

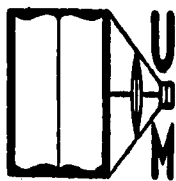
DOCTORAL DISSERTATION SERIES

TITLE REACTION RATES IN  
SULFONATION OF BENZENE  
by Sulfuric Acid

AUTHOR ROBERT C. CROOKS

UNIVERSITY of Michigan DATE 1949

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**1949**

REACTION RATES IN SULFONATION  
OF BENZENE BY SULFURIC ACID

by

Robert C. Crooks

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A dissertation submitted in partial fulfillment of  
the requirements for the degree of Doctor of Philosophy  
in the University of Michigan.

Ann Arbor, Michigan

February, 1949

TO  
JEAN

A C K N O W L E G M E N T

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O B J E C T

The purpose of this investigation was to determine the effect of reaction mixture composition and temperature on the rate of sulfonation of benzene by sulfuric acid.

S U M M A R Y

The rates of sulfonation of benzene by sulfuric acid to produce benzenemonosulfonic acid have been measured over the temperature range 90°C. to 140°C. Sufficient agitation was employed to insure that the reaction solutions were saturated with respect to benzene.

The specific reaction rate is shown to be an exponential function of the solution composition and a logarithmic function of the absolute temperature according to the equation

$$R_L/C_A = 118 (x_A - 1/2x_W + 1/4x_S)^{-9.239 + \frac{5349}{T}}$$

The method of correlation also applies to the rate of mononitration of toluene by mixed acid at 95°F., resulting in the relation

$$\frac{R_N}{x_T C_N} = 2,520,000 (x_N + 5/3x_A - 1/3x_W)^{8.08}$$

## I. I N T R O D U C T I O N

Most chemical processes employed industrially have been developed on an empirical basis. Through many trials and variations tested, they have been developed to a high degree of usefulness. By the formulation of working concepts, it has been possible to predict in some degree the effects of the various factors upon reaction rates. Such has been the experience in sulfonation processes, in which there is lacking fundamental data from which the reaction rates may be computed.

Although sulfonation of benzene has been an important step in the manufacture of phenol, there has been published but little material by which the reaction rates of that system can be predicted. Moreover, the reaction between benzene and sulfuric acid may be regarded as representative of a large class of sulfonation reactions. For these reasons, the reaction rate between benzene and sulfuric acid was chosen as the subject for this investigation, with the intent of relating the rate of reaction with the composition and temperature variables of the system.

Harvey (8) in 1922 conducted a series of sulfonation experiments by passing benzene vapor through batches of sulfuric acid for various periods of times and at various temperatures. His data include no values for reaction times less than three hours in duration, in which time the reactions had progressed by substantial amounts. Variations in the benzene flow rates used in the experiments introduces large uncertainties in the reaction rates obtained from the data.

Ambler and Gibbs (2) and Zakharov (19) proposed processes for the sulfonation of benzene in which excess benzene is circulated through the reaction mixture to remove the water of reaction by entrainment. Process conditions are described, but no information is offered on specific reaction rates.

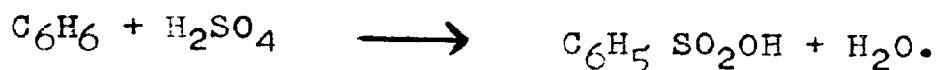
Since it was known that the rate of benzene sulfonation was very sensitive to the reaction solution composition, it was decided to employ the steady-state flow method for the determination of reaction rates. This method was chosen in preference to the batch method in order to avoid the uncertainties inherent in the differentiation of the composition-time data derived from batch experiments.

Several factors led to the decision to measure reaction rates in solutions which were maintained saturated with respect to the benzene component at atmospheric pressure. Benzene has but a limited solubility in sulfuric acid solutions, and its concentration is difficult to determine quantitatively with a satisfactory degree of accuracy. Moreover, representative samples of the reaction solutions are difficult to obtain because of vaporization during sampling. An additional advantage could be realized in that the benzene fugacity would be held constant, thus reducing by one the number of variables to be considered in correlation of experimental data.

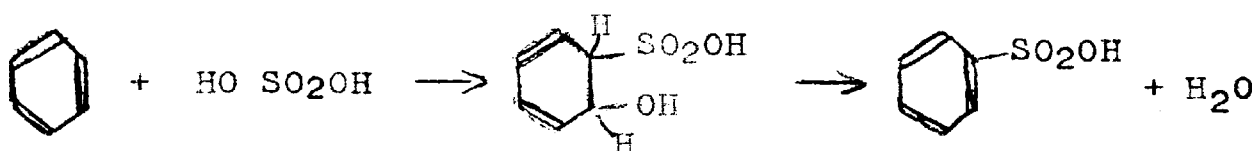
## II. THEORY

A. REACTION MECHANISM

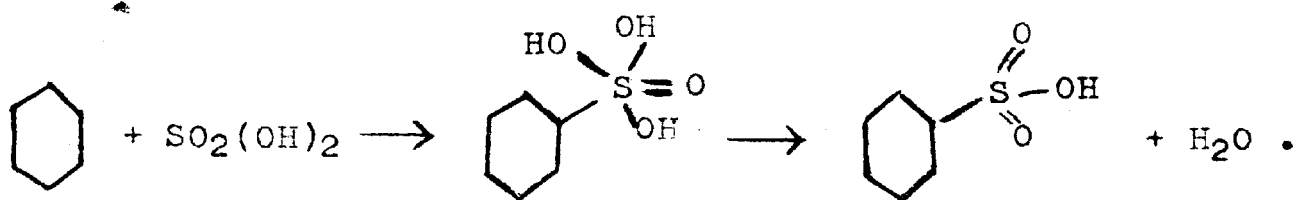
Although the mechanism of the benzene sulfonation process has not been established, many possibilities have been offered. The overall reaction may be expressed as



Wieland (17) interpreted the sulfonation process as proceeding through the addition of  $\text{HO}-\text{SO}_2\text{OH}$  to a double bond of the benzene ring with subsequent dehydration, as

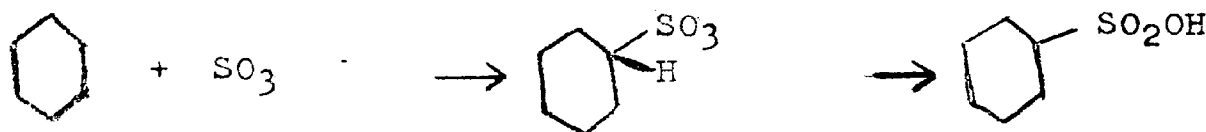


Michael (11) suggested that sulfonation may involve the addition of a hydrogen atom from the benzene ring to an unsaturated oxygen atom of the acid, and the aromatic residue to the attached sulfur. Water is then assumed to separate from the addition product, as



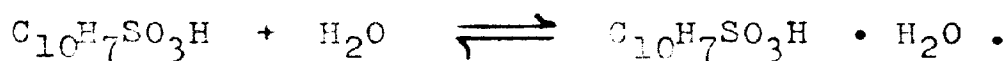
Luder and Zuffanti (9) offer an explanation on an electronic basis. According to this theory,  $\text{SO}_3$  acts as an electrophilic agent to form a coordinate bond with a carbon atom in

the benzene ring, creating an addition compound. A shift of a proton from the ring to an oxygen atom attached to the sulfur atom completes the formation of the sulfuric acid group.



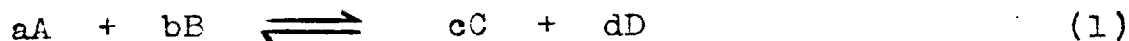
A significant factor in the action of sulfuric acid upon benzene is the effect of water upon the reactivity of the acid. Sulfuric acid is able to react with benzene only when its concentration relative to the water present is greater than a certain critical value. The limiting value of sulfuric acid concentration was designated as the "pi-value" by Guyot (7). The pi-value of sulfuric acid concentration evaluated by Guyot for benzene sulfonation was 64%  $\text{SO}_3$  by weight, corresponding to the sesquihydrate  $\text{H}_2\text{SO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ . Groggins (6) gives a value for the pi-value which corresponds to the dihydrate  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

Spryskov (14,15) showed that the limiting concentration of sulfuric acid necessary for the sulfonation reaction to proceed was influenced by the presence of sulfonate products. He attributed this as due to the dehydrating effect of the sulfonate product, in the case of naphthalene sulfonation, as



## B. REACTION KINETICS

The reaction rate of the general reaction



may be represented by the general equation

$$r = k C_A^a C_B^b \quad (2)$$

$$r' = k' C_C^c C_D^d \quad (3)$$

where,  $r, r'$  = rate of forward and reverse reactions, respectively, in mols of a particular component, per unit time, per unit volume.

$C_A, C_B, C_C, C_D$  = active concentrations of components A, B, C and D, respectively, in mols per unit volume.

$k, k'$  = forward and reverse specific reaction rates, respectively.

The dependence of the reaction rate on component concentrations is based on the mass action law formulated by Guldberg and Waage in 1867.

The effect of temperature on the specific reaction rate constant  $k$  can generally be expressed in the empirical form,

$$\ln k = \text{constant} - \frac{E_A}{RT} \quad (4)$$

Svante Arrhenius (3) recognized the similarity of the empirical equation with the van't Hoff isochore which relates the equilibrium constant of a chemical reaction with the increase in enthalpy,

$$\ln K = \text{constant} - \frac{\Delta H}{RT} \quad (5)$$

By analogy between these equations, Arrhenius suggested that there existed an equilibrium between "normal" and "active" molecules in which the activated molecules possessed an additional amount of energy. He interpreted the quantity  $E_A$  in the empirical equation

as representing the additional amount of energy a molecule must acquire before it could enter into the chemical reaction.

The dependence of the specific reaction rate constant on temperature may then be written as

$$k = A e^{\frac{-E_A}{RT}}, \quad (6)$$

where the constant  $A$  is in the nature of a frequency factor.

The transition-state theory (5) considers chemical reactions as proceeding through the formation of an activated complex from the reactant molecules. The reaction is then completed by the decomposition of the activated complex into the final reaction products. The activated complex is considered to be in thermodynamic equilibrium with the reactant molecules. The rate of reaction in the process may then be viewed as a unimolecular decomposition reaction of the activated complex, as

$$r = k^{\ddagger} c^{\ddagger}. \quad (7)$$

Since a thermodynamic equilibrium has been assumed to exist between the reactant molecules and the activated complex, the equilibrium constant for that part of the reaction may be written for a bimolecular reaction as

$$K^{\ddagger} = \frac{c^{\ddagger}}{c_A c_B}, \quad (8)$$



Since the equilibrium constant  $K^{\ddagger}$  is considered as a thermodynamic equilibrium constant, it may be related to the thermodynamic quantities  $\Delta F^{\ddagger}$ ,  $\Delta H^{\ddagger}$ , and  $\Delta S^{\ddagger}$ , which describe the changes accompanying the formation of the activated state from the reactants. Then



$$-RT \ln K^\ddagger = \Delta F^\ddagger = -T\Delta S^\ddagger + \Delta H^\ddagger, \quad (10)$$

or

$$K^\ddagger = e^{-\frac{\Delta F^\ddagger}{RT}} = e^{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}} \quad (11)$$

By substitution for  $C^\ddagger$  from equation (8) into equation (7), the reaction rate is expressed as

$$r = k^\ddagger K^\ddagger C_A C_B. \quad (12)$$

By substitution for  $K^\ddagger$  from equation (11) into equation (12), the reaction rate becomes

$$r = k^\ddagger e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} C_A C_B, \quad (13)$$

where  $k^\ddagger$  corresponds to the frequency factor  $A$  in the Arrhenius equation (6).



