14) + R(6)*STRMI(1,17) + R(7)*
     2 STRMI(1,16) + R(8)*STRMI(1,19) + R(9)*STRMO(1,4)
      STRMO(1,30) = 0.5*AA + STRMI(1,30)
      STRMO(1,31) = 0.5*AA + STRMI(1,31)
C
C     ******************************************************************
C     NORMALIZATION SECTION
      NOPP = EN(NE,6)
      M = NOPP
      CALL PROCAL
C     SUM THE WEIGHT OF INPUT AND OUTPUT ORGANICS TO BE NORMALLIZED
      SUMIN = STRMI(1,13)*PPSC(M,8) + STRMI(1,16)*PPSC(M,11) +
     1        STRMI(1,17)*PPSC(M,12) + STRMI(1,20)*PPSC(M,15) -
     2        (STRMO(1,10)-(STRMI(1,10)+STRMI(2,10)))*0.516*PPSC(M,5) -
     3        (STRMO(1,15)-(STRMI(1,15)+STRMI(2,15)))*PPSC(M,10)
      SUMOUT = C5PROD*PPSC(M,14)
      DO 40 J=21,31
   40 SUMOUT = SUMOUT + (STRMO(1,J)-STRMI(1,J))*PPSC(NOPP,J-5)
      AA = SUMIN/SUMOUT
      STRMO(1,18) = STRMI(1,18) + AA*C5PROD*0.10
      STRMO(1,19) = STRMI(1,19) + AA*C5PROD*0.90
      DO 70 J=21,31
   70 STRMO(1,J) = STRMI(1,J) + AA*(STRMO(1,J)-STRMI(1,J))
      STRMO(1,3)=0.0
      DO 80 J=6,31
   80 STRMO(1,3)=STRMO(1,3)+STRMO(1,J)
      IF(EN(NE,2).LT.0.5)  GO TO 110
      DIFFPC = (SUMIN-SUMOUT)*100.0/SUMIN
      WRITE(6,1005) SUMIN, SUMOUT, DIFFPC
```

```
      WRITE(6,9997)
      DO 90 J=1,26
      AA = STRMI(1,J+5)*PPSC(1,J)
      BB = STRMI(2,J+5)*PPSC(1,J)
      CC = STRMO(1,J+5)*PPSC(1,J)
   90 WRITE(6,9999) AA,BB,CC
C
C      *****************************************************************
C      CHECK OUTPUT FOR NEGATIVE FLOWS
  110 IF(STRMO(1,4).GT.60.0.OR.STRMO(1,4).LT.40.0)  WRITE(6,4448)
      IF(STRMO(1,15).GT.STRMI(1,15)) GO TO 200
      DO 150 J=6,31
      IF(STRMO(1,J).LT.0.0)  GO TO 200
  150 CONTINUE
      GO TO 260
  200 WRITE(6,252)
      WRITE(6,9998)  (STRMI(1,J),J=1,31)
      WRITE(6,9998)  (STRMI(2,J),J=1,31)
      WRITE(6,9998)  (STRMO(1,J),J=1,31)
      STOP
C
C      *****************************************************************
C     -HEAT BALANCE CALCULATES THE HEAT THAT MUST BE REMOVED BY THE COILS
C        IN THE RACTOR AND TRANSFERS THIS AMOUNT TO THE PRODUCT SEPARATOR
C     -THE HEAT OF REACTION IS CALCULATED KNOWING THE FLOWS OF OLEFIN
C        AND USING VALUES FROM CULPIT ADJUSTED BY A PLANT FACTOR
C     -THE IMPELLER HEAT INPUT IS THE EQUIVALENT OF A 50 HP MOTOR
260   CONTINUE
      ENTHIN=0.0
      NOPP = EN(NE,7)
      DO 21 I=1,NIN
      X=STRMI(I,4)
      DO 22 J=1,NOCOMP
22    XMOLE(J)=STRMI(I,J+5)
      CALL PROMIX(1)
21    ENTHIN=ENTHIN+PPMX(NOPP)*X
      X = STRMO(1,4)
      DO 24 J=1,NOCOMP
   24 XMOLE(J)=STRMO(1,J+5)
      CALL PROMIX(1)
      ENTHO = PPMX(NOPP)*X
      HR = (35280.*STRMI(1,13) + 34440.*(STRMI(1,16)+STRMI(1,17)) +
     1                                  34960.*STRMI(1,20))*0.845
      HI=1260000.0
      HEATLD=ENTHIN-ENTHO+HR+HI
      IF(EN(NE,3).GT.0.5)  WRITE(6,5555) ENTHIN, ENTHO, HR, HI, HEATLD
      NNN = EN(NE,5)
      EN(NNN,5) = HEATLD
      ENC(NE,16) = EN(NE,8)
      RETURN
C
C
  252 FORMAT(///51H **** STOP BECAUSE FLOW IN REACTOR EXIT IS NEGATIVE/)
 1005 FORMAT(/37H ORGANIC INPUT TO BE NORMALIZED (LB.), F11.2, 6X, 25HOU
   1TPUT BEFORE NORMALIZING, F11.2, 6X, 18HPERCENT DIFFERENCE, F9.5/)
 4446 FORMAT( 25H *** CORRELATION LIMIT OF,F7.1, 23H  EXCEEDED FOR STRMI
```

```
     1(1,, I2, 10H) WHICH IS, F7.1,  27H  IN THE REACTOR MODULE ***)
 4448 FORMAT(/  43H *** REACTOR TEMPERATURE OUTSIDE LIMITS ***/)
5555  FORMAT(      5X,11HENTHALPY IN,F12.3,5X,12HENTHALPY OUT,F12.3,5X,16H
     1HEAT OF REACTION,F12.3,/,5X,13HIMPELLER HEAT,F12.3,5X,10HTOTAL LOA
     2D,F12.3)
 9997 FORMAT(/ 12X, 32HMASS FLOWS IN AND OUT OF REACTOR/)
 9998 FORMAT(5F20.5)
 9999 FORMAT(5F15.1)
      END
```

APPENDIX 3

3. Determination of Various Physical Properties

(a) Calculation of Diffusion Coefficient

(i) The Wilke Equation

The following is the calculation of the diffusion coefficient of isobutane in 93 wt % sulphuric acid using the Wilke (11-10) equation.

