

TWO-PHASE CHEMICAL REACTION
IN A CONSTANT-FLOW
STIRRED-TANK REACTOR

by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum Refining Engineering.

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ABSTRACT

The objective of this research was to study the overall reaction rate constant, the reaction rate constants of each reaction involved in the system, and the overall mass transfer coefficient in a system of two liquid phases with chemical reactions taking place in both phases. To accomplish this objective the mononitration of benzene with mixed nitric and sulfuric acids was used.

The overall reaction rate constant of the system was found to be a function of phase volume ratio and temperature. For an average of 30 vol. per cent of acid phase and between 71 and 98°F the activation energy was 9.1 Kcal. per g. mole. Values for the individual rate constants were obtained but some of them are in complete disagreement with the theory. The reason for this could be the fact that the nitronium ion is the reactive entity and not the nitric acid. This suggests that the reaction rate equation should be expressed as a function of the concentration of the nitronium ion and not as a function of the concentration of the nitric acid.

To obtain the necessary data, a single constant-flow stirred tank reactor was used. The data were collected from the steady state of the system with the system attaining steady state in about 3 1/2 hours of operation. Steady state temperature varied from 71 to 98°F. for overall holding times from 25 minutes to 34 minutes.

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INTRODUCTION

Many industrial chemical reactions such as nitrations, alkylations and sulfonations are necessarily carried out in systems of two fluid phases. In some cases fluid-fluid reactions may also be made to take place to facilitate the removal of an unwanted component from a fluid or a desired product of reaction as is the case of "extractive" reaction. This is defined by Piret and co-workers (1) as one in which an immiscible solvent is deliberately added to an homogeneous system in order that extraction of a product and conversion be carried out simultaneously.

Reactions between two relative immiscible liquids are greatly influenced by the mutual solubilities of the two phases. They are favored by intimate intermixing to produce a highly extended interfacial area in the nature of an emulsion and to approach an equilibrium distribution of all components in the two phases. Many of these reactions are carried out in well-agitated tank-type reactors.

Although a large number of publications have been devoted to this subject of chemical reaction in two phases, liquid-liquid, or gas-liquid system accompanied by mass transfer, the problem has been only partially solved. For many of these reactions the theory and mechanism are better understood than they were several years ago. However, from an engineering viewpoint better understanding is needed of the kinetics and of the mass-transfer coefficients between the two phases. Solubilities of the various components in each phase and mixing characteristics at various levels of agitation are also of interest.

This study was undertaken to throw some light on these problems, especially on kinetics and mass transfer. For this purpose, the nitration of benzene to mononitrobenzene with nitric acid, especially as mixed nitric and sulfuric acids, was chosen.

This nitration was carried out in a single constant-flow stirred-tank reactor and data were collected from steady state conditions.

LITERATURE SURVEY

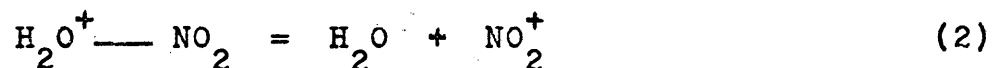
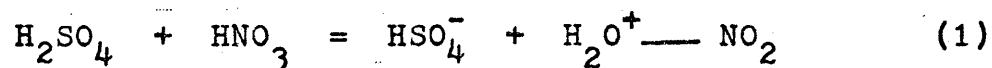
Nitration of benzene, as well as nitration of other aromatic hydrocarbons, is a very important industrial reaction that has been greatly studied and its theory and mechanism are better understood. The most common medium for nitration of aromatic hydrocarbons is mixed acid, this is a solution of HNO_3 , H_2SO_4 and H_2O . For economic reasons H_2SO_4 is used but other strong acids such as perchloric acid, hydrogen fluoride, acidic ion-exchange resins and boron trifluoride can be used. Acetic acid and other relatively weak acids are sometimes used for the nitration of easily nitratable hydrocarbons.

Bennet (2) reports that the function of H_2SO_4 in aromatic nitrations is 3-fold: (a) to produce the nitrating agent (NO_2^+) from HNO_3 , (b) to react either as HSO_4^- or H_2SO_4 with the proton that is released at the site of substitution, and (c) as a solvent for the hydrocarbon.

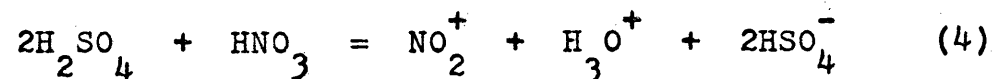
Reference has been made several times to the existence of the nitronium ion and nitration through it. Nitration of aromatic hydrocarbons through the nitronium ion is an old

theory proposed by Euler (3) in 1903, and frequently supported on indirect grounds since that date, (4,5,6); but it was not until 1946 that the existence of the ion was demonstrated (7,8,9,10). Its formation in large amount in certain solutions, notably in sulfuric acid solution, has been demonstrated by cryoscopic measurements and by spectroscopic studies on such solutions.

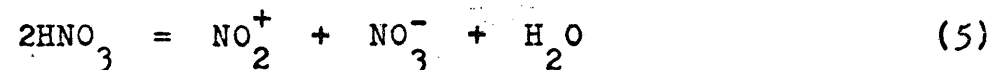
From cryoscopic measurements made by Gillespie and others (8) it was concluded that nitric acid in solvent sulfuric acid produces the nitronium ion according to the following equilibria:



Equations (1) and (3) represent the expected acid-base equilibria. The overall equilibrium may be expressed as:



Cryoscopic (11) and Raman spectroscopic (12) measurements indicate that pure nitric acid contains the nitronium ion, as a result of the ionization:



The extent of ionization of pure nitric acid according to eqn. (5) is small compared with that of nitric acid in sulfuric acid, where it is essentially complete.

The fact that the nitronium ion is present in the nitrating medium does not prove that it is a reactive entity in aromatic nitrations. Evidence that it derives mainly from kinetic studies. The presence of the nitronium ion in aqueous sulfuric acid has already been discussed. The other possible nitrating entities present under these conditions are nitric acid and the nitric acidium ion (H_2NO_3^+) which is formed as follows:

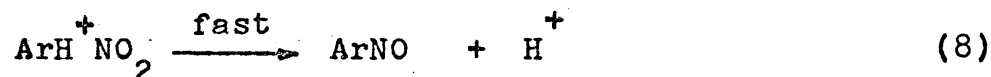
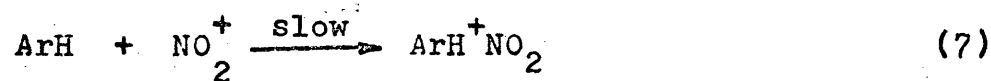


Halberstadt (13) has shown that the variation of the rate of nitration when water is added is not related to the change in concentration of nitric acid. Therefore the possibility that nitric acid be the reactive entity has been eliminated. According to Norman and Taylor (14), if the nitric acidium ion were the reactive species "the rate of nitration should follow the Hammett acidity function, H_0 , whereas in practice it follows the J_0 function over a wide concentration range, as expected if NO_2^+ is the reactive entity".