FIGURE 1. BENZENE SULFONATION EQUIPMENT

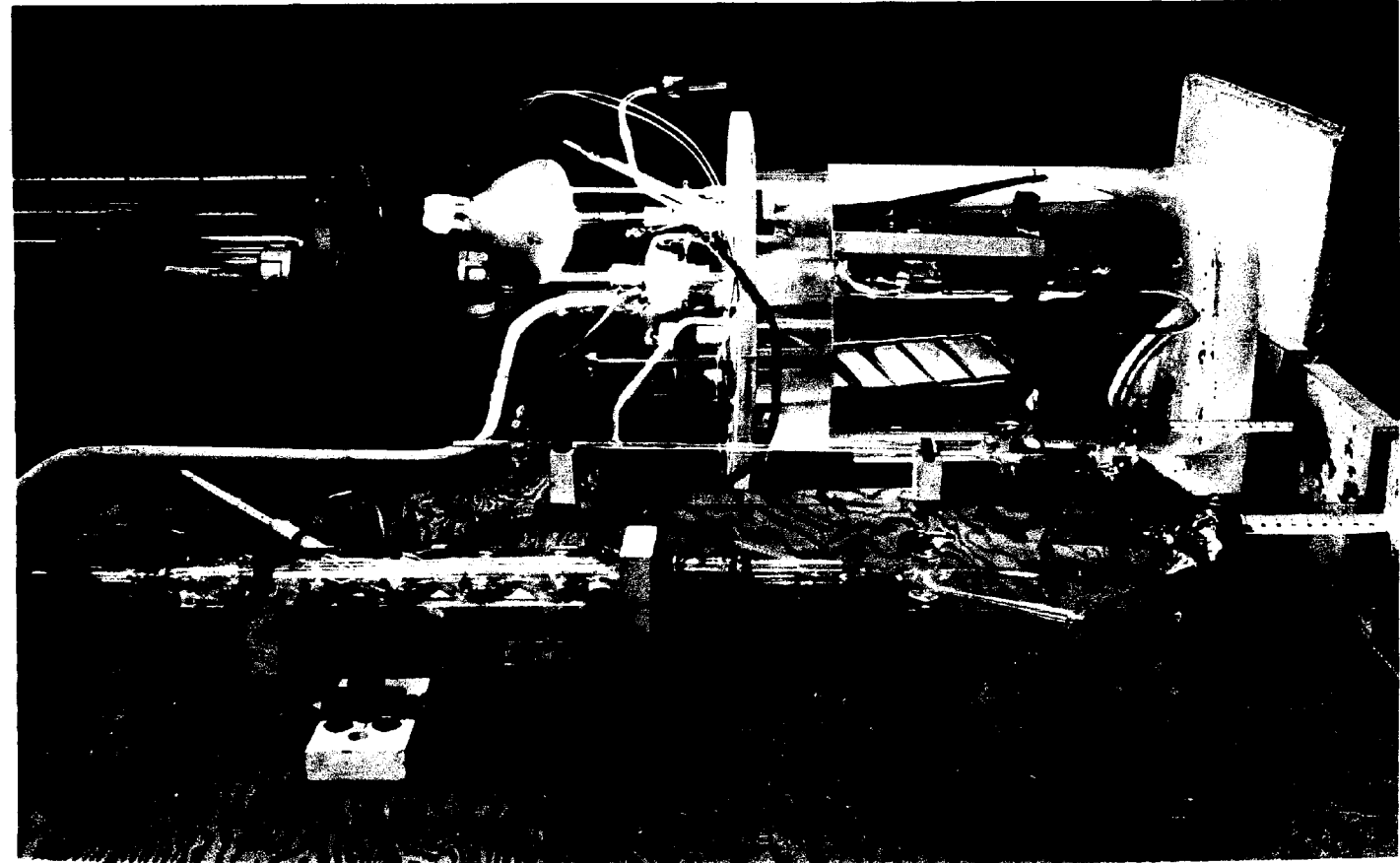


FIGURE 2. SIDE VIEW OF SULFONATION UNIT

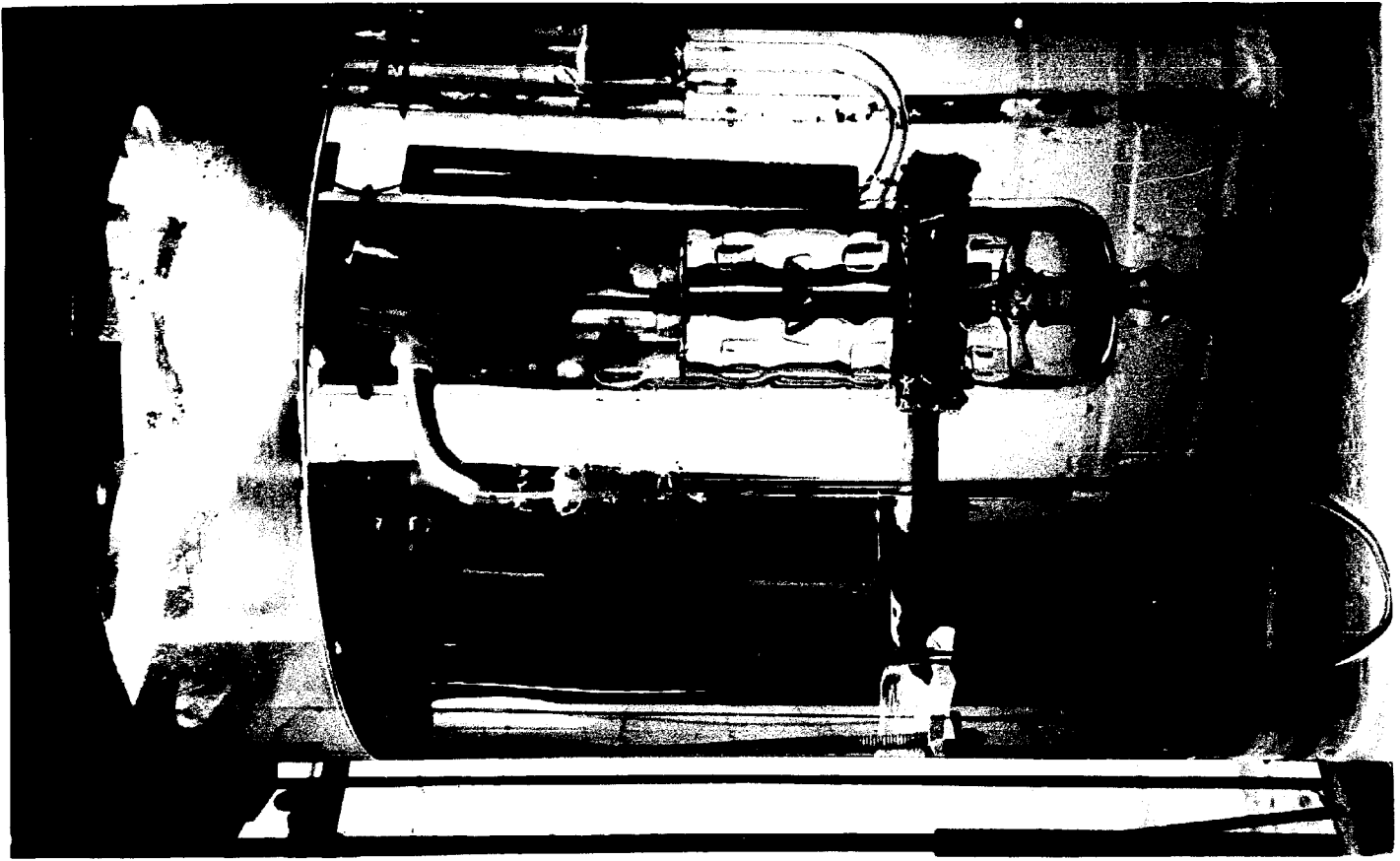


FIGURE 3. REACTION CELL

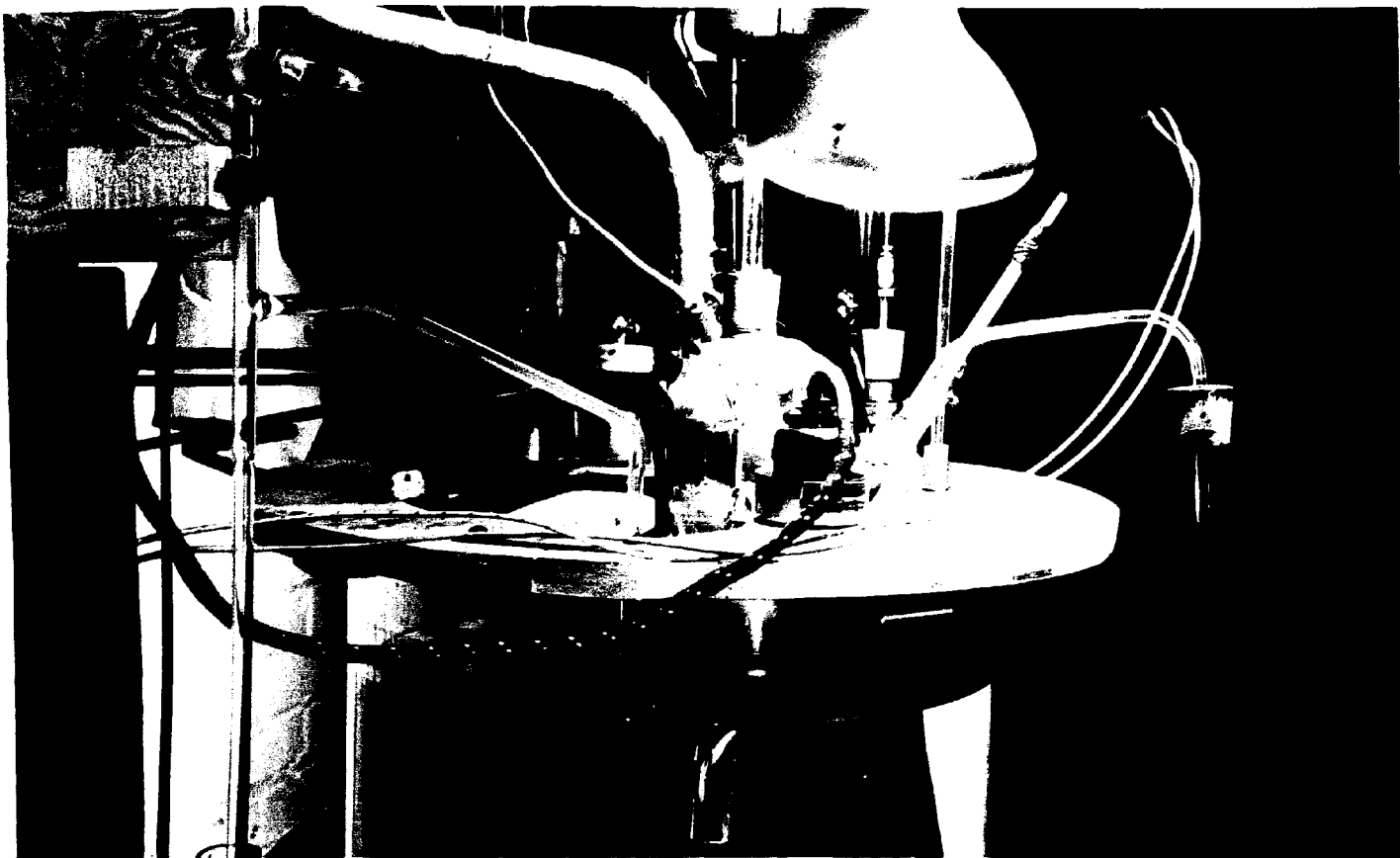


FIGURE 4. TOP OF CONSTANT TEMPERATURE BATH

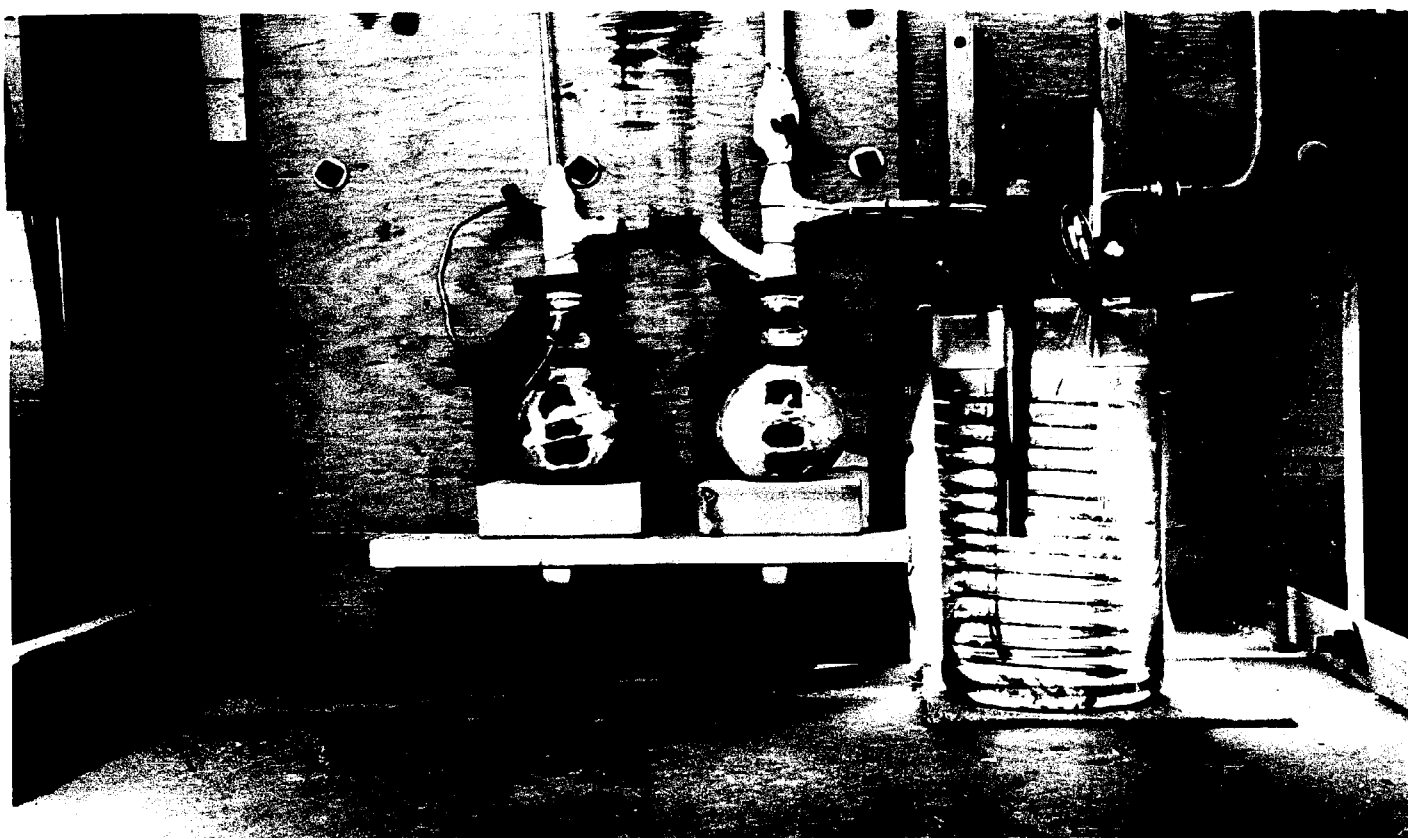


FIGURE 5. VAPORIZER, TRAP AND VACUUM RELEASE

### III. EXPERIMENTAL EQUIPMENT AND METHODS

#### A. GENERAL DESCRIPTION

The equipment was designed and constructed to conduct the benzene sulfonation reaction under steady-state conditions in a continuous-flow type reaction cell. Figure 1 shows a photograph of the experimental equipment, and Figure 6 shows a schematic diagram illustrating the method employed.

#### Material Flows.

Gravity flow of materials was employed throughout the system. Benzene and sulfuric acid reactants were fed continuously from constant-head type reservoirs A and B, shown in Figure 6, through their respective flowmeters D and E. Sulfuric acid was introduced into the cell by way of the drip cup M. Benzene liquid was passed from the hydrostatic leg E into the vaporizer F, and the vaporized benzene was introduced into the bottom of the reaction cell O by way of the insulated and electrically heated line J. Flask G was employed as a liquid trap to prevent unvaporized benzene from entering the reaction cell. Flask H employed a hydrostatic seal and served as a vacuum release to prevent the formation of a vacuum, in the benzene vapor system, which would result in drawing over acid from the reaction cell into the vaporizer lines when the equipment would be allowed to cool. Both flasks were insulated and electrically heated.