$$D_{AB} = \frac{7.4 \times 10^{-8} \, (\psi_B \, M_B)^{\frac{1}{2}} \, T}{\mu \, V_A^{0.6}} \qquad \text{(A-1)}$$

where D_{AB} - diffusion coefficient of solute A diffusing into solvent B, cm^2/sec.

ψ_B - an "association parameter" for the solvent B

M_B - the molecular weight of solvent B

T - the absolute temperature in degrees K

μ - the viscosity of the solution in centipoises

V_A - the molar volume of the solute A as liquid at its normal boiling point, $cm^3/gmole$

for the present system

ψ_B - 1.0

M_B - 98.07

T - 298.2

μ - 17.

V_A - 103.5

substituting into equation

$$D_{AB} = 7.97 \times 10^{-7}\ \text{cm}^2/\text{sec}$$

(ii) The Reddy and Doraiswamy Equation

The following is the calculation of the diffusion coefficient of isobutane in 93 wt % sulphuric acid using the equation developed by Reddy and Doraiswamy (II-11)

$$D_{12} = 10 \times 10^{-8} \frac{M^{1/2}\ T}{\mu V_1^{1/3} V_2^{1/3}} \qquad \text{(A-2)}$$

when $V_2/V_1 \leq 1.5$

where D_{12} - diffusion coefficient of solute 1 diffusing into solvent 2, cm^2/sec.

M - the molecular weight of solvent 2, gm/gmole

T - the absolute temperature, °K

V_1 - the molecular volume of solute 1, cm^3/gmole

V_2 - the molecular volume of solvent 2, cm^3/gmole

μ - viscosity of solvent, centipoise

for the present system

M - 98.07

T - 298.2

V_1 - 103.5

V_2 - 53.6

μ - 17.

substituting into equation

$$D_{12} = 9.86 \times 10^{-7}\ \text{cm}^2/\text{sec}$$

(b) Calculation of Solubility of Isobutane in Sulphuric Acid

The only data available on the solubility of isobutane in sulphuric acid is given by Cupit, Gwyn and Jernigan (II-9) and is shown in Table A-5.