In pure nitric acid, Norman and Taylor (15) point out that "nitric acid itself is not the reactive species, for the addition of nitrate ions and of sulfuric acid, which should not significantly alter the concentration of nitric acid,

affects the rate of nitration appreciably".

Concerning the mechanism by which the nitronium ion reacts with aromatic hydrocarbon, some theories have been proposed. The most accepted theory is that two stages are involved, a slow uptake of nitronium ion followed by rapid transfer of the proton. This mechanism can be written as follows:



where ArH represents the aromatic hydrocarbon. The nitration process is then completed by the following reaction:



Of all the reactions that take place during the nitration, eqns. (1), (2), (3), (7), (8) and (9), reaction (7) is probably the rate-controlling chemical step (16).

As for rate of nitration of aromatic hydrocarbons, Martinsen was the first to obtain a definite order. He found that the nitration of nitrobenzene with nitric acid using sulfuric acid as solvent was a second-order process. This result was later confirmed by Westheimer and Kharasch (5) and Bennett and others (17).

Ingold (18) pointed out that nitration with nitric acid used as a solvent is a first-order process. This process is

what the previous one would become if nitric acid were in constant excess, as it necessarily is when it is the solvent. He also said that for some aromatic nitration in organic solvents, especially nitromethane and acetic acid, usually with nitric acid in constant excess over the aromatic compound, the reaction order is zeroth. This means that nitration proceeds at a constant rate, independently of the concentration of aromatic compound. The reaction will suddenly stop when no more aromatic hydrocarbon is left.

On nitration of benzene, previous studies (19) have shown that the reaction between benzene and nitric acid in mixed acid is essentially irreversible.

Lewis and Suen (19) state that, in the nitration of benzene with mixed acid, reaction occurs in both phases. The rate in the acid phase being several fold the rate in the organic phase. They point out that "the rate of reaction is extremely sensitive to the composition of the acid phase". They also say that "the rate of nitration doubles, other things being equal, for a temperature rise of about 10°C".

Rate equations for mononitration of aromatic hydrocarbons with mixed nitric and sulfuric acids have been developed by Hougen and Watson (20) and Biggs and White (21). Hougen and Watson developed the following equation assuming that agitation is sufficient to approximate equilibrium between the phases.

$$r = k x_{Aa} \gamma_{Aa} x_{Bb} \gamma_{Bb} (V_a + V_b K') \quad (10)$$

where r = moles of A transformed per unit time per unit volume of total system

k = reaction velocity constant ($k = k_a K_B$)

K' = $k_b K_A / k_a K_B$

K_A, K_B = distribution equilibrium constants

x_{Aa} = mole fraction of HNO_3 in acid phase

x_{Bb} = mole fraction of aromatic in organic phase

γ_{Aa} = activity coefficient of HNO_3

γ_{Bb} = activity coefficient of aromatic

V_a, V_b = fractional volumes of a and b phases, respectively

Subscripts A and B refer to HNO_3 and aromatic, respectively
Subscripts a and b refer to phases a and b, respectively

They also say that "the overall reaction velocity constant k is a function of temperature which may be expressed by the Arrhenius equation".

Biggs and White (21) developed a rate equation expressed also as a function of mole fractions, activity coefficients, rate velocity constants and volume fractions.

$$r = x_{Aa} x_{Bb} \gamma_{Aa} \gamma_{Bb} (k_a V_a + k_b V_b) \quad (11)$$

The notation for eqn. (11) is the same as for eqn. (10).

In the same paper they correlated the rate of reaction of benzene as a function of temperature, volume percentage of acid phase and composition of the reactants, v.g. nitric acid and benzene.

Although most of the facts presented in this section were not directly associated with the nitration of benzene, many, if not all of them, represent very well this particular reaction.

EXPERIMENTATION

The experimental equipment, materials of construction, reagents, methods of analyses and procedure used in this study are described in the following sections.

Equipment and Materials of Construction

A flow diagram of the equipment used in this study is shown in figure 1. Mixed acid and benzene flowed by gravity from constant-head tanks through rotameters. Before entering the reactor the reactants were passed through coils immersed in a constant-temperature bath to insure a constant inlet temperature of the reactants. Then they flowed into the reactor where good mixing was provided with two turbine-type impellers driven by a high, variable-speed motor. The product from the reactor overflowed into the separator where the two phases separated completely. In the same way the lighter organic phase overflowed from the separator and the heavier acid phase was syphoned from the bottom of the separator.