A pilot heat indicator was provided as a guide for the regulation of electric current supplied to the heater wires wound

on the benzene vapor lines and the heated flasks G and H. The pilot consisted of a piece of glass tubing which was furnished with electrical heater wire and insulation similar to that on the benzene vapor lines, and electrically connected in series therewith. A laboratory thermometer placed in the pilot tube gave a representative indication of the temperature in the electrically heated tubes and flasks.

The benzene vaporizer was constructed on the principle of flash-vaporization in order to provide a constant rate of vaporization and to minimize the variations in benzene hold-up between the reservoir and the reaction cell. Since a slight amount of pressure was required to force the benzene into the reaction cell against the hydrostatic pressure at the bottom of the reaction mixture, a stopcock was placed at the bottom of the hydrostatic leg E. Thereby a hydrostatic head of benzene was established in the leg to place the required pressure on the benzene vapor.

The level of the mixture of liquid and vapor in the reaction cell was established by the position of the liquid overflow outlet in the side of the cell. The liquid product overflowed through the side outlet into a U-tube, from which it was withdrawn by a siphon tube whose outlet was immersed in the liquid seal cup U located outside the bath. The product then flowed through a side outlet from the siphon seal into the product receiver W. Excess benzene vapor, released from the reaction mixture in the cell, passed through the insulated and electrically heated line L to the condenser AA, and the condensate was collected in the benzene receiver X.

### Reaction Unit.

In the reaction cell O, benzene vapor was maintained in intimate contact with the acid phase by the cell stirrer. A copper-constantan thermocouple Q, in a well which was immersed in the reaction liquid, was employed to measure the temperature in the reaction cell. The dibutyl phthalate bath N, in which the cell was immersed, was electrically heated and thermostatically controlled to maintain the desired temperature in the reaction cell. In order to remove the heat of reaction generated in the cell, it was necessary to maintain the bath at a temperature several degrees below the temperature of the cell. Agitation in the bath was provided by a stirrer. Power for both the reaction cell stirrer and the bath stirrer was furnished, through pulleys and round leather belting, by an electric motor equipped with a two-groove sheave.

### Measurements and Sampling Methods.

Flow rates of benzene feed, acid feed, product, and benzene condensate were determined by time and level measurements on the calibrated reservoirs and receivers. The flowmeters were used only as a guide in adjusting flow rates of benzene and acid feeds to the reaction cell.

Obtaining a representative sample of the acid phase presented several problems. A sample taken from the product overflow line at V, just before the product entered the receiver, would not be representative of the liquid phase in the cell, for the reaction would continue during the transit time of the liquid passing from the cell to the sampling point. By withdrawing a portion of the

reaction mixture directly from the reaction cell through the cell sampling tube R into a flask containing a measured quantity of water, the reaction could be halted, but the comparatively large amount of water used to stop the reaction would introduce errors in the subsequent analysis of the sample for water content. Moreover, a substantial quantity of benzene was lost by flash-vaporization when a sample was withdrawn directly from the cell. Therefore, for each run samples were taken of both the overflow product and of the cell reaction mixture, and a relation was obtained between the two samples by a material balance on their total sulfur contents. The cell sample was used for the determination of sulfuric acid and benzenesulfonic acid, and the overflow sample was used for the determination of water. The water content of the overflow sample was then corrected for the after-reaction effect by stoichiometric relationships between the overflow and cell samples. Appendix A shows the method of computation.

The cell sample was obtained as illustrated in Figure 14. A glass siphon tube passed from an Erlenmeyer flask through one of the cell front openings into the reaction mixture. A slight vacuum furnished by the siphon bottle arrangement would draw a sample from the cell into the Erlenmeyer flask. The reaction would then be halted by admixture of the sample with a measured quantity of water previously placed in the sampling flask.

The volume of the reaction liquid in the cell was measured, after completion of a run, by shutting off the flows of reactants and observing the liquid height in the reaction cell, which was calibrated as shown in Figure 9.



## B. EQUIPMENT DETAILS

### Reaction Cell.

The reaction cell was of pyrex all-glass construction as shown in Figures 3 and 8. It was designed to provide a high degree of agitation between the benzene vapor phase and the liquid solution phase for the purpose of maintaining an equilibrium distribution between the two phases. Distribution of benzene vapor into the liquid phase was provided for by a group of four glass tubes arranged radially at the bottom of the stirrer shaft. Benzene vapor passing through the bottom tube connection of the reactor entered the 12-mm. tubular opening on the agitator shaft bottom, passed radially through the 8-mm. tube distributors, and was subdivided into small bubbles by the shearing forces present at the ends of the rotating distributor tubes.

A total of five four-bladed paddles, including the distributor arms, were spaced at equal intervals along the agitator shaft; a total of nineteen baffle arms were attached to the cell wall, in four groups of four baffles and one group of three baffles. The baffle arm groups were positioned midway between the agitator paddle blade groups to check the rotary motion imparted to the liquid by the agitator, and to intensify the turbulence of the mixing action.

The 8-mm. side arm provided for the introduction of liquid reactant, the 11-mm. side arm served as an overflow through which the product left the cell, and the 20-mm. side outlet permitted excess benzene vapor to escape to a condenser. A 14-mm. sleeve provided a liquid seal to prevent escape of vapor through the agitator shaft opening at the top of the reaction cell.

The volumetric capacity of the cell at the level of the 11-mm. overflow tube bottom edge was determined to be 455 ml. with the agitator shaft in position. The volumes contained in the cell at other levels is shown by the calibration chart, Figure 9.

A thermocouple well, constructed of 8-mm. pyrex tubing and provided with a standard taper joint, was mounted in the right-front opening of the reaction cell. The end of the thermocouple well projected to a depth of approximately 1-1/2 inches below level of the reaction mixture. A copper-constantan thermocouple was used in this well. The thermocouple was compared with NBS calibrated thermometers, and the thermocouple calibration is shown in Table 1.

T A B L E 1

THERMOCOUPLE CALIBRATION

<u>Temp.</u> <u>°C.</u>	<u>E.m.f.</u> <u>Millivolts</u>	<u>Temp.</u> <u>°C.</u>	<u>E.m.f.</u> <u>Millivolts</u>
80	3.189	116	4.981
82	3.408	118	5.076
84	3.497	120	5.170
86	3.586	122	5.265
88	3.677	124	5.360
90	3.768	126	5.456
92	3.859	128	5.551
94	3.951	130	5.647
96	4.043	132	5.743
98	4.135	134	5.839
100	4.228	136	5.935
102	4.322	138	6.032
104	4.414	140	6.128
106	4.508	142	6.226
108	4.602	144	6.323
110	4.697	146	6.422
112	4.792	148	6.523
114	4.886	150	6.627

Cold junction at 0°C.

### Constant Temperature Bath.

A pyrex jar measuring 12 inches in diameter and 18 inches in height served as a container for the constant temperature bath. Dibutyl phthalate was employed as a bath liquid because of its characteristics of low vapor pressure, freedom from darkening upon exposure to elevated temperatures, high flash-point and reasonable cost. The propeller for stirring the bath liquid was constructed of a two-inch diameter copper disk with slits along its radii in a manner to form an eight-bladed propeller. Power supplied to the propeller shaft operated the stirrer at a speed of approximately 850 r.p.m.

Two knife-type heaters rated at 500 watts each, and one knife-type heater rated at 250 watts, all ratings at 115 volts, were employed as source of heat. A mercury-in-glass type thermoregulator furnished a constant-temperature control for the bath. A 10-ampere capacity "Adjustavolt" variable transformer was used to control the heating rate of the bath heaters. Additional sensitivity of temperature control was obtained by using two of the heaters continuously, and the third heater intermittently as dictated by the thermoregulator unit. The performance of the constant temperature regulation was such that no movement of the mercury column could be detected in a thermometer having one-degree Centigrade divisions.

### Power.

The reaction cell stirrer and the bath stirrer were driven by a single electric motor of the repulsion-induction type, rated at one-sixth horsepower and operating at a speed of 1140 r.p.m.

By means of a double-groove sheave, the motor operated 3/16-in. diameter round leather pulleys which supplied power to the stirrer shafts via intermediate idler pulleys. Various cell stirrer speeds ranging from 650 r.p.m. to 1770 r.p.m. were obtained by selection of different pulley diameter combinations of the intermediate and driven pulleys.

#### Reactant Reservoirs.

Calibrated constant-head type reservoirs as shown in Figure 10 were employed as a source and measure of benzene and sulfuric acid reactants. In each case the reservoir was constructed of 100 mm. O.D. pyrex tubing, with appropriate openings at top and bottom, and had a capacity of 5,000 milliliters. A glass siphon tube extended from the interior lower portion of the reservoir to a flowmeter outside, and was equipped with stopcocks to permit starting of siphon and control of flow rate. Another glass tube passed through the central top opening of the reservoir and a sleeve type seal of rubber tubing; this tube regulated the hydrostatic pressure head at the siphon inlet for maintenance of constant feed rate. Thereby was established an adjustable level in the reservoir, at which level the pressure would be of exactly atmospheric value, and the subsequent hydrostatic pressure causing liquid movement would be held constant.

The calibration constants for the reservoirs, corrected for the presence of the air inlet and siphon tubes, are:

Benzene reservoir	68.2 ml./cm.
Acid reservoir	69.1 ml./cm.

### Receivers.

Calibrated receivers as shown in Figure 11 were employed to receive and measure the liquid product and excess benzene discharged from the reaction cell. Each receiver was constructed of 80 mm. O.D. pyrex tubing and had a total capacity of 2300 ml.

Calibration constants for the receivers are:

Benzene receiver	44.5 ml./cm.
Product receiver	43.9 ml./cm.

### Flowmeters.

Pyrex glass capillary tube flowmeters were used to indicate instantaneous flow rates of benzene and sulfuric acid reactants to the reaction cell. Figure 12 shows the construction of the benzene flowmeter. The standard taper glass joint was connected to the reservoir siphon, and the bottom stopcock permitted introduction of manometer fluid. Water was used as a manometer fluid, and the pressure drop across the capillary was indicated by elevation difference between the water-benzene levels in the manometer legs.

Figure 13 shows the construction of the acid flowmeter. The acid being measured was used as the manometer fluid in the single-leg manometer.

Calibration constants for the flowmeters are listed in Table 2 .

T A B L E 2  
FLOWMETER CONSTANTS AT 25°C.

<u>Flowmeter</u>	<u>K</u>	<u>Material</u>
Benzene	35	Benzene
Acid	48	95.0% H <sub>2</sub> SO <sub>4</sub>
Acid	44	90.0% H <sub>2</sub> SO <sub>4</sub>
Acid	40	85.2% H <sub>2</sub> SO <sub>4</sub>
Acid	46	80.4% H <sub>2</sub> SO <sub>4</sub>

#### Vaporizer.

This unit provided for the vaporization of the benzene feed to the reaction cell, and is illustrated in Figure 5. A pyrex glass helical coil of 8mm. O.D. tubing, with 13 turns on a coil inside diameter of 7.5 cm., was immersed in a dibutyl phthalate liquid heating medium. A pyrex jar, six inches in diameter and twelve inches high, served as a container. Heat was supplied by a chromel-A resistance wire coil, with a heating capacity of 500 watts, immersed in the liquid bath. A bimetallic thermoregulator with relay controlled the bath temperature.

#### Trap and Vacuum Release.

These units were precautionary measures installed to facilitate the handling of benzene vapor. They were constructed of 300-ml. boiling flasks with asbestos heat insulation and wound with electric resistance heating wire. They are illustrated in Figure 5, and Figure 6 indicates their manner of operation. The right-hand flask served to trap and vaporize those portions of unvaporized benzene that might leave the vaporizer unit. The left-hand flask was provided with a hydrostatic liquid seal of mineral oil, and prevented

the formation, in the vapor system, of a vacuum which would result in drawing over acid liquid from the reaction cell into the benzene vapor lines.

#### Sampling Aids.

An aspirator arrangement, shown diagrammatically in Figure 14, was used to obtain reaction mixture samples directly from the reaction cell. A 125-ml. Erlenmeyer flask, with a side tube added, was connected to a glass sampling tube which extended to within the reaction mixture in the cell. The one-gallon bottle with a water siphon functioned to aspirate a liquid reaction mixture sample from the cell into the sampling bottle.

### C. MATERIALS

#### Sulfuric Acid.

Reagent grade C.P. sulfuric acid manufactured by the General Chemical Company was mixed with distilled water to the various concentrations desired for acid reactant solutions.

#### Benzene.

A technical grade benzene manufactured by The Barrett Division, Allied Chemical and Dye Corporation, was used as reactant. Its freezing point was determined to be  $5.28^{\circ}\text{C}.$ , as compared to a value of  $5.51^{\circ}\text{C}.$  determined on pure benzene (17). The benzene purity indicated by the freezing point lowering was 99.65% benzene, expressed on a mol basis.

#### D. RUN PROCEDURE

Each experimental run was devoted to the attainment of a steady-state condition of operation in the reaction cell. In each run, the reaction process was conducted under conditions of constant reactant feed rates, compositions, and reaction mixture temperatures, for a period of time sufficient for a steady-state condition of component concentrations in the cell to be attained.

Sulfuric acid feed stock solutions were made up by mixing the approximate quantities of acid and water, checking the concentration by titration against standard NaOH solution, making necessary adjustments in the concentration, and rechecking the final concentration by analysis.

To begin a run, the reservoirs and receivers were first readied, during which time the electric heaters in the constant-temperature bath, vaporizer and benzene vapor lines were turned on to bring the various units to their operating temperatures. Approximately one and one-half to two hours were required to heat the constant-temperature bath to the desired operating temperature. Cooling water was then supplied to the benzene condenser, and flows of benzene and acid solution were initiated by starting the siphons of their respective reservoirs. The flow rates were regulated by adjusting the elevations of the air inlet tubes, which established constant hydrostatic head conditions, and adjusted to their approximate values by reference to the flowmeters.