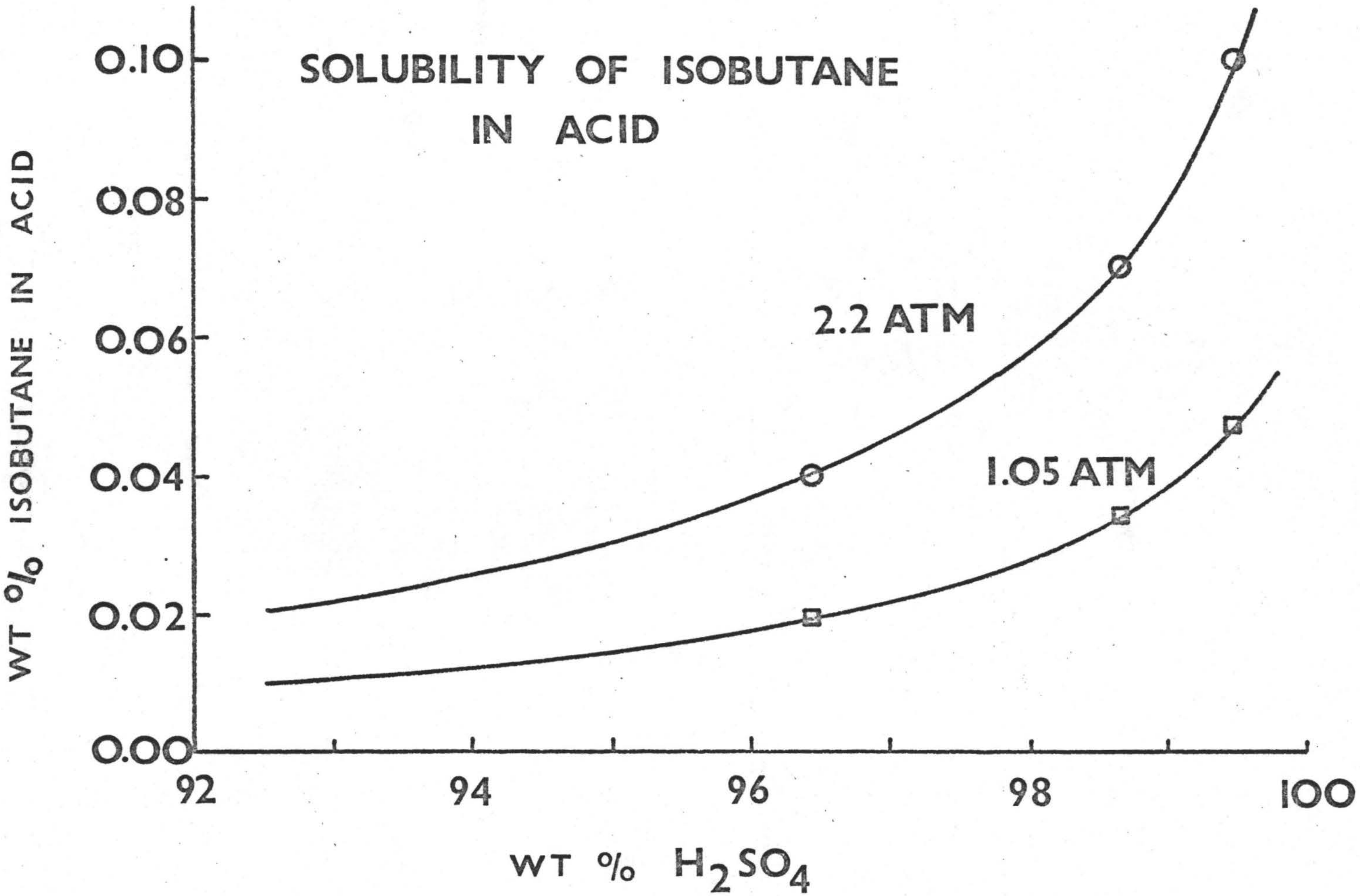
TABLE A-5

EFFECT OF WATER ON LIQUID SOLUBILITY OF ISOBUTANE IN H_2SO_4 AT 56 F

Wt % H_2SO_4	Wt % Isobutane in Acid
99.5	0.10
98.7	0.070
96.5	0.040

Since there is no data available concerning the relationship between the solubility of isobutane in acid and temperature, the assumption must be made that the solubility is the same at both 56°F and 77°F (25°C). All experiments in this study were done at 25°C. Another assumption that can reasonably be made is that the solubility is directly proportional to the pressure. The pressure at which the present work was done was consistently at about 80 cm of Hg (1.05 atm). The pressure of isobutane at 56°F is 2.2 atm. Therefore, it can be expected that the solubility of isobutane in sulphuric acid at 1.05 atm will be 1.05/2.2 times smaller than it is at 2.2 atm. The results of this are shown in Figure A-1. Since all the experiments in this study were done with acid which was very close to 93%, then it is possible to take from Figure A-1 the value of 0.01 wt % isobutane as its solubility

FIGURE A-1


SOLUBILITY OF ISOBUTANE IN ACID
2.2 ATM
1.05 ATM
WT % ISOBUTANE IN ACID
0.10
0.08
0.06
0.04
0.02
0.00
92
94
96
98
100
WT % H_2SO_4

in acid.

(c) Absorption Rate of 1-Butene into Sulphuric Acid

In 1930, H.S. Davis and R. Schuler published a paper entitled "The Relative Rates of Absorption of the Gaseous Olefins into Sulfuric Acid at 25°C" (11-12). In their experimental work, they had a cylindrical horizontal vessel half filled with sulphuric acid. Above the acid they introduced an olefin and proceeded to record the change in pressure of the olefin with time as it was absorbed into the acid. It was also possible to rotate the vessel to study its effect. When they analyzed their data, they found that if the log of the total pressure was plotted against time, a straight line resulted. These lines were then reduced to single point values through the following argument.