The reactor was a round-bottom baffled tank of Pyrex

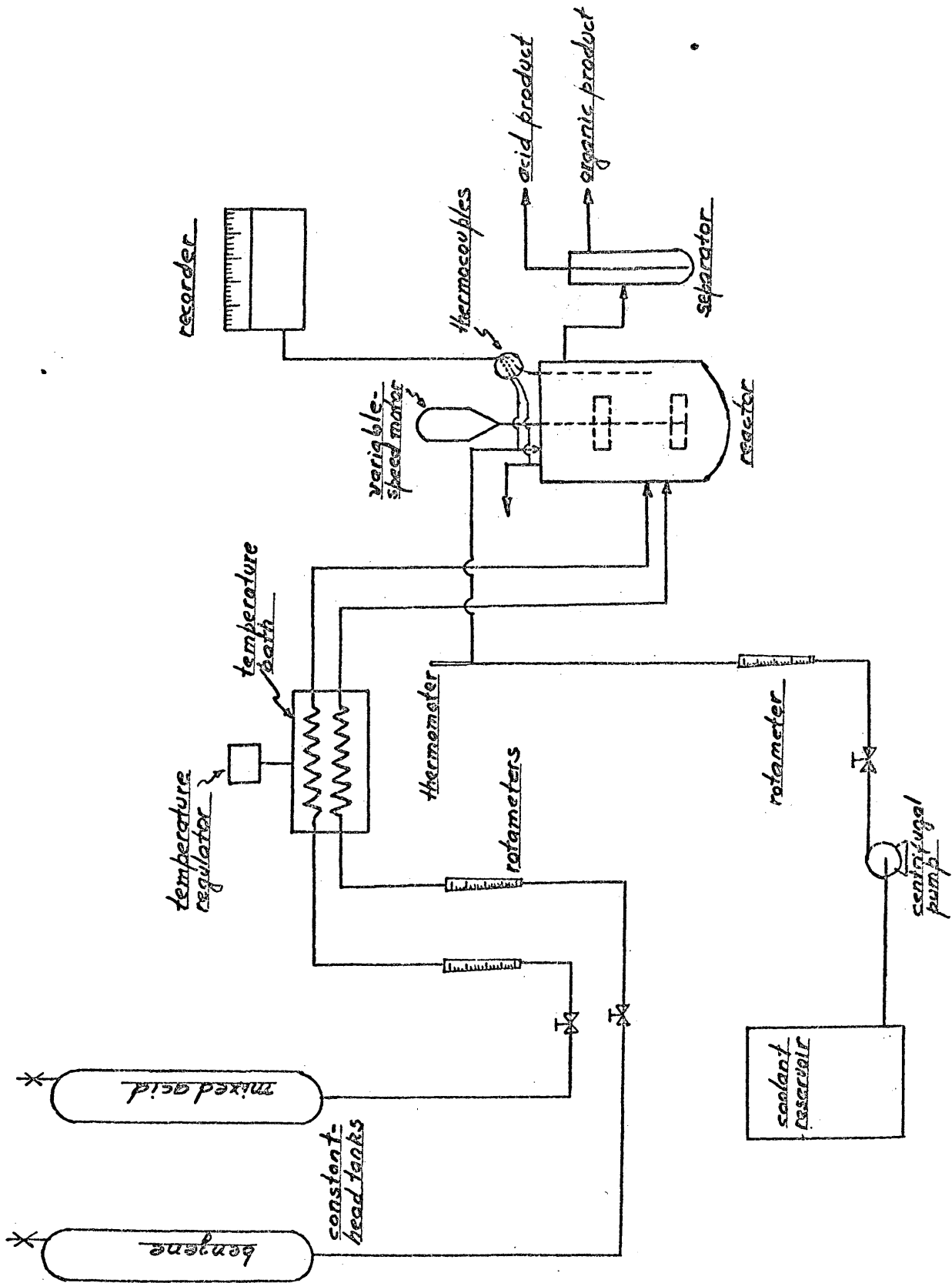


Figure 1: Flow diagram

glass, with four 1/2-in. equally spaced baffles. The round bottom of the reactor together with the baffles, which maintained a fairly uniform fluid level, provided a good circulation of the reactants that improved the emulsion characteristics of the two phases. The reactor (figure 2), 4 in. wide and 7 in. high from bottom to outlet, was insulated with a 1-in. thick layer of asbestos cement. The reactants occupied a volume of 1.18 liters. The constant-head tanks and the separator were also of glass, and the separator was insulated.

Stainless steel, type 304, was used for the stirrer shaft, the impellers, cooling coils of the reactor, and the heating coil for the mixed acid feed. Copper tubing was used for the heating coil of the benzene stream. Cooling coils of the reactor were 20.5 ft. long, 1/4 in. in outside diameter, and 0.02 in. thick. Effective heat-transfer area was 1.26 sq. ft. The heating coil for mixed acid was 20 ft. long and 1/4 in. in outside diameter, the one for benzene was 14 ft. long and 1/4 in. in outside diameter. The two impellers, attached to the stirrer shaft, were turbine-type with six blades. The motor used for mixing was a 45,000-rpm 1/5-hp, variable-speed motor, manufactured by Precise Products Corporation.

The mixed acid and benzene flow rates were measured with precision-made rotameters manufactured by Fisher and Porter Company. The coolant, pumped by a centrifugal pump, also