The temperature of the reaction cell was determined by potentiometric readings on the copper-constantan thermocouple



located in the cell. Since the reaction was exothermic, the temperature of the bath fluid was maintained somewhat lower than the temperature in the reaction mixture in order to remove the heat of reaction. The bath thermoregulator was adjusted, as necessary, to maintain the desired operating temperature in the reaction cell; a steady-state operating condition in the temperature difference between the reaction mixture and the bath was attained usually within thirty to forty-five minutes.

Readings of liquid levels in the reservoirs and receivers were taken on a preset schedule at accurately timed intervals of approximately fifteen minutes, and the rates of flow were computed therefrom. Minor adjustments in rates of flow of the reactants were made, as necessary, with the guidance of flowmeter readings.

The reaction was maintained under conditions of constant temperature and feed rates of reactants for a period of from one and one-half to five hours, depending on the rate of reactant flows, to attain steady-state operating conditions in the reaction mixture. Samples of overflow product were taken at intervals to check the degree of approach to steady-state conditions by means of density measurements. These measurements were made after the runs were completed, and served as confirmation of a steady-state condition in the reaction unit. Since there was an appreciable difference between the densities of the feed and product solutions, constancy in the density of the reaction mixture was taken as an index to achievement of steady-state conditions. The Westphal balance used to determine these densities was quite sensitive and reproducible in action.

When steady-state conditions were judged to be attained, samples for analyses were taken of the overflow product, cell reaction liquid, and benzene condensate. The overflow product sample was obtained through the three-way sampling stopcock on the overflow line. Benzene condensate samples were obtained through the three-way sampling stopcock on the condensate line below the condenser. The cell liquid sample was obtained by aspirating approximately thirty milliliters of reaction liquid into an Erlenmeyer flask as illustrated in Figure 14. In order to stop the progress of the reaction, a predetermined quantity of distilled water was previously pipetted into the flask. The quantity of water used was sufficient to lower the acid concentration below the "p-value," thereby bringing the reaction to a halt.

After the cell sample had been taken, the volume of liquid phase present in the cell reaction mixture was determined. Preparatory to this measurement, the reaction process was first continued for a period of approximately fifteen minutes after the cell sample had been withdrawn to allow replacement of the liquid removed in the sampling process, and to achieve steady-state conditions in the liquid overflow from the cell. The following operations were performed as quickly as possible and in the order mentioned to permit measurement of the liquid volume in the reaction mixture: (1) Acid feed shut off, (2) benzene pressure released at stopcock on benzene vapor feed line, (3) stirrer motor shut off, and (4) benzene feed to the vaporizer shut off. The liquid in the cell rapidly separated from the bubbles of benzene vapor, and the height at which the liquid stood in the cell was read from the metal scale mounted at the side of the cell. The volume of liquid in the cell

was then determined by reference to the cell calibration curve shown in Figure 9. Corrections for liquid volume drained from the acid flowmeter and the volume of cell liquid which backed into the benzene vapor inlet tube were applied to the volume determined from the liquid level in order to find the true volume of liquid existant in the reaction cell at the moment of shut-down.

## E. ANALYTICAL METHODS

### Sulfuric Acid in Reaction Solution.

Sulfuric acid was determined by precipitation as barium sulfate and weighing the ignited precipitate. Using a dropper bottle to facilitate weighing and transfer operations, approximately eight grams of liquid sample were transferred to a 250 ml. volumetric flask. The sample weight was obtained by the difference between the initial and final dropper bottle weights. The volumetric flask was filled with distilled water to the calibration mark and the solution thoroughly mixed. Two 25-ml. aliquot portions were placed in 400-ml. beakers for sulfate analysis; at the same time two 25-ml. aliquot portions were placed in Erlenmeyer flasks for subsequent determination of total acidity by titration. In the 400-ml. beakers, the sulfate samples were diluted with 200 ml. distilled water, heated to boiling temperature, the sulfate precipitated as  $\text{BaSO}_4$  by addition of 25 ml.  $\text{M}/4 \text{ BaCl}_2$ , and the precipitate digested for one hour. The barium sulfate precipitates were transferred to porous-bottom porcelain crucibles, washed, dried and ignited at a low red heat for about fifteen minutes. After cooling in a desiccator, the precipitates were weighed in the crucibles. The percentage of sulfuric acid in the sample was computed from the barium sulfate weights as described in Appendix A.

### Sulfuric Acid in Acid Reactant Feed.

Concentrations of  $\text{H}_2\text{SO}_4$  present in the acid reactant feed solutions were determined volumetrically by titration with standardized NaOH solution. The procedure employed for this determination

was identical with the method described below for the determination of total acidity of reaction solution samples.

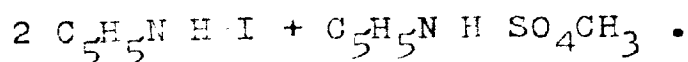
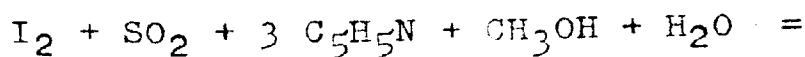
#### Total Acidity of Reaction Solution.

The 25-ml. aliquot portions of reaction solution sample, previously placed in Erlenmeyer flasks as described under "Sulfuric Acid in Reaction Solution," were used for the determination of total acidity. These samples were titrated to a phenolphthalein endpoint with standardized N/4 NaOH solution. Deleterious effects of carbon dioxide on the phenolphthalein endpoints were eliminated by boiling each sample for a three-minute period prior to reaching the endpoint.

The total acidity of the reaction solution was employed in conjunction with the sulfuric acid content, as determined by the BaCl<sub>2</sub> method, to compute the concentration of benzenemonosulfonic acid present in the solution.

#### Determination of Water Content.

The concentration of water present in the reaction mixture was determined by titration with a Karl Fischer iodine reagent in reference to a standardized solution of water in methyl alcohol. Preparation of the iodine and alcohol-water standard titration solutions is described in Appendix B. The chemical reaction involved in the titration may be represented approximately by the equation



The reaction is not stoichiometrically quantitative by the above equation, but is highly reproducible in quantitative action, and thereby suited for quantitative analytical operations.

The end point was determined by the dead-stop method of Foulk and Bawden (4) as applied by Wernimont and Hopkinson (15). To this purpose, two platinum wire electrodes sealed into soft glass tubes were immersed in the sample being titrated, and an electromotive force of 20 millivolts was impressed across the platinum electrodes by connection to the "e.m.f." terminals of a Leeds and Northrup Student Type potentiometer. The end point of the back-titration of excess iodine reagent was indicated by approach of the galvanometer needle on the potentiometer to its zero position. The end point occurred at the stage of the titration where the free iodine, which acts as a depolarizing agent on the electrodes, disappeared, and the polarization action at the electrode surfaces halted the flow of electric current. An electric stirrer kept the sample well mixed during the titration. Atmospheric moisture was excluded by use of paraffin-coated cork stopper provided with appropriate access openings for stirrer shaft, burette tip and electrode leads on the alcohol-water burette; a similar stopper with only a burette opening was mounted on the iodine burette. Soxhlet extraction flasks of 150-ml. capacity were used for titration flasks.

Reaction mixture samples were analyzed for water content by the following procedure: A sample containing 30 mg. to 40 mg. of water was accurately weighed, using a dropper bottle as a weighing bottle, into the Soxhlet flask used in the titration operation. The sample was placed in the flask with a minimum of exposure to the room air in order to reduce moisture pickup by absorption; a

paraffin-coated cork stopper was immediately placed over the flask opening as a guard to block entrance of atmospheric moisture. Five milliliters of pyridine were then pipetted into the flask and admixed with the sample. This addition of pyridine was employed to neutralize the concentrated acids in the sample which, in their concentrated state, would decompose the iodine reagent with a copious evolution of white fumes.

The sample flask, with the guard stopper removed, was then mounted on the iodine burette guard stopper, and an accurately measured portion of 15 or 20 ml. of iodine reagent was run into the flask. Iodine reagent in excess was thus added in order that the solution might be back-titrated with the standardized alcohol-water solution. The flask was transferred immediately to the alcohol-water burette, and the excess iodine titrated to the electro-endpoint with the alcohol-water solution. The dead-stop endpoint in the titration of free iodine was reported to have an endpoint of better reproducibility than had the reverse manner of titrating unreacted water with iodine solution.

The water equivalent of the quantity of iodine solution used in the analysis of the sample was determined by making a blank analysis in which the sample was omitted, but the 5-ml. pyridine addition was included. The difference between the quantities of alcohol-water solution used in the sample and blank titrations was taken to represent the quantity of water present in the original sample (12).

Benzene condensate samples were also analyzed for water content by the Karl Fischer method. Since most of the water was

present as a separate aqueous phase in the condensate samples, it was necessary for sampling purposes to bring the benzene and water into a single liquid phase prior to analysis. Absolute methyl alcohol was employed as a solubilizing agent.

Each benzene condensate sample had been collected, during the sulfonation run, in a 100-ml. volumetric flask in a quantity of approximately 85 ml. The flask had been preweighed, the combined weight of flask with sample was obtained, absolute methyl alcohol then added, and the final weight obtained. An aliquot portion of benzene condensate sample was pipetted into the titration flask, a 5-ml. portion of pyridine measured into the sample, and the sample then analyzed for water in the same manner as in the case of the reaction mixture sample. The pyridine addition was included in this analysis in order that the blank titration values obtained as above would be applicable. The absolute methyl alcohol used for solubilizing the sample was analyzed for water content, and corrections were applied in computations for water content of the sample.



Legend of Figure 6

A	Acid reservoir	O	Reaction cell
B	Benzene reservoir	Q	Cell thermocouple
C	Benzene flowmeter	R	Cell sample line
D	Acid flowmeter	S	Bath thermoregulator
E	Hydrostatic leg	T	Overflow siphon
F	Benzene vaporizer	U	Siphon seal cup
G	Benzene trap	V	Overflow sample line
H	Vacuum relief	W	Product receiver
I	Oil seal line	X	Benzene condensate receiver
J	Benzene vapor line, supply	Y	Condensate sample line
K	Pressure-release line	Z	Condenser vent
L	Benzene vapor line, discharge	AA	Condenser
M	Acid drip cup	BB	Cooling water
N	Constant temperature bath	CC	Electric power