$$\ln \frac{1}{1-x} = kt \qquad \text{(A-3)}$$

where x - fraction of olefin dissolved in acid

t - time in seconds

k - constant in $\sec^{-1}$

or

$$\frac{1}{1-x} = e^{kt} \qquad \text{(A-4)}$$

Let $y = 1-x$

which is the fraction of olefin in the gas so that

$$\frac{1}{y} = e^{kt} \qquad \text{(A-5)}$$

but

$$y = \frac{P}{P_o}$$

where P - pressure of the system

P_o - initial pressure of the system

therefore

$$P = P_o \, e^{-kt} \tag{A-6}$$

but they wanted the rate of drop in pressure which can be obtained by differentiation (A-6)

$$\frac{dP}{dt} = -k \, P_o \, e^{-kt} \tag{A-7}$$

Davis then defined a constant which he called C, the specific absorption coefficient

$$C = \frac{V}{AP} \, \frac{dP}{dt} \text{ at constant volume.} \tag{A-8}$$

He knew that V, the volume of the vessel, and A, the surface area of the acid, were constant. He also knew that

$$\frac{dP}{dt} \quad P = \frac{-kP_o \, e^{-kt}}{P_o \, e^{-kt}} = -k \tag{A-9}$$

therefore

$$C = \frac{-Vk}{A} \tag{A-10}$$

and C was a constant measuring the volume of gas transferred/square cm of surface area/second. Note that the cc transferred are measured at the pressure of the system.

The results of these experiments are shown in Table A-6.

TABLE A-6

EFFECT OF ACID CONCENTRATION ON THE SPECIFIC ABSORPTION COEFFICIENT

RPM	$C \times 10^4$ $cm^3/cm^2/sec$			
	Acid Concentration wt %			
	95.8%	87.0%	80.0%	70.0%
0	771	95.5	9.3	0.619
28	2050	66.1	4.0	0.429

Since C, the specific absorption coefficient, is so strongly dependent on acid concentration, it is not enough just to find a value for it at about 93% acid which is the approximate concentration which all the experiments in this study were done at. It was found that a semi log plot of C versus acid concentration resulted in a straight line. This plot is shown in Figure A-2. A linear least squares fit gave the following equation.