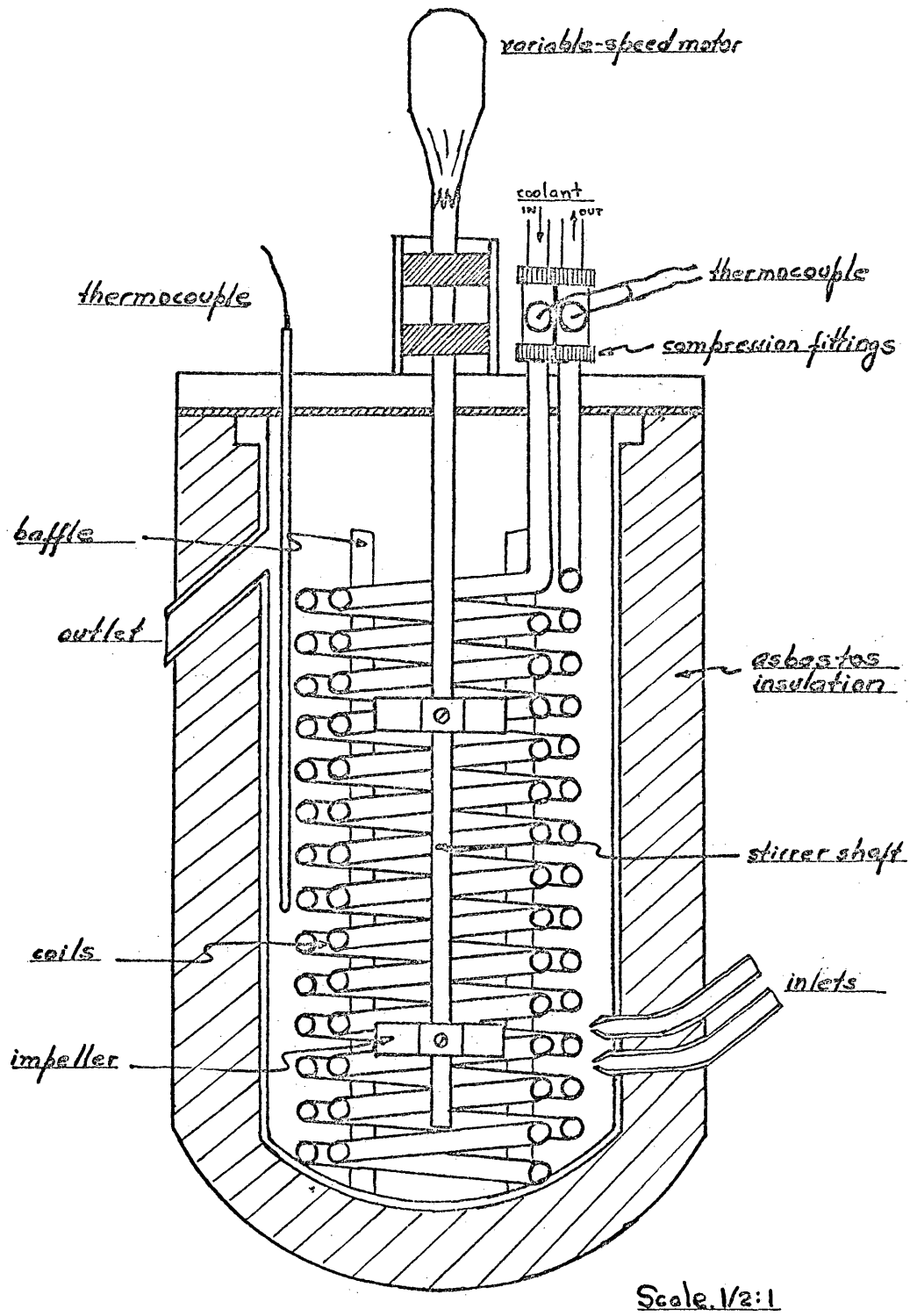


Figure 2: Reactor

flowed through the same type of rotameter. Stainless steel needle valves were used to control flow rates of both mixed acid and benzene.

The constant-temperature bath, used to keep a constant inlet temperature of reactants, had about 20 liters capacity. Commercial mineral oil was used as the heating medium. Heating coils were used and the temperature was regulated by an automatic on-off temperature regulator.

A copper-constantan thermocouple with stainless steel sheath was used to measure the temperature inside the reactor. Difference in temperature between the inlet and outlet temperature of the cooling water was measured with iron-constantan thermocouples. Both the temperature inside the reactor and the difference in temperature of the coolant were recorded on a dual-channel Hewlett-Packard strip chart recorder, Model 7100B.

A Bausch and Lomb Abbe refractometer was used to measure refractive index of the organic phase.

Reagents

Reagent-grade nitric (69-71 per cent) and sulfuric (95-98 per cent) acids were used to prepare the mixed acid and some solutions used for chemical analyses. Reagent-grade benzene manufactured by Industrial Chemicals Corporation was used in this study. Minimum purity of benzene was 99.5 mole per cent. Nitrobenzene of reagent grade was used for preparing

standardization curves used in refractive index analyses.

Reagent-grade ferrous sulfate heptahydrate was used to prepare the solutions for the analyses of nitric acid.

Reagent-grade sodium hydroxide was used in chemical analyses. 'Baker Analysed' Reagent potassium biphthalate was used as the primary standard.

Methods of Analysis

Standard methods of analysis were used for determining total acidity (22), nitric (23) and nitrous acid (24) in the acid phase. No chemical analysis was made to determine the sulfuric acid, but was determined by the difference between total acidity and nitric acid.

Refractive index was used to determine the composition of the organic phase. The refractive index was determined after the organic phase was washed with water to remove the acids and then dried with calcium chloride. Acid content of this phase was determined by the same standard methods mentioned above. A qualitative test (25) was made for dinitrobenzene.

Experimental Procedure

To obtain the necessary data for this study the equipment was set as shown in figure 1. A single constant-flow stirred-tank reactor was used and the data were collected from the steady state. To insure a constant composition of mixed acid feed, large amounts were prepared initially.

A run was started by filling the reactor with the reactants in the same proportion used in the feed. The bath through which the reactants were passed had been previously set at the desired temperature. Also the coolant flow rate was set and the inlet temperature to the reactor was kept constant by heating and cooling provided in the reservoir from which it was pumped. Immediately after the reactor was filled with the reactants, the stirrer was turned on and the valves in the feed streams were opened to obtain the desired flow rates of the reactants. For all runs the agitator speed was in the neighborhood of 3,400 rpm.

The system was brought to steady state conditions in about 3 to 3 1/2 hours of operation. For all runs, the temperature of the reactor was recorded from the beginning of the reaction. For the first 2 1/2 hours of operation, the approach of the reactor temperature to a constant value served as an indication of the approach to the steady state. After these 2 1/2 hours of operation, samples were taken from the reactor every 10 minutes, and chemical analyses were made until three consecutive samples showed constant nitric acid composition in both acid and organic phase. These samples were taken from the separator which was insulated to keep the same temperature as that of the reactor. Keeping the separator at reactor temperature maintained physical equilibrium in the separator the same as that in the reactor.

After the steady state was reached and the chemical

analyses were made, the stirrer was turned off and the valves in the feed streams and coolant stream were closed. Then the reactor was disassembled and the reactor contents were collected to measure the volume of both phases. The densities of both the acid phase and the organic phase were determined with pycnometers. The reactor was then cleaned and assembled for another run.

CALCULATION PROCEDURES

The equations used for calculations and calculation procedures are presented in this section. A digital computer program was written to make the necessary calculations.

The overall rate of reaction at the steady state was determined from the following material balances around the reactor:

$$v_{11}a_{11} - v_1a_1 - (-r_a) V_a - hA (a_1 - a_2) V = 0 \quad (12)$$

$$-v_2a_2 - (-r_o) V_o + hA (a_1 - a_2) V = 0 \quad (13)$$

equations (12) and (13) represent the material balances in the acid phase and organic phase respectively. Adding these two equations we get the following overall difference equation:

$$v_{11}a_{11} - v_1a_1 - v_2a_2 = (-r_a) V_a + (-r_o) V_o \quad (14)$$

$$\text{where } (-r_a) V_a + (-r_o) V_o = (-r) V \quad (15)$$

The overall rate of reaction can be expressed as:

$$(-r) V = v_{11} a_{11} - v_1 a_1 - v_2 a_2 \quad (16)$$

In this study no attempt was made to determine the order of the reactions since a great deal of research has been devoted to this subject. Therefore, based on previous works, the reactions are assumed first order with respect to the nitric acid and first order with respect to the benzene. Now we can write the rate equations as follows:

$$-r_a = k_a a_1 b_1 \quad (17)$$

$$-r_o = k_o a_2 b_2 \quad (18)$$

$$-r = k a b \quad (19)$$

$$a = \frac{a_1 V_a + a_2 V_o}{V} \quad (20)$$

$$b = \frac{b_2 V_o}{V} \quad (21)$$

Now by substituting eqn. (19) into eqn. (16) we get the following expression for the overall reaction rate constant.