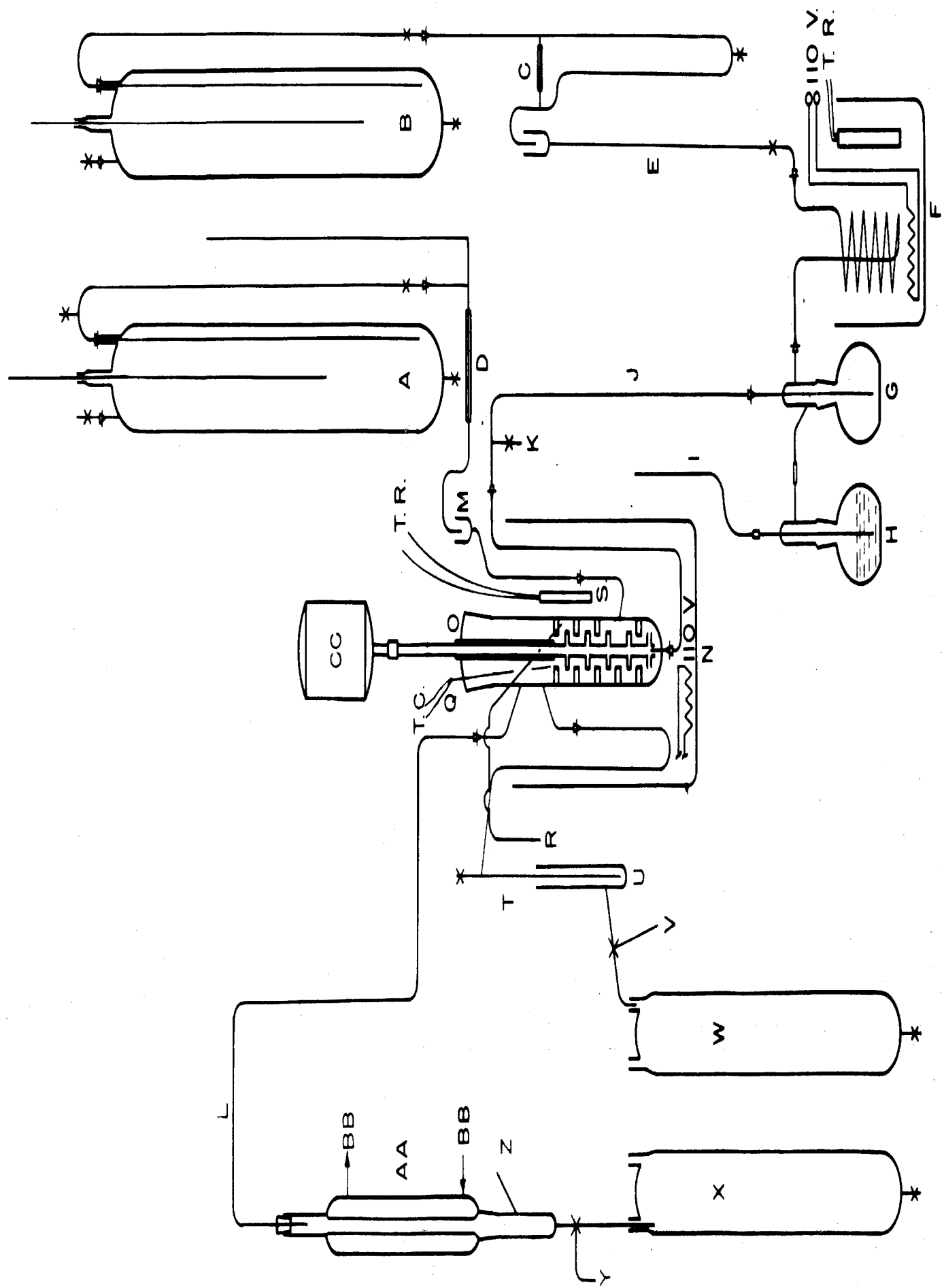


FIGURE 6. SCHEMATIC DIAGRAM OF EQUIPMENT

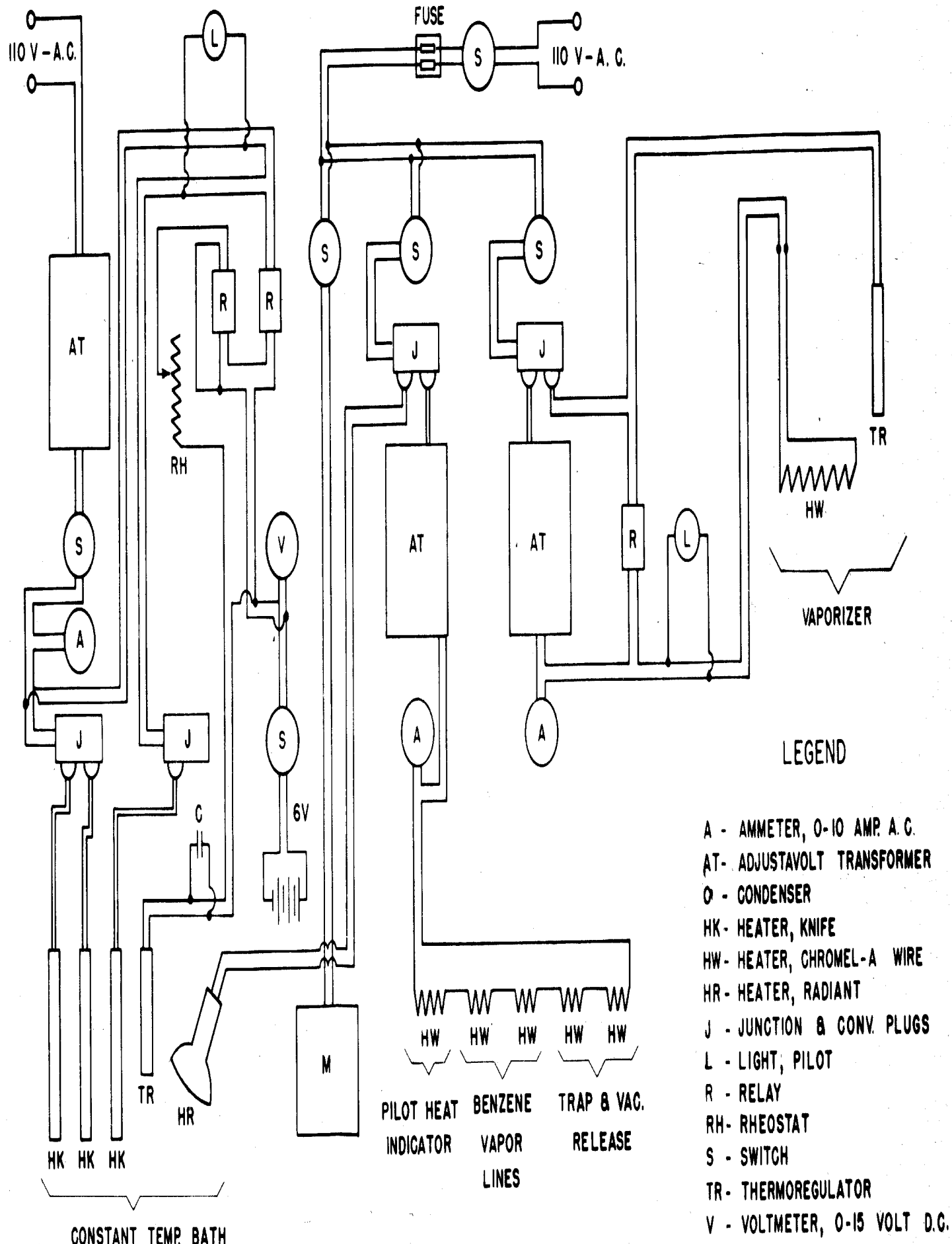
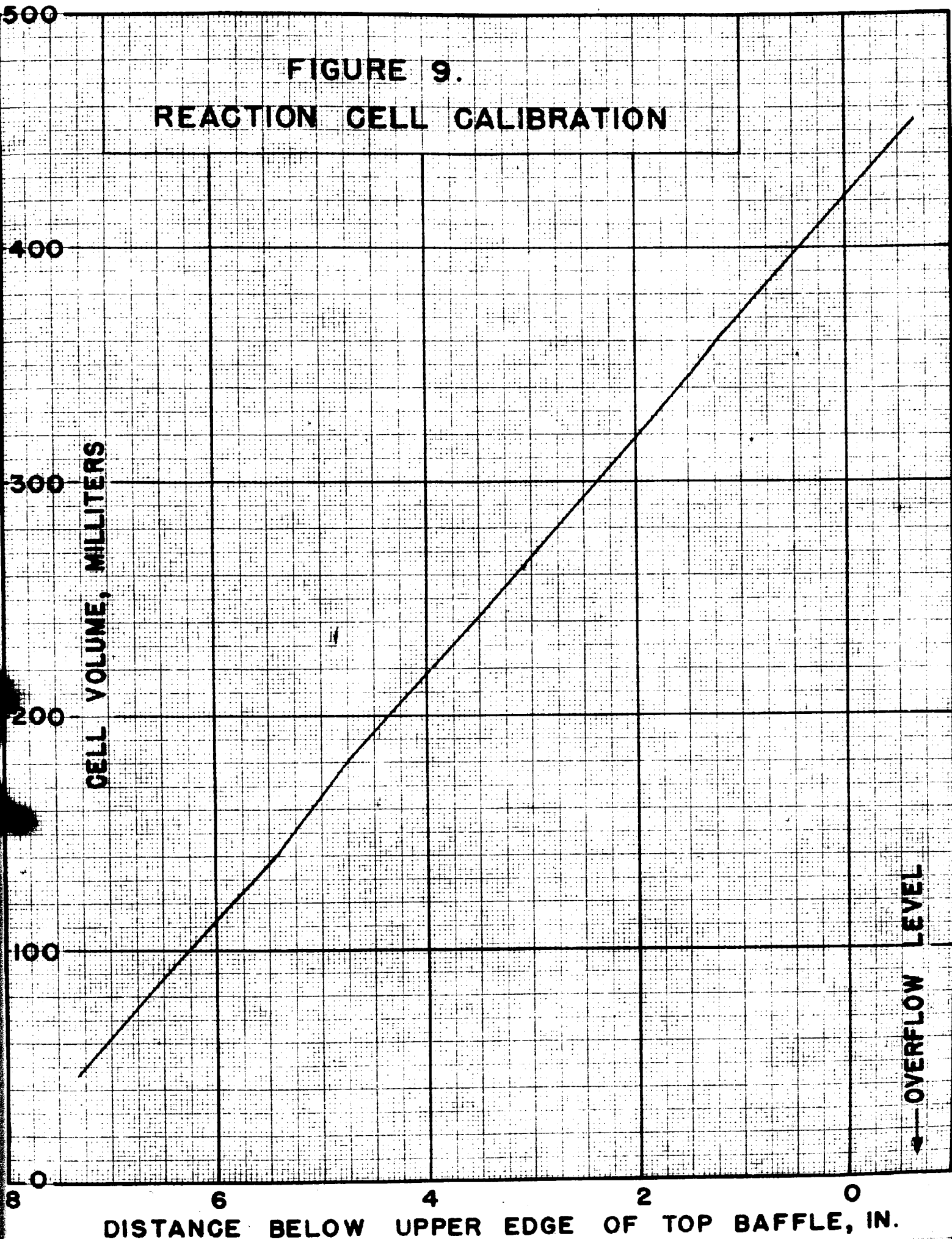