$$\log_{10} C = -13.85 + 0.135\ (\%\ H_2SO_4) \qquad \text{(A-11)}$$

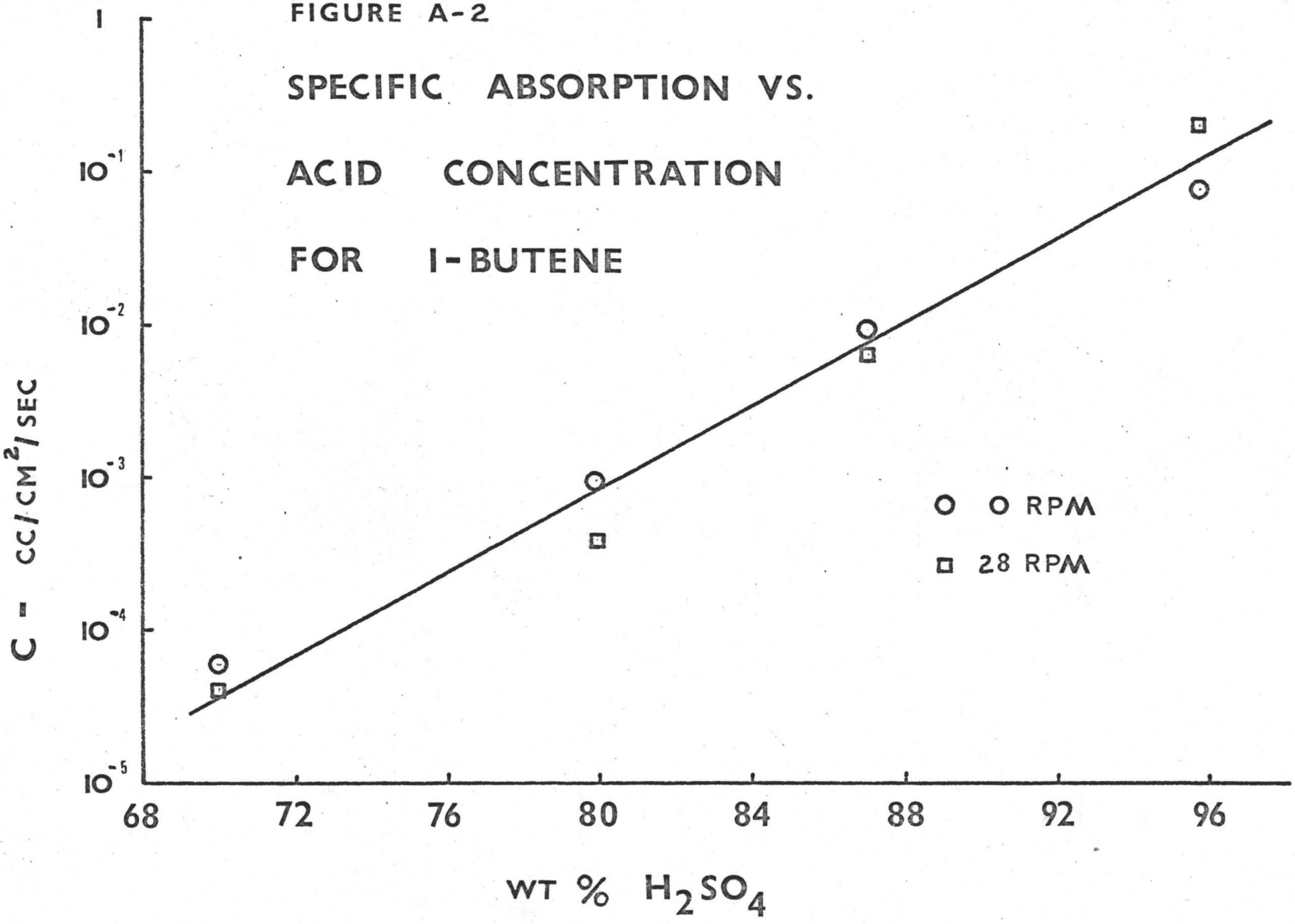


FIGURE A-2

SPECIFIC ABSORPTION VS. ACID CONCENTRATION FOR 1-BUTENE

APPENDIX 4

4. Experimental Details

(a) Description of Reactor Column

Figure A-3 is a schematic diagram of the continuous flow bubble column used in this study. Figure A-5 shows a photograph of the complete apparatus. The bubble column was built by A. Yau (11-1) and used without modification. The reactor column was made of a 5/8-in I.D. glass tube 26-in long. Three sample outlets were located at approximately 8-in, 13-in. and 18-in. from the bottom of the tube. In the present work, only the top port was used and is the only one shown on the diagram. The other tubes were sealed off. The bottom of the reactor column was fitted with a 24/40 ground glass joint.