$$k = \frac{v_{11} a_{11} - v_1 a_1 - v_2 a_2}{a b V} \quad (22)$$

It is also possible to calculate the reaction rate constants of both the acid phase and the organic phase reactions. For this the following procedure is suggested. First,

substitute eqns. (17) and (18) into eqn. (15) to get the following equation:

$$k_a a_1 b_1 V_a + k_o a_2 b_2 V_o = (-r) V = R \quad (23)$$

Now, if the sulfuric acid content of the acid phase and the temperature of the reaction are not changed and if the degree of agitation is high enough to keep the acid phase saturated with benzene, then we can say that the concentration of benzene in the acid phase, b_1 , is a constant. Under these conditions k_a is also a constant and the product of k_a and b_1 is another constant.

$$\text{let } k_a b_1 = K_a \quad (24)$$

Eqn. (23) can now be rewritten as follows:

$$K_a a_1 V_a + k_o a_2 b_2 V_o = R \quad (25)$$

In eqn. (25) we only have two unknowns, K_a and k_o . By chemical analysis a_1 , a_2 and b_2 can be determined, $(-r) V$ is calculated from eqn. (16), and V_a and V_o are determined by direct measurements. To solve for K_a and k_o we need another independent equation:

$$K_a a_1' V_a' + k_o a_2' b_2' V_o' = R' \quad (26)$$

This other equation can be obtained from a run under the same conditions as those for eqn. (25) except for a different proportion of acid phase to organic phase. This variation will increase or decrease the reaction rate by increasing or

decreasing the amount of acid phase. Provided the sulfuric acid content of the acid phase is not changed and the temperature is the same as for eqn. (25) the rate constants will be the same in each phase.

After solving these two equations, (25) and (26), simultaneously we obtain the following expressions for K_a and k_o :

$$K_a = \frac{R a_2' b_2' V_o' - R' a_2 b_2 V_o}{a_1 V_a a_2' b_2' V_o' - a_1' V_a' a_2 b_2 V_o} \quad (27)$$

$$k_o = \frac{R' - K_a a_1' V_a'}{a_2' b_2' V_o'} \quad (28)$$

Once these reaction rate constants have been determined, the nitric acid transferred from the acid phase to the organic phase can be calculated from either eqn. (12) or (13). Also from the same equations, the overall mass transfer coefficient, h_A , can be calculated.

DISCUSSION OF RESULTS

The effects of temperature and phase ratio on the overall reaction rate constant and an attempt to correlate individual reaction rate constants and overall mass transfer coefficient according to the suggested procedure were the main objective of this study. Among all the runs made, the concentration of the sulfuric acid in the acid phase varied from 0.9105×10^{-2} to 0.9235×10^{-2} g. mole H_2SO_4 per ml. acid phase. As can be seen from Appendix I, Table 2, this was almost a constant value. Although no attempt was made to study the effect of the concentration of sulfuric acid on the rate of reaction and reaction rate constants, it was observed from batch runs that this has a considerable effect on the rate of reaction. Chemical analysis showed that no sulfuric acid was present in the organic phase when the steady state conditions were reached. Neither nitrous acid nor dinitrobenzene were detected in any of the runs. Chemical analysis also showed that the composition of nitric acid in the organic phase was almost constant. These results are shown in Appendix I, Table 2. This indicates that the organic

phase at the high degree of agitation used, 3,400 rpm, was saturated with nitric acid. However it is not clear whether or not the effects of mass transfer were completely eliminated since saturation concentration should be some function of temperature and steady state temperatures were different for these studies.

The overall reaction-rate constant was calculated according to eqn. (22). A plot of $\ln k$ versus $1/T$ is shown in figure 3.

Substituting eqn. (19) into eqn. (23) and solving for k , we get the following expression:

$$k = k_a \frac{a_1 b_1 V_a}{abV} + k_o \frac{a_2 b_2 V_o}{abV} \quad (29)$$

As it can be seen, the overall reaction-rate constant is not solely a function of temperature. In the plot of figure 3 the straight line represents an average for 30 vol. per cent of acid phase. For this average and within the temperature range shown in the graph, the activation energy was found to be 9.1 Kcal. per g. mole as calculated from the Arrhenius equation. Therefore for the same percentage (30 vol. per cent of acid phase), k can be expressed as follows:

$$k = 8.3 \times 10^6 e^{-9,100/R_1 T} \quad (30)$$

The overall reaction rate constant is also a function of the sulfuric acid concentration. Therefore, eqn. (30) should