FIGURE 7. ELECTRICAL WIRING DIAGRAM



**FIGURE 9.**  
**REACTION CELL CALIBRATION**



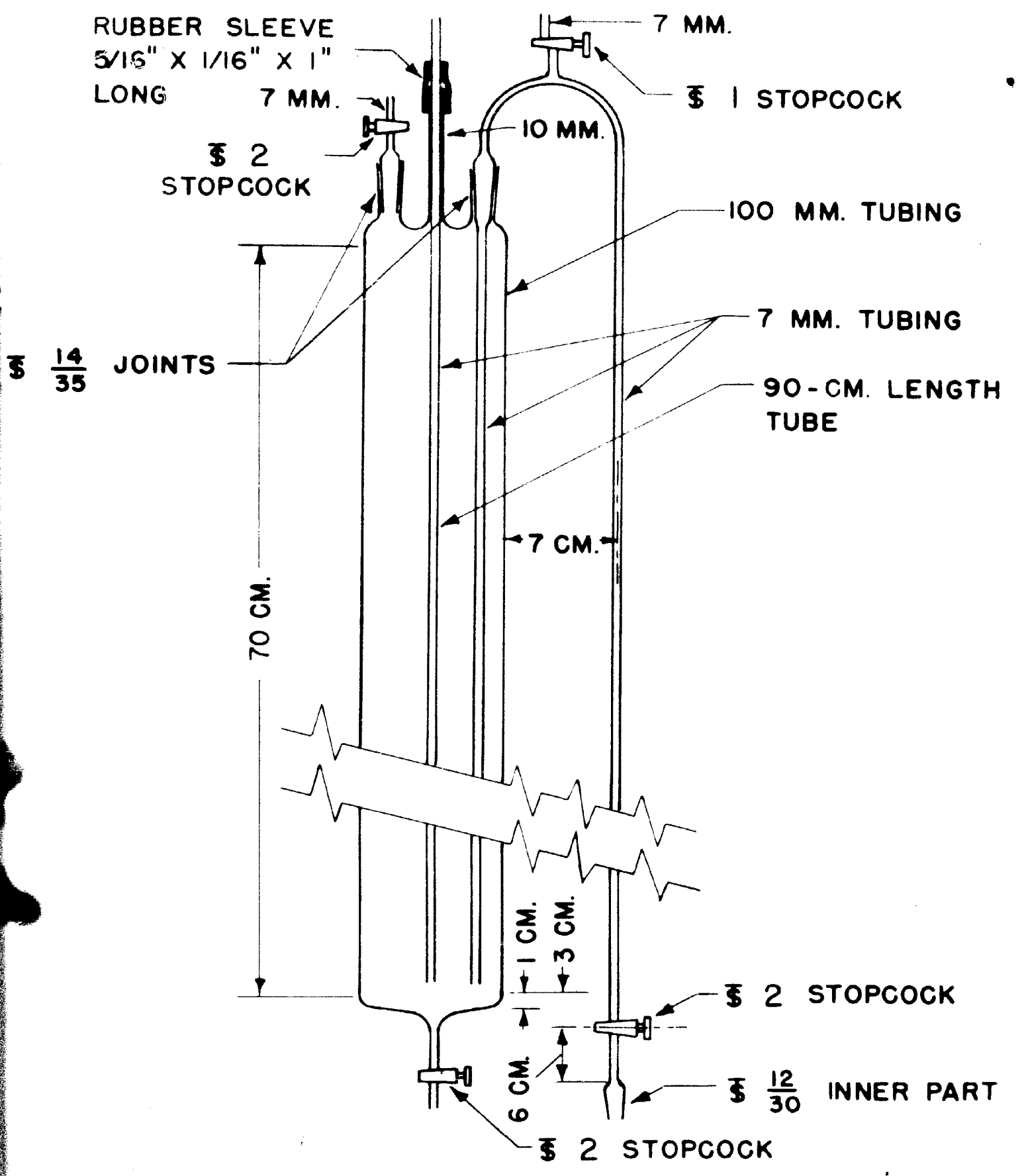


FIGURE 10.  
RESERVOIR

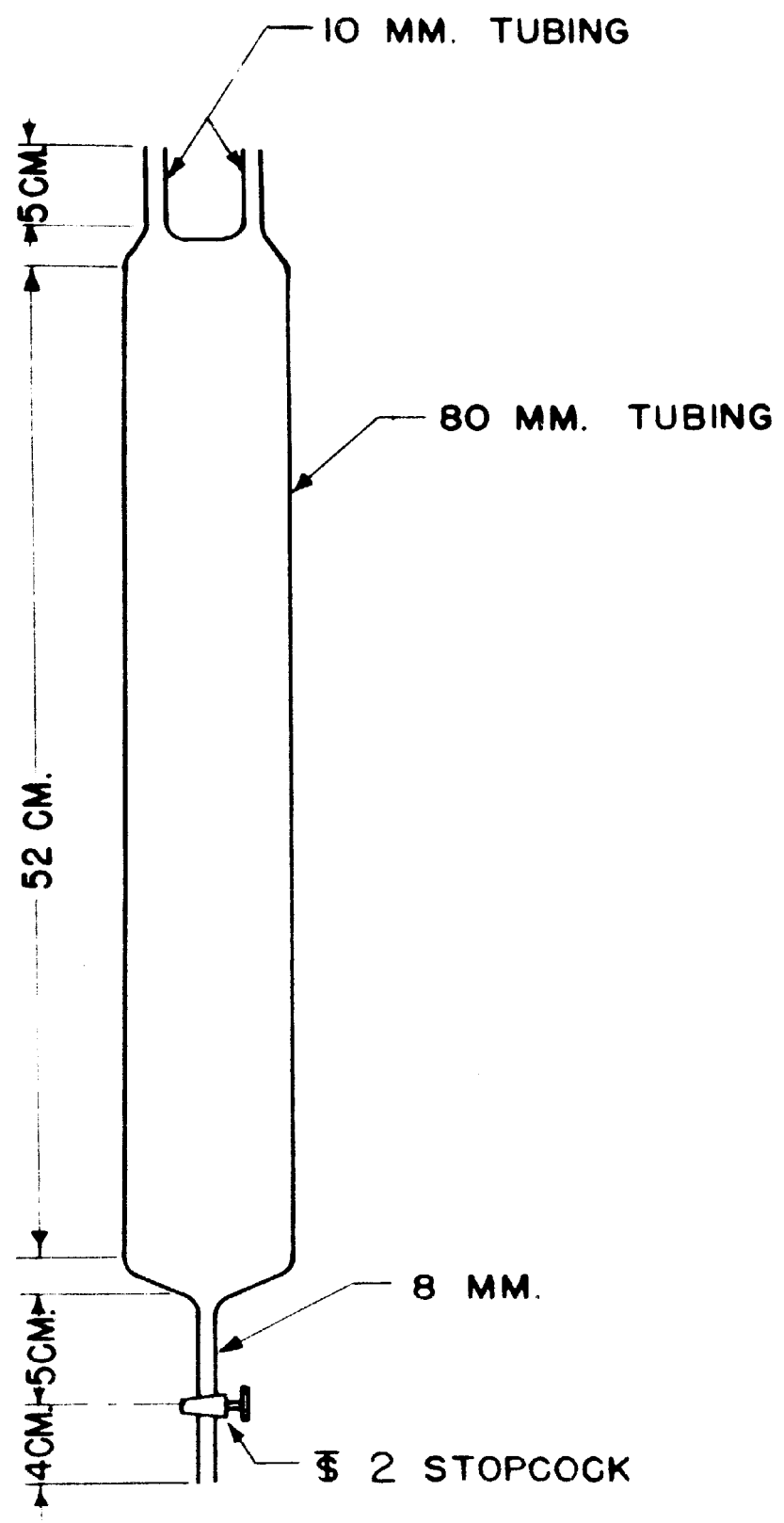


FIGURE II.  
RECEIVER

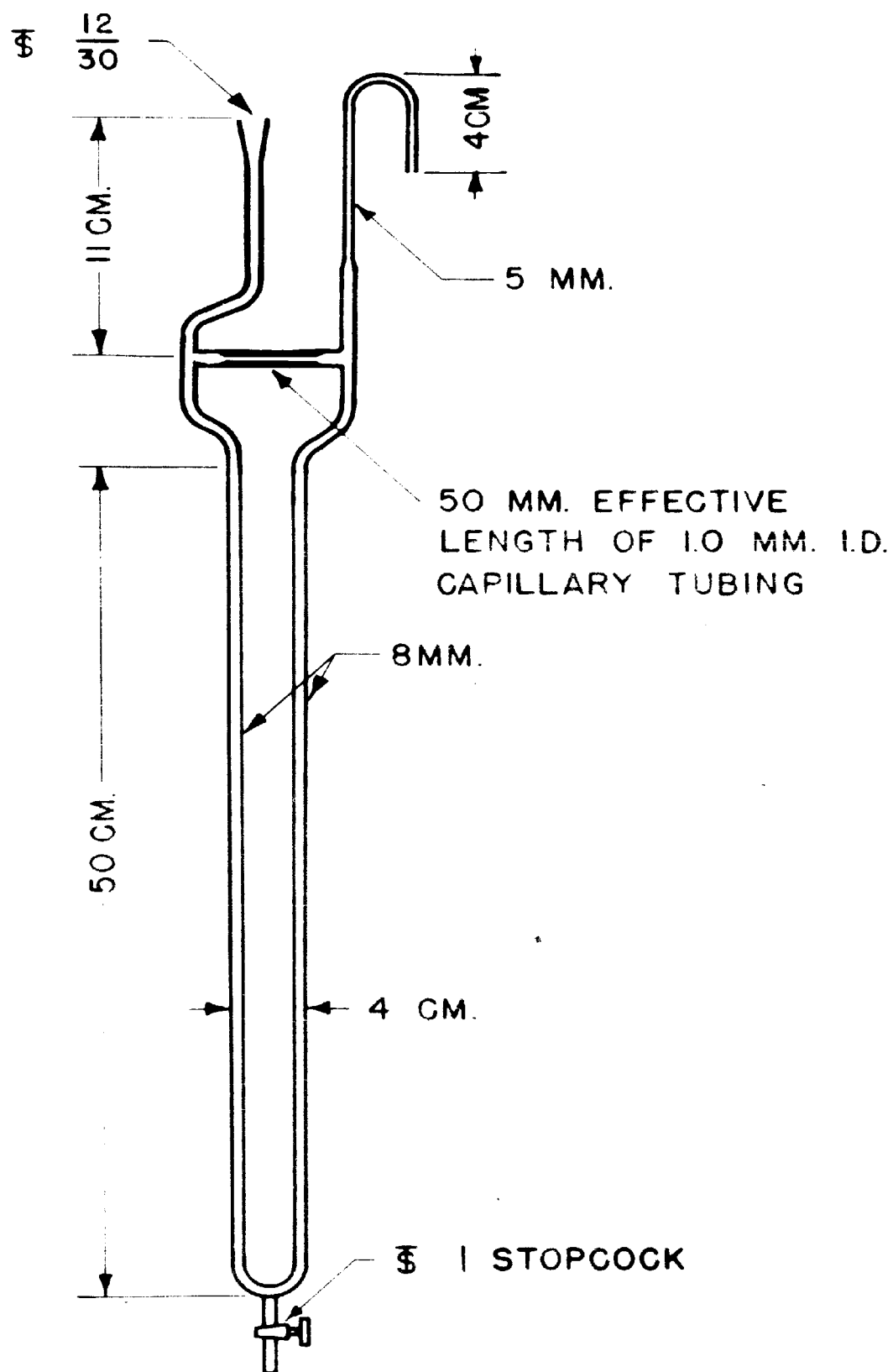


FIGURE 12  
BENZENE FLOWMETER



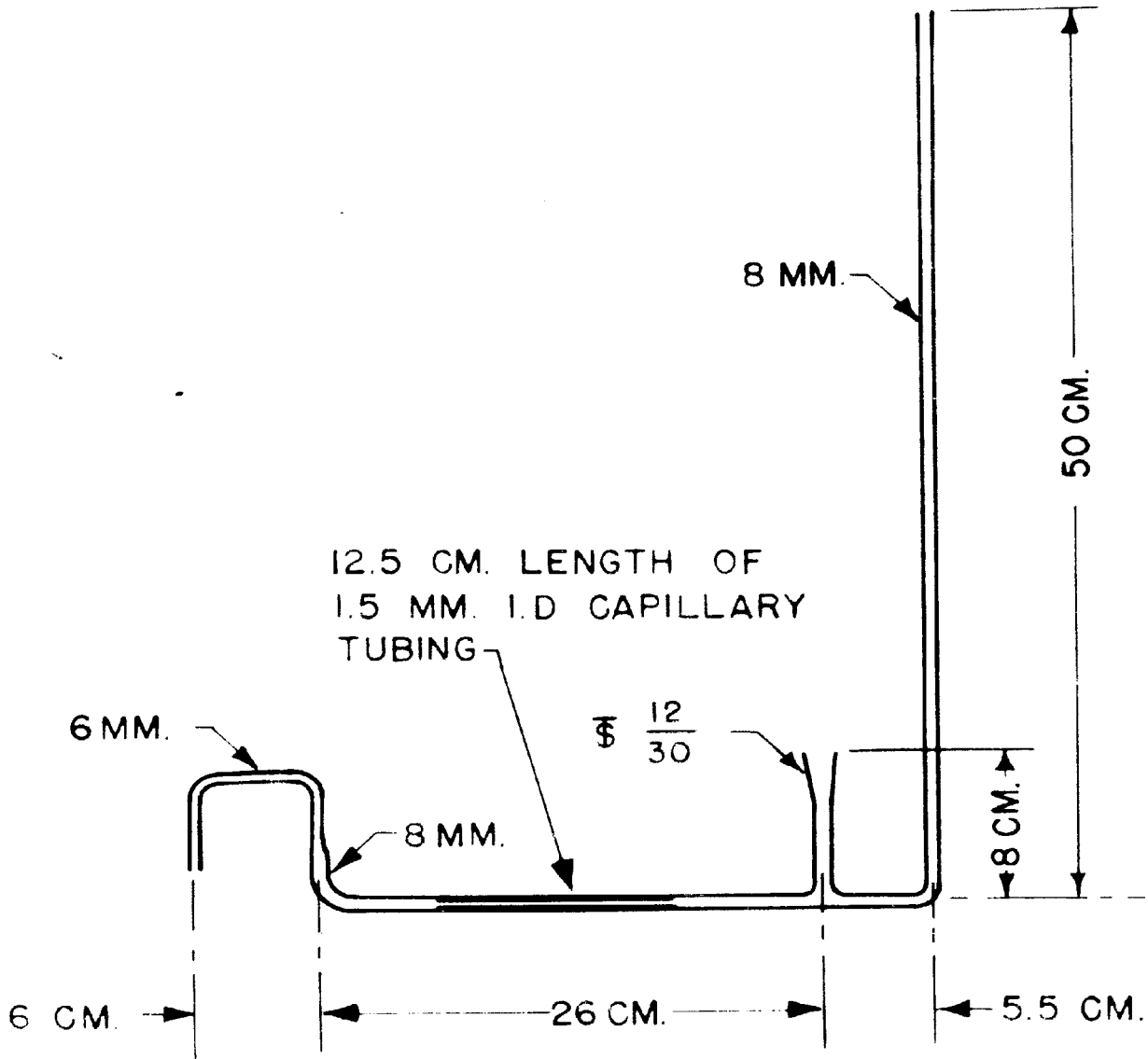


FIGURE 13  
ACID FLOWMETER

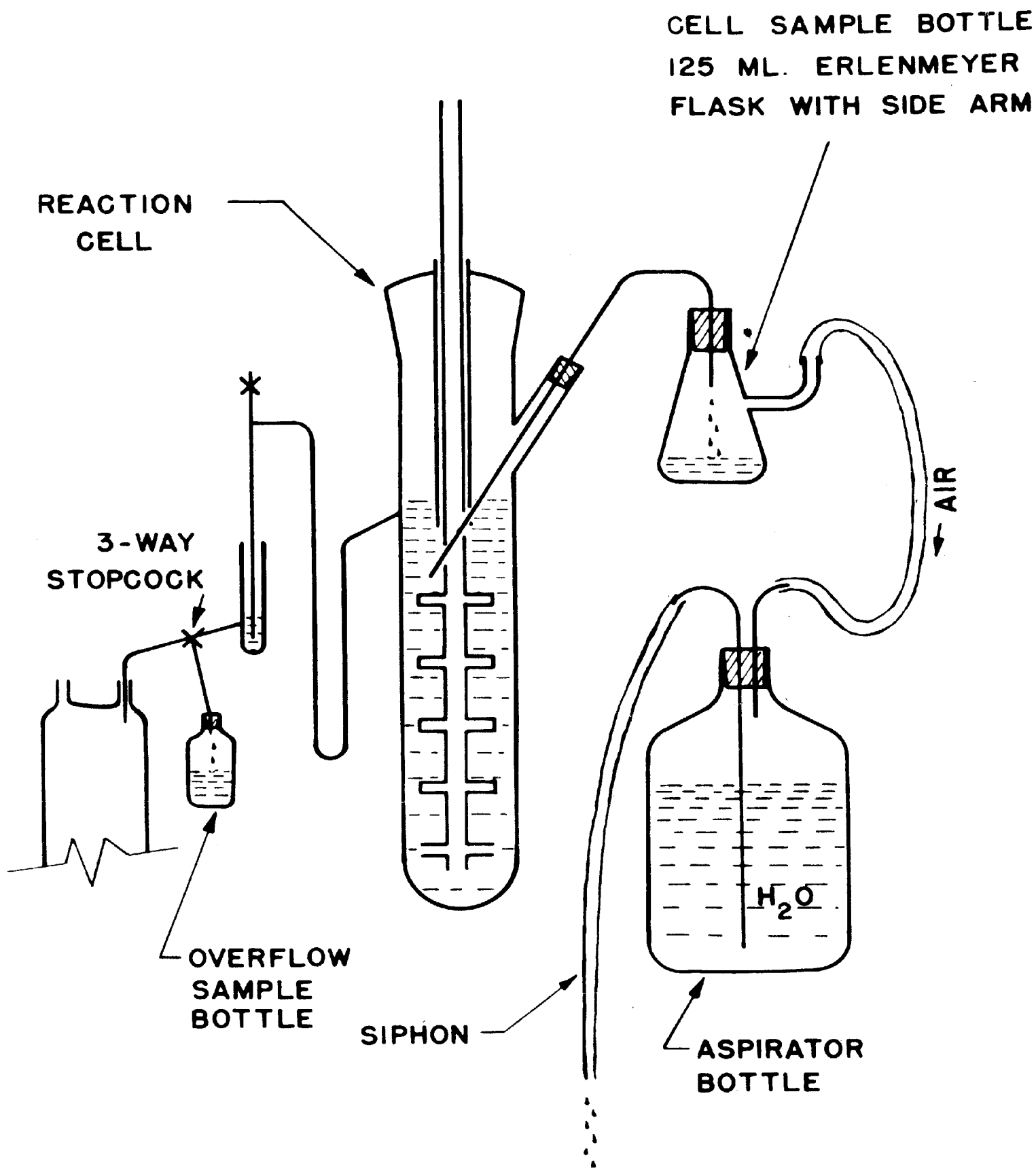


FIGURE 14. SAMPLING METHOD

#### IV. EXPERIMENTAL RESULTS

Reaction rates in the sulfonation of benzene by sulfuric acid were obtained in thirty runs over the temperature range 90°C. to 140°C. in sulfuric acid solutions saturated with respect to benzene. Sulfuric acid-water solution mixtures in concentrations varying from 80.4% to 95.1% sulfuric acid by weight, were employed as reactant feed solutions. The quantity of benzene vapor introduced into the cell was approximately twelve times the amount which entered the reaction. Benzene-sulfonic acid product was formed in these runs to concentrations which varied from a minimum of 2.53% to a maximum of 41.83% by weight.

The experimental errors present in measurements of the quantities observed in this work are estimated to be approximately as follows:

Volumetric rates	-----+ 0.5%
Temperature	-----+ 0.05°C.
Wt. percent H <sub>2</sub> SO <sub>4</sub>	-----+ 0.05%
Wt. percent BSA	-----+ 0.2%
Wt. percent H <sub>2</sub> O	-----+ 0.05%
Reaction mixture volume	-----+ 3 ml.