The arrangements for acid and hydrocarbon gas inlets are shown in Figure A-4. A machined Teflon plug Y was fitted into the ground glass joint. At the bottom of the plug, two holes were drilled. The vertical hole T was tapped for 1/16-in. stainless steel Swagelok male connector. The nozzle for the hydrocarbon inlet was made of a 7-in. 0.028 in O.D. stainless steel needle tubing V inserted into a 1/16-in. O.D. stainless steel tubing W. The tip of the nozzle was fitted with a 1/4-in AWG #20 Teflon thin wall tubing X. The assembly was held in place by the 1/16-in Swagelok male connector. The hole which was drilled 45° to the vertical, was tapped for 1/8-in stainless steel Swagelok mole connector and was used as the acid inlet U. The reactor

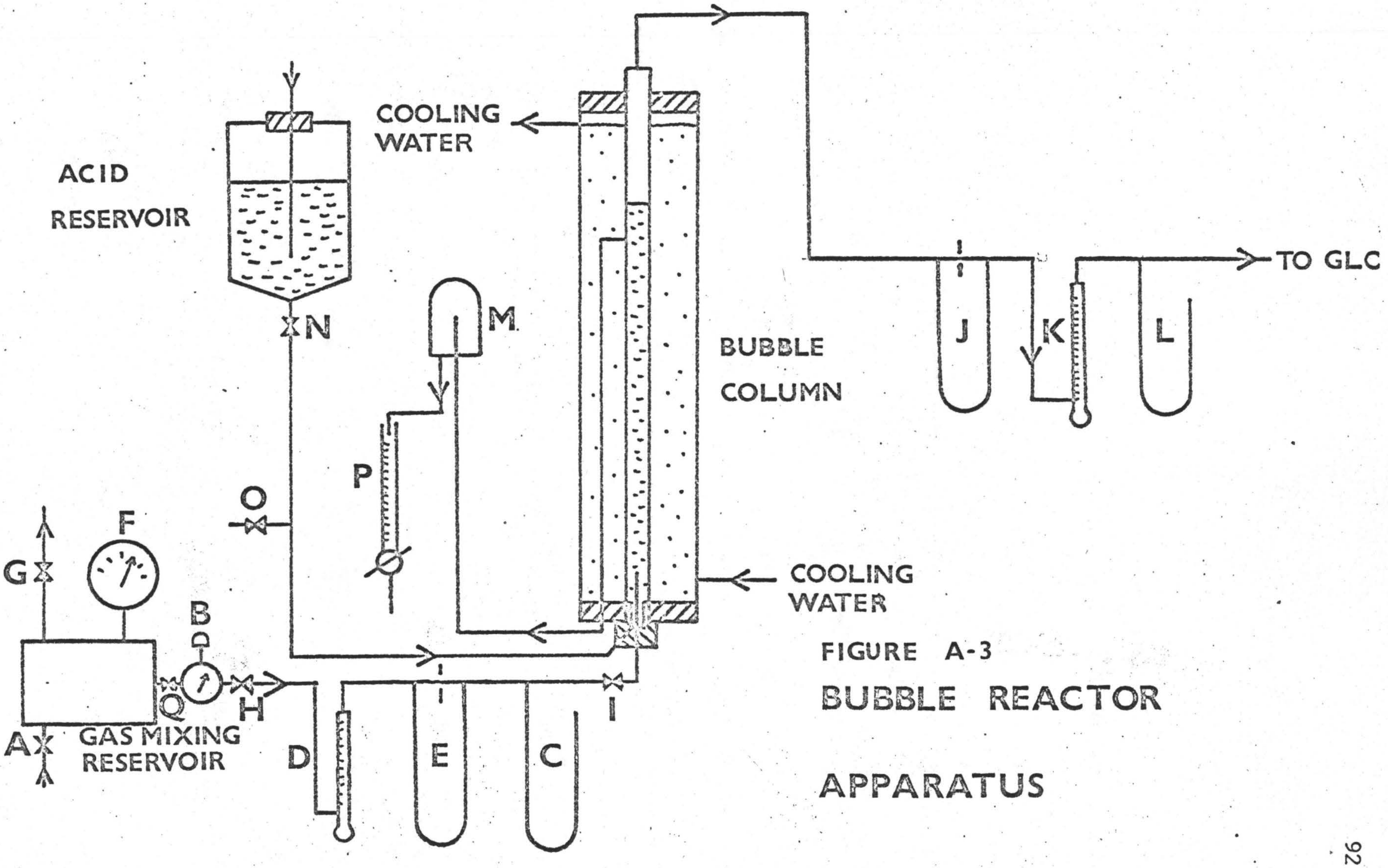


FIGURE A-3

BUBBLE REACTOR

APPARATUS

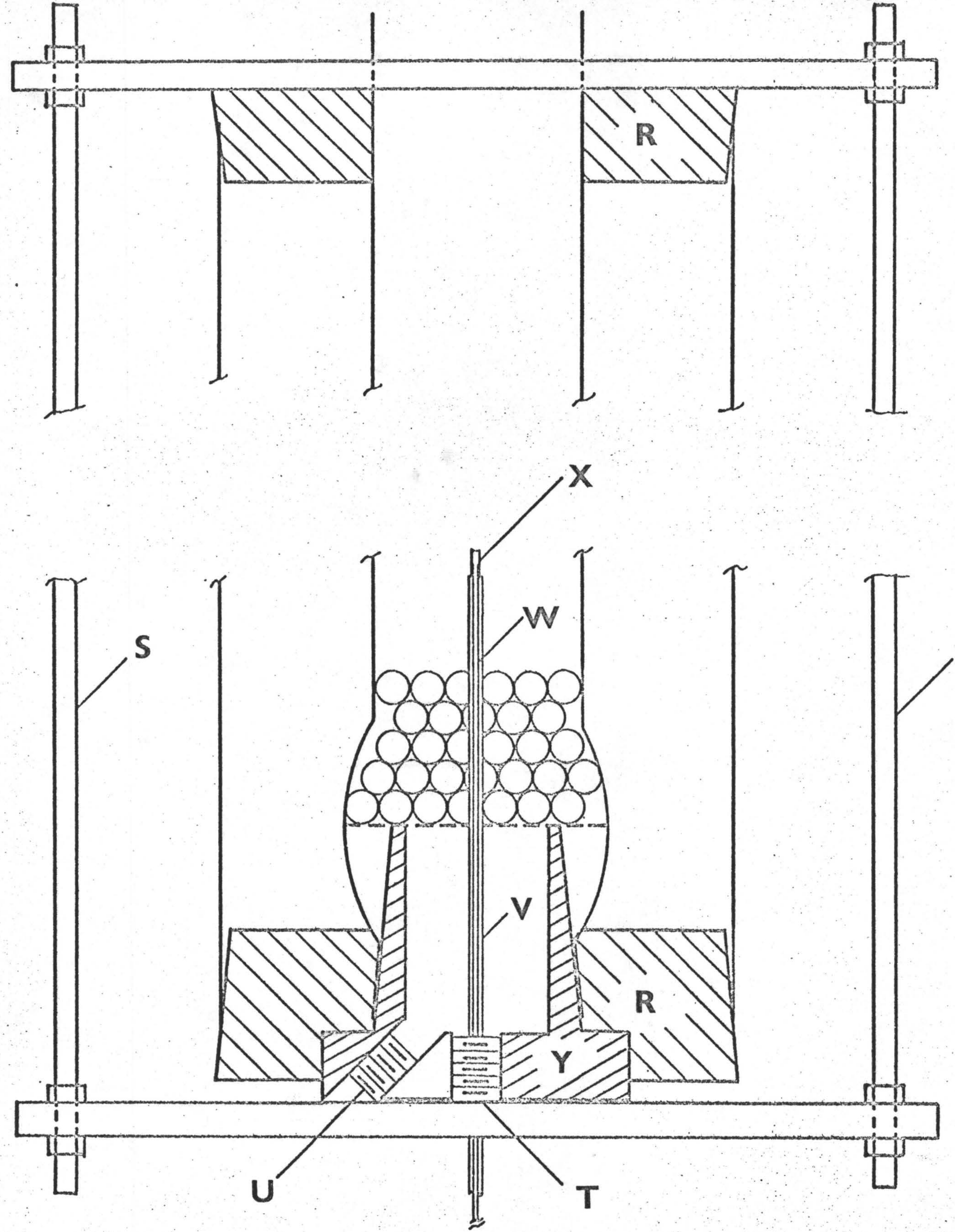
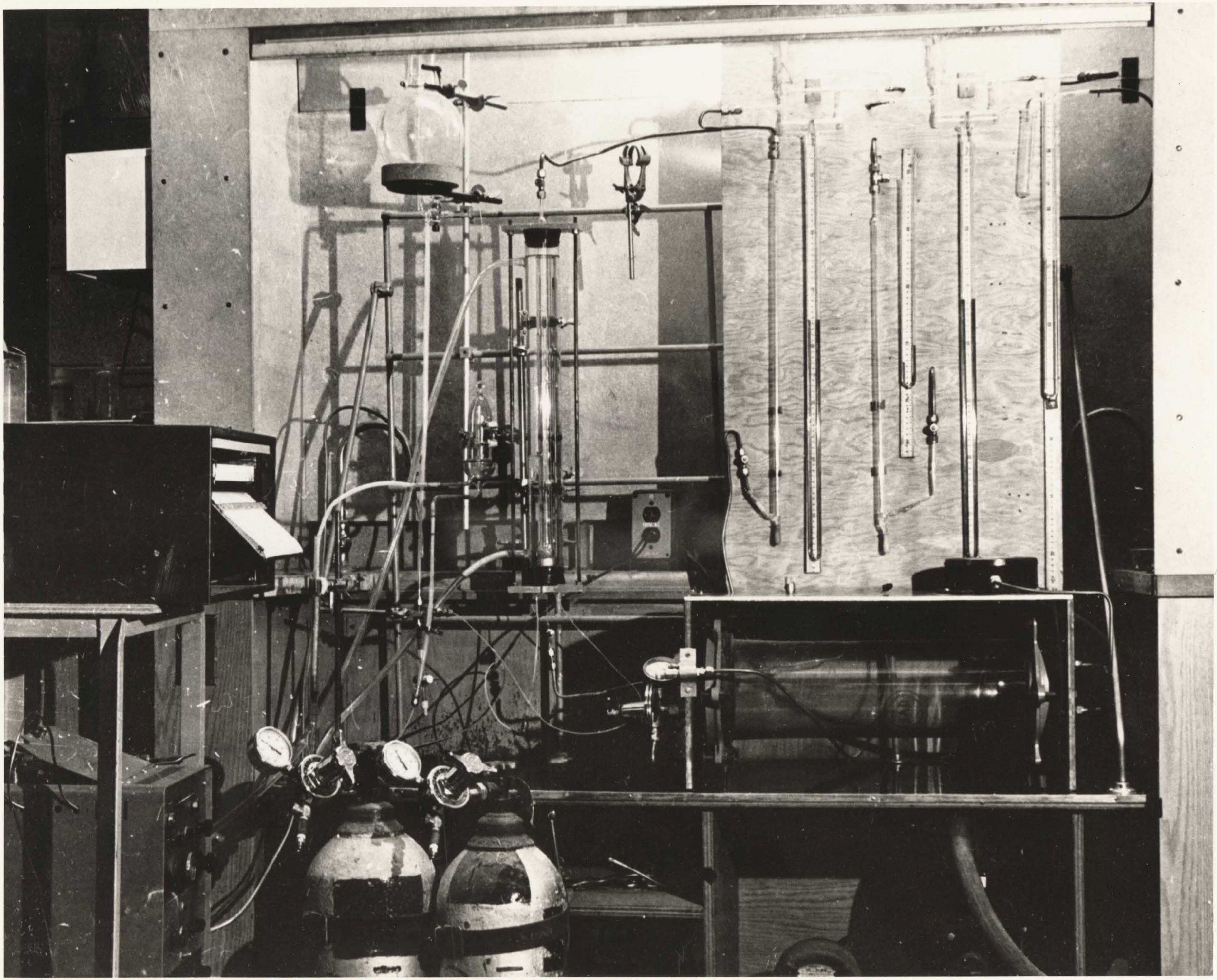


FIGURE A-4
DETAILS OF NOZZLE SECTION

FIGURE A-5



column and the cooling jacket were held together by means of rubber stoppers R and tie rods S as shown in Figure A-4.