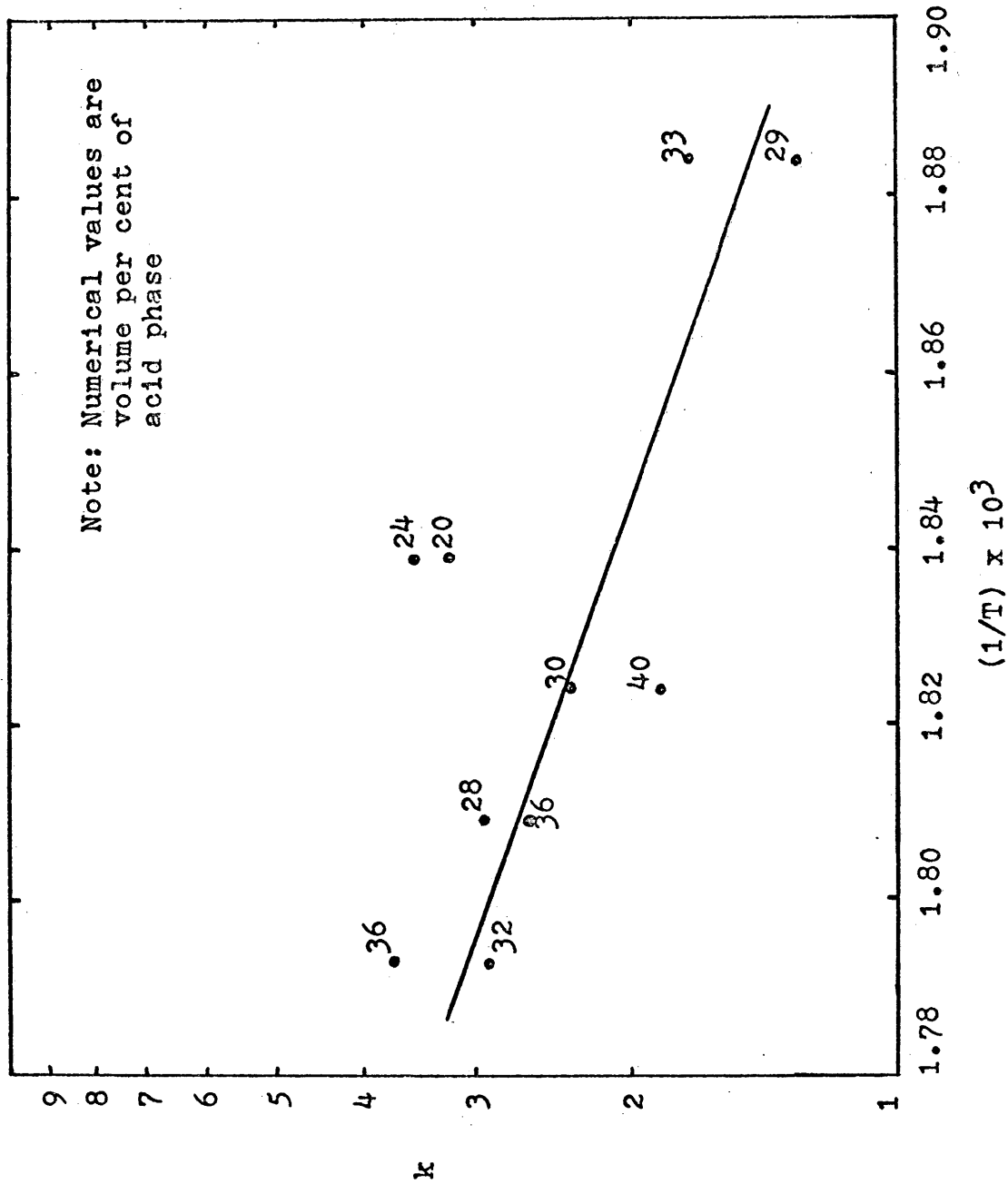


Figure 3: Effect of temperature and volume ratio on the overall rate constant

only be used within the range of sulfuric acid concentration used in this research (Appendix I, Table 2).

An attempt was made to calculate individual reaction-rate constants according to the procedure suggested before, but results are inconsistent with each other, and in some cases they are in a complete disagreement with the theory. These results are shown in Appendix II.

An explanation of these results could be the fact that it is not the nitric acid that is the reactive entity but the nitronium ion (NO_2^+); therefore, the reaction-rate equation should perhaps be correlated as a function of the concentration of the nitronium ion instead of as a function of the nitric acid, as previous authors have done. The concentration of these two compounds are different, and that of the former one can be determined by spectroscopic and cryoscopic techniques. However, at fixed sulfuric acid concentration, the nitronium ion and nitric acid concentrations are directly related. Rate constants based on one of these species should be related to the rate constant based on the other species. These facts validate the suggested procedure as a possible way to determine individual reaction rate constants, and consequently, rate of reaction in each phase and overall mass transfer coefficient.

The nitric acid transferred from the acid phase to the organic phase at steady state was calculated with these results and according to eqn. (12). These results are given

in figure 4. The overall mass transfer coefficients are shown in figure 5.