Experimental data obtained in the thirty-one runs performed are shown in Table 3, "Operating Conditions," and Table 4, "Reaction Mixture Analytical Data." As an illustration of the procedure followed in securing these data, a detailed treatment of Run No. 20 is shown in Appendix A.

### Operating Conditions.

The data tabulated in the columns of Table 3, "Operating Conditions," were obtained as follows:

Col. 1 : Run Number.

Col. 2 : Cell Temperature, °C. This was obtained by measuring the e.m.f. of the copper-constantan thermocouple in the reaction cell, using a Leeds and Northrup portable precision potentiometer, Model 8662.

Col. 3 : Barometer, mm. Hg. These values were obtained from readings on a mercurial barometer. They are corrected to a standard temperature of 0°C.

Col. 4 : Stirrer R.P.M. The reaction cell stirrer speed was measured by obtaining timed revolution counter readings at the driven pulley on the stirrer shaft.

Col. 5 : Reaction Liquid Volume, Ml. The quantity of reaction liquid phase was determined by noting the liquid level position in the reaction cell. This position was determined after the flows of reactants and the stirrer were halted simultaneously and at a time when the cell had been in operation under steady flow conditions. The volume of liquid present in the cell was then found from the cell calibration curve shown in Figure 9. A correction of 8 ml. volume was added to the calibration curve reading to allow for liquid in tubing connections.

- Col. 6 : Space Velocity. This is calculated by dividing the hourly volume rate of acid feed (Col. 9) by the volume of the liquid phase in the cell (Col. 5).
- Col. 7 : Acid Feed,  $H_2SO_4$  Wt. %. The concentration of sulfuric acid in the feed solution was determined by titration with standard NaOH.
- Col. 8 : Acid Feed, Density. These values were obtained from the composition-density table for sulfuric acid in Perry's (13) "Handbook for Chemical Engineers," and are corrected to room temperature.
- Col. 9 : Acid Feed, ml./hr. The volumetric acid feed rates were obtained from timed observations of liquid levels in the acid reservoir. The volumetric rate in ml./hr. is numerically equal to the product of the rate of liquid level lowering and the reservoir calibration constant, 69.1 ml. per cm. height.
- Col. 10: Acid Feed, Gm./hr. The gravimetric acid feed rates in gm./hr. are equal to the product of the density (Col. 8) and the volumetric feed rate (Col. 9).
- Col. 11: Benzene Feed, ml./hr. The volumetric benzene feed rates were obtained from timed observations of liquid levels in the benzene reservoir. The volumetric rate in terms of ml./hr. of liquid benzene is equal to the product of the rate of

liquid level lowering and the benzene reservoir calibration constant, 68.2 ml. per cm. height.

Col. 12: Benzene Feed, Gm./Hr. These values are equal to the product of the volumetric feed rate (Col. 11) and the density of liquid benzene at room temperature.

Col. 13: Benzene Condensate, Ml./Hr. The volumetric benzene condensate rates were obtained from timed observations of liquid levels in the condensate receiver, and include the small quantities of water vapor present in the benzene leaving the reaction cell. The volumetric rate in ml./hr. liquid is equal to the product of the rate of liquid level rise and the condensate receiver calibration constant, 44.5 ml. per cm. height.

Col. 14: Benzene Condensate, Gm./Hr. These values are equal to the product of the volumetric condensate rate (Col. 13) and the density of liquid benzene at room temperature.

Col. 15: Product, Ml./Hr. The volumetric product rates were obtained from timed observations of liquid levels in the product receiver. The volumetric rate of product in ml./hr. is equal to the product of liquid level rise and the product receiver calibration constant, 43.9 ml./cm. height.

Col. 16: Product, Gm./Hr. The gravimetric rate of product overflowing from the reaction cell was obtained

by an overall total material balance:

$$(\text{Gm./hr. Product}) = (\text{Gm./hr. Acid Feed}) + (\text{Gm./hr. Benzene Feed}) - (\text{Gm./hr. Condensate}),$$

or  $(\text{Col. 16}) = (\text{Col. 10}) + (\text{Col. 12}) - (\text{Col. 14}).$

Col. 17: Product, Density at 25°C., Gm./Ml. The product densities were measured with a Westphal balance and corrected for temperature.

Col. 18: Reaction Rate, (Mol. BSA)/(Hr.)(Lit.). The reaction rates were calculated from the concentration of benzenesulfonic acid in the product, the weight rate of product formed, the reaction liquid volume in the cell, and the molecular weight of benzene sulfonic acid, 158.17.

$$R_L = \frac{(\text{Wt. \% BSA})(\text{Product rate})}{(100)(\text{Reaction liquid volume})(158.17)}$$

Col. 19: Reaction Rate, (Mol. BSA)/(Hr.)(Mol. H<sub>2</sub>SO<sub>4</sub>).

These reaction rates are numerically equal to the ratio of  $R_L$  and the molar concentration  $C_A$  of sulfuric acid, or,  $R_L/C_A$ .

#### Analytical Data.

Analytical data describing the compositions of the reaction liquid mixtures are shown on Table 4, "Reaction Mixture Analytical Data." A detailed treatment of Run No. 20 is shown in Appendix A to illustrate the analytical procedures employed.

In order to reduce sampling errors, two samples from each reaction mixture were withdrawn and analyzed. In each run, with

the exception of Runs 1, 2, 3, 4 and 6, one sample was withdrawn directly from the cell, and one sample was taken from the overflow line. Sampling errors arising from loss of benzene vapor from the cell sample and water produced by after-reaction in the overflow sample are corrected by relating these two samples through a material balance on sulfur contents.

Compositions of reaction mixture samples withdrawn directly from the reaction cell are shown in columns 2 to 6 of Table 4. Water determinations were made on cell samples of the first ten runs, and on the overflow samples for the remainder of the runs. Column 6 shows the percentage of sulfur in the cell samples as calculated from the sulfuric acid (Col. 2) and benzene sulfonic acid (Col. 3) concentrations.

Columns 7 through 11 show the compositions of the overflow product samples. Column 11 shows the sulfur contents as calculated from the concentrations of sulfuric acid (Col. 7) and benzene sulfonic acid (Col. 8).

Columns 12 through 15 show the compositions of the cell reaction mixtures as adjusted for sampling errors. These values are obtained from the cell and overflow sample compositions which were adjusted as follows:

$$\text{Col. 12: } \underline{\text{H}_2\text{SO}_4}. \quad \% \text{H}_2\text{SO}_4 = (\text{Col.2})(\text{Col.11})/(\text{Col.6})$$

$$\text{Col. 13: } \underline{\text{BSA}}. \quad \% \text{BSA} = (\text{Col.3})(\text{Col.11})/(\text{Col.6})$$

$$\text{Col. 14: } \underline{\text{H}_2\text{O}}.$$

$$\text{Runs 5, 7-10: } \% \text{H}_2\text{O} = (\text{Col.4})(\text{Col.11})/(\text{Col.6})$$

$$\text{Runs 11-31:}$$

$$\% \text{H}_2\text{O} = (\text{Col.9}) - \left[ (\text{Col.12}) - (\text{Col.7}) \right] \frac{(\text{M.W. H}_2\text{O})}{(\text{M.W. H}_2\text{SO}_4)}$$



The ratio (Col.11)/(Col.6) represents the sulfur material balance correction factor to adjust the total sulfur content of the cell sample equal to the sulfur content of the overflow sample; it is the correction factor which compensates for the loss of benzene experienced in taking samples from the reaction cell.

The quantity  $[(\text{Col. 12}) - (\text{Col. 7})] (\text{M.W. H}_2\text{O}) / (\text{M.W. H}_2\text{SO}_4)$  represents the correction for the water produced by after-reaction in the overflow sample.

Columns 16-18 show the compositions of the reaction mixtures on a "benzene-free" basis. The values shown therein were obtained from the corrected cell analyses by dividing Columns 12-14 by their total, Column 15. It was assumed that the differences between 100% and the totals shown in Column 15 was due to benzene dissolved in the reaction mixtures.

Column 19 shows the concentrations of water present in the excess benzene vapor which left the reaction cell during operation under steady-state conditions.

#### Material Balances.

Table 5, "Material Balances," compares the entering and leaving rates of key constituents for each run. The quantities of sulfur, oxygen and benzene (both free and combined benzene) entering and leaving the cell are shown on an hourly basis. These values were computed from rate and composition quantities in the previous tables; the computation procedure is illustrated in Appendix A.

Correlation Data.

Table 6, "Correlation Summary," presents derived values employed in correlation of the data. The product densities (Col. 4) at the reaction temperatures were computed from their densities referred to 25°C. and the experimentally determined volumetric expansion coefficient of  $0.0006 \text{ } ^\circ\text{C}^{-1}$ . The total moles per liter of reaction mixture (Col.9) were computed from the product mol fraction compositions, Columns 5-7, and the densities at the reaction temperatures. Values for  $(R_L/C_A)_{\text{calc.}}$  were computed from the empirical equation (Eq. 18) of correlation.

TABLE 3

## OPERATING CONDITIONS

Run No.	Cell Temp.	Barometer	Stirrer Speed	Reaction Space Liquid Vol.	Space Velocity	Acid Feed		Benzene Feed				Benzene Condensate				Product			Reaction Rate
						H <sub>2</sub> SO <sub>4</sub>	Density	Rate	Rate	Rate	Rate	Rate	Rate	Rate	Rate	Density at 25°C.	R <sub>L</sub>	R <sub>L</sub> /C <sub>A</sub>	
	°C.	mm. Hg.	R.p.m.	ml.	Ml. acid feed/ml. vol./hr.	Wt. %	Gm. ml.	ml. hr.	Gm. hr.	ml. hr.	Gm. hr.	ml. hr.	Gm. hr.	ml. hr.	Gm. hr.	Gm. ml.	Mol. BSA Hr. Lit	Mol. BSA (Hr.) (Mol. H <sub>2</sub> SO <sub>4</sub> )	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
1	100	737	650	370	0.76	95.68	1.830	280	513	614	536	440	364	420	666	1.565	4.07	0.470	
2	100	737	650	363	2.23	94.98	1.827	876	1599	374	762	550	462	1152	1661	1.626	3.34	0.947	
3	100	745	970	379	2.13	94.81	1.826	808	1478	975	765	556	486	1086	1757	1.628	3.87	0.864	
4	100	741	970	354	2.62	94.79	1.827	676	1301	374	849	659	374	1166	1876	1.631	9.48	0.913	
5	100	736	1260	326	2.66	94.94	1.828	669	1587	954	632	632	551	1172	1869	1.629	9.60	0.924	
6	140	737	970	338	2.65	95.06	1.872	697	1678	1097	950	683	591	1299	2037	1.592	13.55	1.587	
7	140	740	1260	312	2.87	95.17	1.828	696	1638	1146	999	717	626	1306	2012	1.591	15.04	1.791	
8	140	736	970	330	2.72	95.17	1.824	697	1636	1110	964	672	583	1292	2016	1.590	14.09	1.682	
9	140	740	650	347	2.58	95.06	1.827	696	1637	1112	969	669	583	1293	2023	1.591	13.44	1.604	
10	140	737	1770	253	3.09	95.06	1.824	873	1593	1120	972	699	606	1260	1958	1.591	15.81	1.877	
11	140	741	1260	324	0.93	95.14	1.830	317	580	420	368	238	208	480	739	1.560	6.03	0.817	
12	100	736	1260	361	3.99	95.14	1.826	1202	2194	1241	1060	797	693	1616	2580	1.636	14.83	1.429	
13	100	740	1770	283	3.98	95.14	1.826	1047	1912	1236	1078	846	736	1414	2253	1.632	15.03	1.463	
14	100	733	650	365	1.55	86.12	1.768	596	1054	359	312	311	270	641	1096	1.724	1.10	0.083	
15	140	739	650	365	3.05	95.06	1.832	1084	1986	1182	1036	668	586	1558	2436	1.597	15.48	1.811	
16	140	735	1260	314	3.04	95.06	1.829	954	1745	1146	1001	688	601	1372	2146	1.590	15.57	1.844	
17	100	735	650	376	1.13	95.03	1.829	426	778	468	409	277	242	591	945	1.603	5.03	0.537	
18	100	729	650	360	2.02	95.03	1.829	728	1331	771	674	478	417	980	1587	1.621	6.21	0.831	
19	100	740	650	367	1.82	89.98	1.809	743	1344	372	326	221	193	691	1476	1.688	3.94	0.330	
20	100	729	650	366	3.82	89.98	1.809	1437	2599	668	599	460	402	1661	2796	1.710	6.35	0.501	
21	100	747	650	402	0.93	89.98	1.809	372	674	248	217	151	132	451	759	1.662	2.30	0.205	
22	100	739	650	366	3.90	85.18	1.783	1428	2546	655	572	601	525	1512	2593	1.747	1.68	0.120	
23	140	736	650	370	1.01	85.18	1.782	375	668	435	379	359	313	441	735	1.656	2.22	0.208	
24	140	737	650	364	1.82	80.42	1.724	696	1201	266	249	258	224	736	1225	1.701	0.93	0.0753	
25	120	745	650	407	0.85	80.42	1.727	346	598	110	97	100	87	361	606	1.705	0.239	0.0186	
26	120	750	650	361	1.96	85.18	1.763	708	1263	611	534	534	467	761	1330	1.707	2.14	0.1715	
27	120	735	650	359	1.96	86.38	1.809	710	1264	650	603	508	444	874	1443	1.662	5.16	0.470	
28	120	742	650	352	2.87	95.03	1.827	1612	1848	1215	1058	788	637	1404	2220	1.614	12.62	1.342	
29	90	732	650	356	2.03	95.06	1.827	721	1318	812	708	530	462	972	1564	1.630	7.71	0.747	
30	140	734	0	392	3.07	95.06	1.828	1204	2200	1262	1118	606	703	1656	2614	1.628	12.86	1.34	
31	90	735	650	413	1.34	84.90	1.770	551	976	78.6	68.5	30.8	33.8	686	1011	1.741	0.663	0.0482	