(b) Materials

The following materials were used in this study:

1-butene (Matheson of Canada Limited, C.P. Grade)

Isobutane (Matheson of Canada Limited, C.P. Grade)

Sulphuric Acid (Fisher Scientific Company, Reagent Grade)

(c) Experimental Procedure

At the beginning of every experiment, the gas mixing reservoir was evacuated using the vacuum pump. It was then filled with isobutane and evacuated again. The two hydrocarbon gases were then put into the reservoir separately and allowed to stand for at least four hours. Usually the period was overnight.

After the gases were thoroughly mixed, three samples were separately taken and analysed on a Varian Aerograph Hydrogen Flame Detector Chromatograph Model 600-B using a 25 foot 1/4-in. O.D. copper tube packed with 20% propylene carbonate.

The gas mixture was then started flowing through the column followed by the acid. When the flows settled down, the required values were set and the apparatus was left for about two hours. At this time the flows were measured and the output gas analysed. The bubble frequency was measured by a General Radio Type 1531-A strobotac.

Samples of acid were taken from both the acid in the reservoir and the acid in the column. From each sample, two 20 ml aliquots were taken and made up to 500 ml in volumetric flasks. Two samples from each of the two volumetric flasks were then titrated against 1N sodium hydroxide using phenolpthalein as an indicator. The four results were averaged and used to calculate the wt % concentrations.

APPENDIX 5

5. Raw Experimental Data

Key for Tables A-8 and A-9:

1	Run Number	
2	Gas input flowrate at std. press. and temp. of system, cm^3/min.	
3	Gas output flowrate at std. press. and temp. of system, cm3/min.	
4	Bubble frequency, bubbles/min	
5	Pressure inside inlet soap film meter, cm Hg	
6	Pressure at exit of column, cm Hg	
7	Temperature of water bath, °C	
8	Atmospheric pressure, cm Hg	
9	Height of acid above nozzle, cm.	
10	Concentration of fresh acid, wt %	
11	Concentration of column acid, wt %	
12	Acid flowrate, cm^3/min	
13	Volume percent propane	into reactor
14	Volume percent isobutane	into reactor
15	Volume percent n-butane	into reactor
16	Volume percent 1-butene	into reactor
17	Volume percent butadiene	into reactor
18	Volume percent propane	out of reactor
19	Volume percent isobutane	out of reactor
20	Volume percent n-butane	out of reactor

21 Volume percent 1-butene out of reactor

22 Volume percent isopentane out of reactor

TABLE A-7

RAW EXPERIMENTAL DATA

1	2	3	4	5	6	7	8	9	10	11	12
1	16.54	16.55	1800	90.09	78.07	31.5	76.44	44.0	94.36	93.70	2.13
3	18.12	14.35	1400	91.43	77.42	27.7	76.27	43.8	94.16	93.57	2.11
4	17.87	17.00	1380	93.49	77.96	28.0	76.28	41.5	94.16	93.65	1.38
5	20.41	15.65	1208	84.58	76.70	25.0	75.22	44.6	93.60	92.34	0.85
7	18.77	18.05	1201	85.61	77.39	25.0	75.34	42.6	93.60	92.70	0.87
8	18.71	17.34	1222	90.32	77.25	25.0	75.16	42.2	93.60	93.01	0.74
12	18.25	12.78	1490	90.29	76.66	25.0	75.65	47.4	94.50	93.32	1.90
13	17.94	12.65	1370	88.09	74.82	25.0	73.74	45.7	94.50	93.52	1.85
14	17.66	14.03	1400	91.96	77.09	25.0	75.85	40.6	94.50	93.16	2.00
15	17.12	14.75	1350	90.64	76.18	25.0	74.74	40.6	94.50	93.41	0.78

TABLE A-8

RAW EXPERIMENTAL DATA

1	13	14	15	16	17	18	19	20	21	22
1	0.34	98.69	0.95	0.02	0.00	--	--	--	--	--
3	0.27	82.67	0.88	16.18	0.00	0.27	98.11	1.04	0.00	0.58
4	0.35	94.69	0.98	3.97	0.00	0.26	98.18	1.05	0.00	0.50
5	0.39	81.25	0.98	17.38	0.00	0.50	97.46	1.26	0.00	0.78
7	0.35	95.11	1.02	3.52	0.00	0.36	97.98	1.17	0.14	0.35
8	0.45	90.69	1.07	7.79	0.00	0.44	96.49	0.97	1.89	0.22
12	0.40	76.26	1.01	27.33	0.00	0.48	97.03	1.58	0.00	0.92
13	0.32	72.20	1.01	26.42	0.05	0.50	97.15	1.59	0.00	0.76
14	0.48	83.16	1.21	15.15	0.00	0.60	97.52	1.30	0.00	0.60
15	0.53	86.09	0.92	12.46	0.00	0.43	98.28	1.04	0.00	0.25