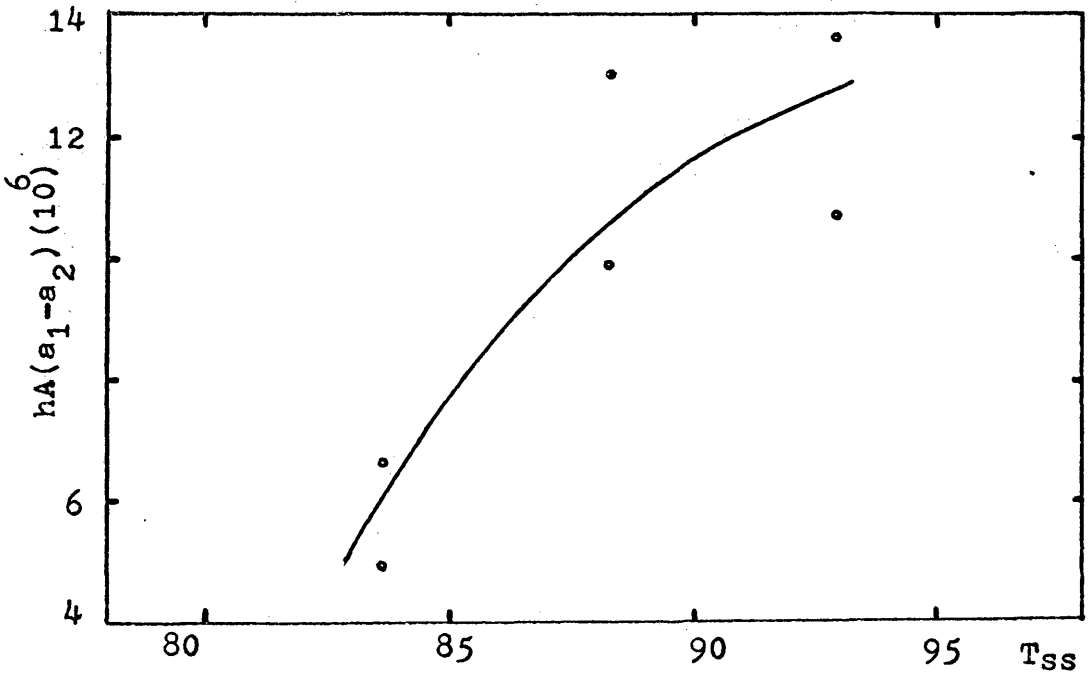


Figure 4: Effect of temperature on mass transfer

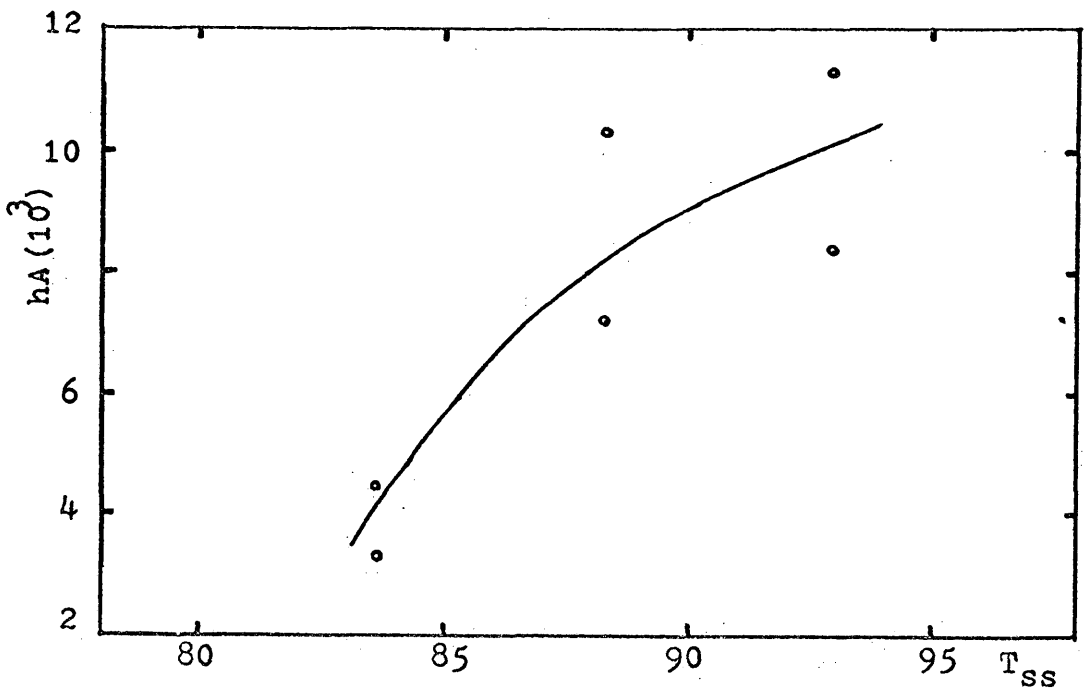
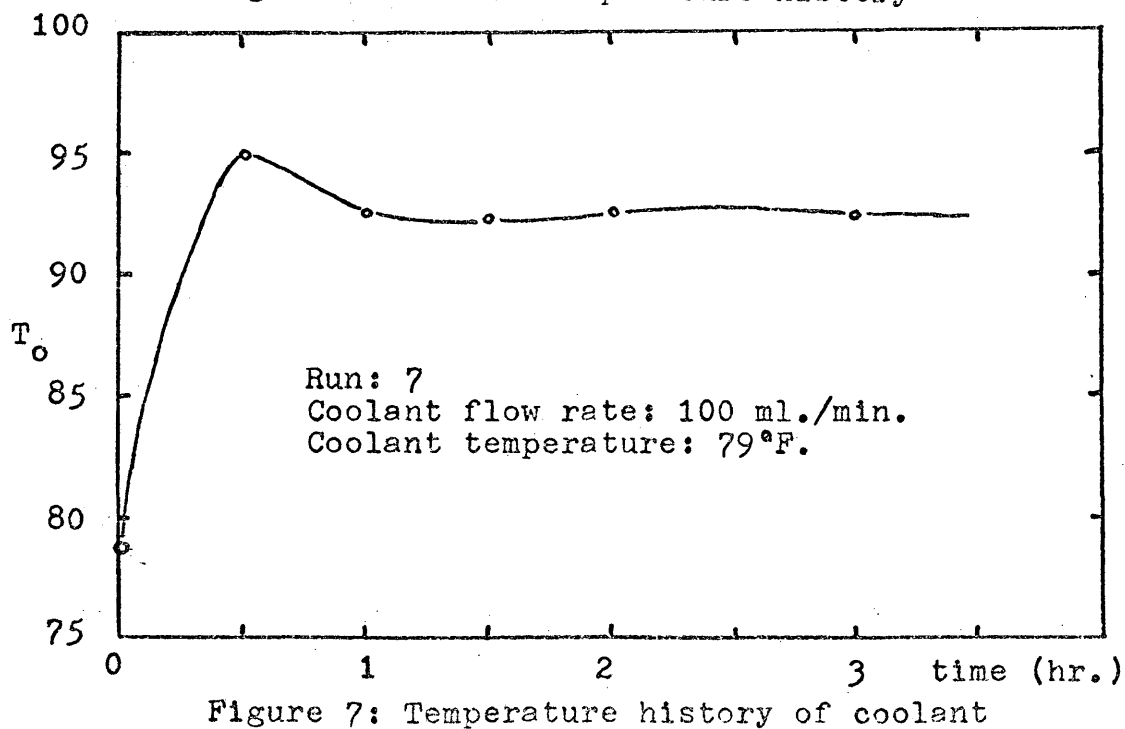
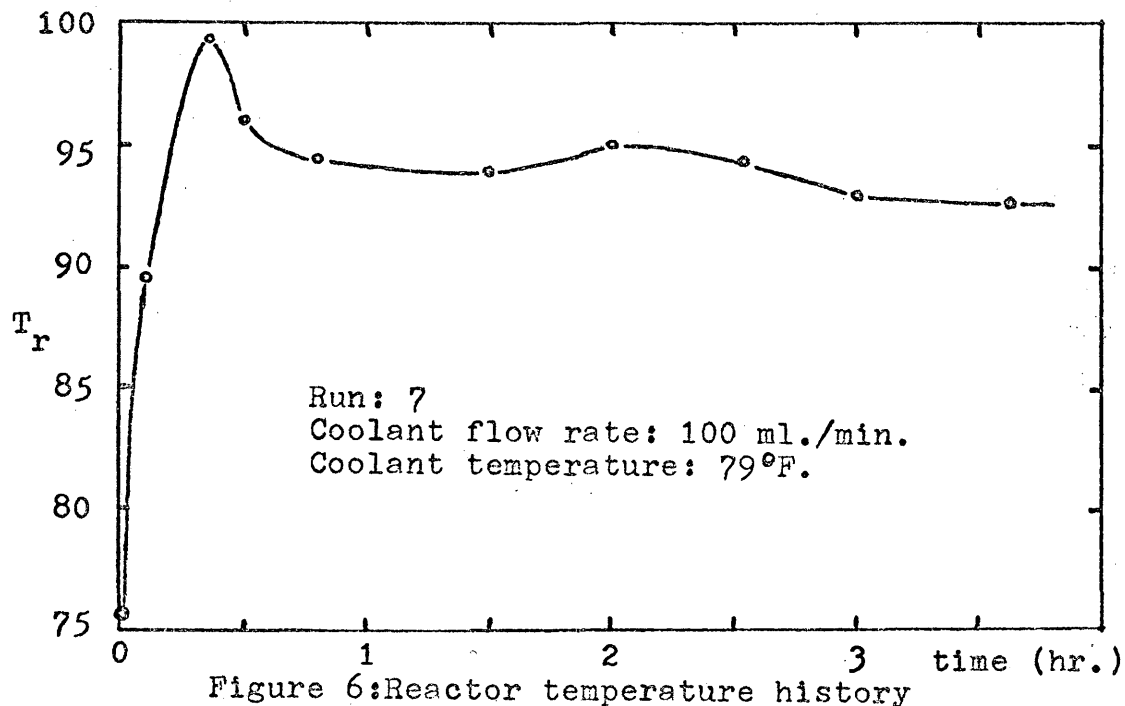


Figure 5: Effect of temperature on overall mass transfer coefficient

Reactor temperature and cooling water temperature rise were monitored during the approach to steady state for each of the experimental runs. Typical curves are presented in figures 6 and 7.



CONCLUSIONS AND RECOMMENDATIONS

From the results obtained in this study, the following conclusions were drawn:

1. Overall rate constant has been found as a function of temperature and volume per cent of acid phase which has not been done previously.

2. The rates of reaction are extremely sensitive to the composition of the acid phase, especially the concentration of sulfuric acid which acts as a catalyst.

3. The individual rate constants could be determined if the rate equations are accurately expressed as a function of the nitronium ion instead of as a function of the nitric acid.

It is recommended that further studies be conducted to correlate the concentration of the nitronium ion as a function of temperature, concentration of sulfuric acid and concentration of nitric acid. The author believes that the reaction rate constant of acid phase reaction is not only a function of temperature but also a function of the sulfuric acid concentration in the acid. This is not the case for the reaction rate constant in the organic phase reaction since no sulfuric

acid was found in that phase.

APPENDIX IDataTable 1

<u>run</u>	<u>v_{1i}</u>	<u>v_{2i}</u>	<u>V_a</u>	<u>V_o</u>	<u>T_i</u>
1	11.6	23.2	386	782	78
2	11.6	34.8	337	809	78
3	11.6	23.2	272	879	78
4	11.6	34.8	222	887	78
5	11.6	23.2	484	728	100
6	11.6	34.8	345	814	100
7	11.6	23.2	434	772	123
8	11.6	34.8	314	810	123
9	11.6	23.2	430	756	78
10	11.6	34.8	373	783	78

Table 2

<u>run</u>	<u>a₁x10³</u>	<u>a₂x10⁴</u>	<u>b₂x10²</u>	<u>Sx10³</u>	<u>T_{ss}</u>
1	1.826	1.607	1.084	9.152	70.9
2	1.721	1.516	1.086	9.201	70.9
3	1.649	1.578	1.100	9.152	83.7
4	1.647	1.564	1.107	9.221	83.7
5	1.530	1.605	1.046	9.106	88.3
6	1.421	1.516	1.073	9.194	88.3
7	1.432	1.556	1.056	9.105	92.9
8	1.365	1.516	1.077	9.194	92.9
9	1.251	1.610	1.040	9.235	97.8
10	1.237	1.516	1.055	9.201	97.8

Table 3

<u>run</u>	<u>$a_{11} \times 10^3$</u>	<u>$a_1 \times 10^3$</u>	<u>$a_2 \times 10^4$</u>	<u>$R \times 10^2$</u>	<u>Conversion</u>
1	3.018	1.826	1.607	1.040	0.291
2	3.071	1.721	1.516	0.706	0.318
3	3.018	1.649	1.578	1.732	0.287
4	3.060	1.647	1.564	1.444	0.259
5	2.976	1.530	1.605	1.002	0.408
6	3.065	1.421	1.516	1.088	0.417
7	2.977	1.432	1.556	1.315	0.426
8	3.065	1.365	1.516	1.268	0.424
9	3.050	1.251	1.610	1.616	0.501
10	3.071	1.237	1.516	1.223	0.491

Table 4

<u>run</u>	<u>(d)_{a1}</u>	<u>(d)_{o1}</u>	<u>(d)_{ss}</u>		<u>$n_D^{25 C}$</u>
			<u>acid</u>	<u>organic</u>	
1	1.573	0.879	1.568	0.896	1.5004
2	1.573	0.879	1.568	0.897	1.4985
3	1.573	0.879	1.568	0.898	1.4992
4	1.573	0.879	1.568	0.898	1.4990
5	1.573	0.879	1.568	0.898	1.5021
6	1.573	0.879	1.568	0.897	1.5017
7	1.573	0.879	1.567	0.899	1.5022
8	1.573	0.879	1.568	0.898	1.5015
9	1.573	0.879	1.567	0.900	1.5024
10	1.573	0.879	1.567	0.899	1.5023

$n_D^{25 C}$ = refractive index of the organic phase at 25.0 C.

(d)_{a1} = specific gravity of acid phase initially

(d)_{o1} = specific gravity of organic phase initially

(d)_{ss} = specific gravity at steady state

Specific gravity measurements were made at room temperature.

APPENDIX II.Individual Rate Constants

<u>T_{ss}</u>	<u>K_a x 10²</u>	<u>k_o</u>
70.9	2.47	-5.33
83.7	3.51	1.06
88.3	0.17	7.42
92.9	0.59	7.50
97.8	4.58	-6.96

APPENDIX IIINomenclature

- A = mass transfer area, cm^2
 a = overall concentration of nitric acid, g. mole nitric acid per ml.
 a_{11} = concentration of nitric acid in the acid feed stream, g. mole nitric acid per ml. mixed acid
 a_1, a_2 = concentrations of nitric acid in the acid phase and organic phase respectively, g. mole nitric acid per ml.
 b = overall concentration of benzene, g. mole benzene per ml.
 b_1, b_2 = concentrations of benzene in the acid phase and organic phase respectively, g. mole benzene per ml.
 h = mass transfer coefficient, per minute per cm^2
 k = overall reaction rate constant, ml. per minute per g. mole
 $k_a = k_{a1}$, per minute
 k_a, k_o = reaction rate constants in the acid phase and organic phase respectively, ml. per minute per g. mole
 $R = (-r) V$, g. mole per minute
 R_1 = universal gas constant

$-r$ = overall rate of reaction, g. mole per minute per ml.

$-r_a, -r_o$ = rates of reactions in the acid phase and organic phase respectively, g. mole per minute per ml.

s = concentration of sulfuric acid in the acid phase, g. mole sulfuric acid per ml. acid phase

T = absolute temperature

T_1 = inlet temperature of reactants, °F.

T_o = outlet temperature of cooling water, °F.

T_r = reactor temperature, °F.

T_{ss} = reactor temperature at steady state, °F.

V = total volume of reactants, ml.

V_a, V_o = volumes of the acid phase and organic phase respectively, ml.

v_1, v_2 = outlet volumetric flow rates of the acid phase and organic phase respectively, ml. per minute

v_{11}, v_{1i} = inlet volumetric flow rates of the acid phase and organic phase respectively, ml. per minute

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