TABLE 4

## REACTION MIXTURE ANALYTICAL DATA

Weight Percent

Run No.	Cell Analysis					Overflow Product Analysis					Corrected Cell Analysis				Cell Analysis Benzene-Free Basis			Benzene Condensate
	H <sub>2</sub> SO <sub>4</sub>	BSA	H <sub>2</sub> O	Total	Sulfur	H <sub>2</sub> SO <sub>4</sub>	BSA	H <sub>2</sub> O	Total	Sulfur	H <sub>2</sub> SO <sub>4</sub>	BSA	H <sub>2</sub> O	Total	H <sub>2</sub> SO <sub>4</sub>	BSA	H <sub>2</sub> O	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	55.12	35.76	7.74	98.64	25.27	---	---	---	---	---	---	---	---	---	55.98	36.34	7.68	---
2	62.63	30.40	7.74	100.77	26.64	---	---	---	---	---	---	---	---	---	62.14	33.17	7.69	---
3	62.65	30.26	8.64	101.75	26.25	---	---	---	---	---	---	---	---	---	64.60	27.76	7.64	---
4	64.28	28.70	7.56	98.54	26.42	---	---	---	---	---	---	---	---	---	65.23	27.10	7.67	---
5	64.34	26.61	7.44	98.39	26.43	61.89	29.82	---	---	26.31	64.05	26.49	7.41	97.95	65.39	27.05	7.56	---
6	55.91	35.57	7.54	100.50	25.48	---	---	---	---	---	---	---	---	---	56.24	35.79	7.97	---
7	55.44	36.50	7.52	99.76	25.58	54.10	37.36	---	---	25.26	54.74	36.89	7.42	99.05	55.33	36.73	7.94	0.66*
8	55.28	36.63	7.54	99.65	25.54	53.92	37.53	---	---	25.29	54.76	36.48	7.47	98.71	55.23	36.80	7.97	0.54*
9	55.30	36.70	7.74	99.74	25.52	54.04	37.90	---	---	25.36	54.96	36.47	7.69	99.12	55.24	36.65	8.11	0.40*
10	55.40	36.35	7.26	99.03	25.46	54.21	37.52	---	---	25.33	55.07	36.13	7.24	98.44	55.52	36.43	8.05	0.40*
11	49.17	41.53	---	---	24.55	43.20	43.39	8.32	99.91	24.55	40.17	41.83	8.14	99.14	49.60	42.19	8.21	---
12	64.79	27.64	---	---	26.78	62.78	29.56	7.30	99.64	26.51	64.13	27.36	7.16	98.65	65.01	27.73	7.26	---
13	64.52	28.18	---	---	26.60	62.38	29.57	7.25	99.20	26.39	63.51	27.74	7.15	98.40	64.54	28.19	7.27	---
14	70.82	6.13	---	---	27.04	78.76	6.01	15.15	99.92	26.96	78.70	6.11	15.11	99.92	78.77	6.11	15.12	---
15	56.42	36.92	---	---	25.74	53.32	36.56	8.92	99.90	25.50	56.67	36.67	7.96	99.52	56.14	35.54	8.02	---
16	55.82	36.43	---	---	25.64	54.42	37.30	8.00	98.72	25.35	58.20	36.04	7.64	99.18	55.66	36.33	8.01	0.82
17	59.60	32.09	---	---	26.99	57.43	33.78	7.82	99.93	25.62	58.76	31.64	7.74	99.14	59.87	32.24	7.89	0.11
18	62.58	29.33	---	---	26.90	60.46	31.45	7.84	99.81	26.15	61.75	29.44	7.54	98.53	62.46	29.79	7.73	0.964
19	72.75	16.42	---	---	27.12	71.70	17.35	11.20	100.25	26.85	72.34	16.32	11.08	99.74	72.53	16.36	11.11	0.997
20	75.92	13.16	---	---	27.48	70.57	13.96	11.03	99.36	27.47	75.87	13.15	10.94	99.96	75.90	13.16	10.94	0.057
21	69.23	19.38	---	---	26.56	60.64	19.74	11.31	99.69	26.44	68.92	19.29	11.26	99.47	69.29	19.39	11.32	0.083
22	61.56	3.74	---	---	27.42	61.37	4.90	14.70	100.07	27.41	61.53	3.74	14.67	99.94	61.58	3.74	14.68	0.136
23	67.81	17.74	---	---	26.76	67.44	18.36	14.90	100.04	25.71	67.66	17.70	14.86	100.22	67.51	17.66	14.83	1.73
24	76.78	4.62	---	---	26.94	76.58	4.92	19.32	100.72	26.01	76.71	4.62	19.28	100.61	76.25	4.59	19.16	2.86
25	77.41	2.92	---	---	25.82	77.20	3.24	19.55	99.99	25.89	77.64	2.53	19.47	99.64	77.92	2.54	19.54	1.26
26	75.96	8.19	---	---	26.69	75.61	9.87	14.97	100.45	26.72	76.03	8.20	14.89	100.12	75.94	9.19	14.87	0.61
27	68.33	20.32	---	---	26.46	67.59	21.28	11.37	100.24	26.41	68.21	20.28	11.26	99.75	68.38	20.33	11.29	0.42
28	60.36	31.80	---	---	26.18	59.13	33.15	7.98	100.16	26.05	60.06	31.64	7.71	99.41	60.41	31.83	7.76	0.26
29	65.16	20.37	---	---	27.35	62.49	25.76	7.54	99.79	26.46	63.73	27.75	7.31	98.79	64.51	28.09	7.40	0.040
30	62.32	30.77	---	---	26.61	61.27	31.29	7.67	100.23	26.37	61.76	30.49	7.60	99.85	61.85	30.54	7.61	0.50
31	60.71	4.30	---	---	27.26	60.19	4.60	15.20	100.19	27.19	60.51	4.29	15.14	99.94	60.56	4.29	15.15	.068

\* Calc'd from water phase separated from benzene condensate.

T A B L E 5

RUN MATERIAL BALANCES

Run No.	GRAMS		PER		HOUR	
	SULFUR		OXYGEN		BENZENE	
	IN	OUT	IN	OUT	IN	OUT
1	160.5	168.2	340.1	357.7	536.5	510.6
2	484.8	495.8	1037.4	1060.7	761.5	740.5
3	458.1	468.7	982.3	1017.0	764.8	748.1
4	496.0	495.6	1064.2	1065.2	849.2	848.4
5	492.7	491.6	1054.7	1054.7	832.0	832.8
6	521.6	519.2	1114.8	1131.0	949.7	945.4
7	509.7	510.4	1087.7	1080.2	999.1	1007.0
8	509.0	510.0	1086.1	1080.2	963.7	969.4
9	508.7	513.0	1087.3	1089.6	968.8	962.8
10	495.0	496.0	1057.9	1046.7	972.0	984.0
11	180.3	181.3	384.9	384.9	367.5	366.7
12	682.4	684.1	1456.7	1458.9	1079.8	1076.1
13	594.5	594.5	1269.1	1267.2	1077.5	1079.7
14	293.3	295.6	724.9	731.0	311.7	303.0
15	617.1	621.0	1319.0	1325.2	1036.5	1026.2
16	542.3	543.9	1159.0	1163.3	1001.4	995.5
17	241.8	242.1	517.1	518.3	408.9	407.2
18	413.4	415.0	883.8	889.2	673.6	666.3
19	395.3	397.9	908.5	915.5	325.5	315.5
20	764.4	768.0	1757.1	1767.7	599.0	584.3
21	198.2	200.6	455.7	461.5	216.9	208.3
22	708.9	710.8	1750.1	1747.3	572.2	573.9
23	186.1	188.9	459.5	465.6	379.1	371.6
24	315.6	318.8	838.9	846.0	249.2	246.0
25	157.3	157.4	418.0	418.9	96.6	95.7
26	351.7	342.4	868.3	849.6	534.1	524.3
27	377.6	381.1	868.0	877.3	603.2	589.9
28	574.1	578.2	1227.5	1236.5	1058.5	1044.9
29	409.5	413.8	875.2	883.6	707.5	694.6
30	683.6	689.4	1461.2	1475.1	1117.5	1097.1
31	270.9	274.8	671.7	680.0	68.5	55.8

TABLE 6

## CORRELATION SUMMARY

Run No.	Reaction Temp. °C.	Product Density 25°C.	Density At React. Temp.	Product Mol Fraction Benzene-Free Basis			$\left[ x_A \frac{1}{2} x_W + \frac{1}{4} x_S \right]$	Total Mol. Per Lit	Mol. H <sub>2</sub> SO <sub>4</sub> Per Lit	REACTION RATE			
				H <sub>2</sub> SO <sub>4</sub> C <sub>A</sub>	BSA x <sub>S</sub>	H <sub>2</sub> O x <sub>W</sub>				C <sub>L</sub>	C <sub>A</sub>	R <sub>L</sub>	$\frac{R_L}{C_A}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	100	1.585	1.517	0.4652	0.1873	0.3475	0.3382	18.61	8.66	4.07	0.470	0.468	+0.002
2	100	1.626	1.556	.5063	.1524	.3413	.3738	19.47	9.86	9.34	0.347	0.778	+0.169
3	100	1.626	1.558	.5234	.1395	.3371	.3887	19.60	10.28	8.87	0.864	0.962	-0.098
4	100	1.631	1.561	.5269	.1357	.3374	.3921	19.70	10.38	9.48	0.913	0.994	-0.081
5	100	1.629	1.559	.5302	.1360	.3338	.3873	19.60	10.40	9.00	0.924	1.061	-0.137
6	140	1.592	1.489	.4616	.1822	.3862	.3241	18.49	8.54	13.55	1.587	1.906	-0.319
7	140	1.591	1.488	.4560	.1877	.3863	.3247	18.41	8.40	15.04	1.791	1.811	-0.120
8	140	1.590	1.488	.4547	.1879	.3874	.3230	18.42	8.38	14.02	1.582	1.778	-0.096
9	140	1.591	1.488	.4523	.1861	.3816	.3180	18.53	8.38	13.44	1.604	1.878	-0.071
10	140	1.591	1.488	.4553	.1852	.3889	.3218	18.50	8.42	18.81	1.577	1.753	+0.124
11	140	1.560	1.458	.4117	.2172	.3711	.2804	17.92	7.38	6.03	0.817	1.082	-0.235
12	100	1.636	1.566	.5340	.1412	.3248	.4009	19.43	10.38	14.83	1.429	1.200	+0.229
13	100	1.632	1.562	.5307	.1437	.3286	.4038	19.36	10.28	18.83	1.463	1.153	+0.310
14	100	1.724	1.650	.4769	.0230	.5001	.2327	27.77	13.24	1.10	0.083	0.070	+0.013
15	140	1.587	1.484	.4600	.1821	.3578	.3268	18.88	8.55	18.48	1.911	1.850	-0.039
16	140	1.590	1.488	.4569	.1850	.3881	.3241	18.48	8.44	18.57	1.844	1.800	+0.044
17	100	1.603	1.534	.4874	.1628	.3498	.3832	19.21	9.36	5.83	0.537	0.584	-0.047
18	100	1.621	1.531	.5078	.1501	.3421	.3743	19.46	9.88	8.21	0.831	0.784	+0.047
19	100	1.688	1.615	.5066	.0708	.4228	.3130	23.88	11.94	3.84	0.330	0.315	+0.015
20	100	1.710	1.636	.5284	.0868	.4148	.3382	23.87	12.66	6.35	0.501	0.446	+0.055
21	100	1.662	1.590	.4847	.0841	.4312	.2901	25.18	11.24	2.30	0.205	0.214	-0.009
22	100	1.747	1.672	.4979	.0142	.4879	.2575	27.83	13.91	1.68	0.120	0.116	+0.004
23	140	1.656	1.549	.4240	.0888	.5072	.1876	28.15	10.66	2.22	0.208	0.236	-0.028
24	140	1.701	1.591	.4157	.0195	.5688	.1352	28.76	12.37	0.33	0.0753	0.0703	+0.0050
25	120	1.705	1.613	.4192	.0888	.5724	.1351	30.57	12.81	0.239	0.0186	0.0187	-0.0001
26	120	1.707	1.615	.4670	.0350	.4980	.2208	28.78	12.50	2.14	0.1715	0.1800	-0.0085
27	120	1.662	1.572	.4799	.0885	.4316	.2662	28.84	10.36	5.16	0.470	0.498	-0.018
28	120	1.614	1.527	.4955	.1613	.3482	.3611	19.06	9.40	12.82	1.342	1.378	-0.033
29	90	1.630	1.568	.5278	.1425	.3287	.3886	19.85	10.32	7.71	0.747	0.752	-0.005
30*	140	1.628	1.522	.5060	.1549	.3391	.3751	18.97	9.60	12.86	1.34	3.11	-1.77
31	90	1.741	1.676	.4861	.0162	.4978	.2412	28.32	13.77	0.663	0.0462	0.0476	+0.0006

\* Reaction liquid in Run No. 30 was not saturated with benzene.

## V. DISCUSSION

In these experiments, the rate of reaction between benzene and sulfuric acid was determined in solutions which were maintained at a saturation concentration with respect to benzene. Sufficient agitation was employed to maintain the liquid reaction phase in equilibrium with the benzene vapor phase. Therefore, the specific reaction rates determined in this work are for those benzene concentrations which correspond to saturation at atmospheric pressure.

### A. EFFECTIVENESS OF AGITATION

#### Saturation of Reaction Liquid.

Since it was desired to measure the sulfonation rate of benzene in sulfuric acid solutions saturated with respect to benzene, the degree of agitation necessary to maintain the benzene concentration at the saturation level was investigated. A series of runs performed at the highest rates of reaction was made with all run variables -- space velocity, reactant feed composition, temperature -- other than the rate of stirring held constant. Figure 15 shows a group of runs performed with an acid feed of 95.1%  $H_2SO_4$  by weight, a space velocity of  $3.07 \pm 0.03 \text{ hr.}^{-1}$ , and a temperature of  $140^\circ C.$ , with agitation speeds of 0, 650, 1260 and 1770 r.p.m. Therein is plotted the rates of reaction versus the speeds of stirring. From the graph it is evident that the rate of reaction was substantially independent of the degree of agitation over a range of 650 to 1770 r.p.m., and was considerably retarded when no agitation was

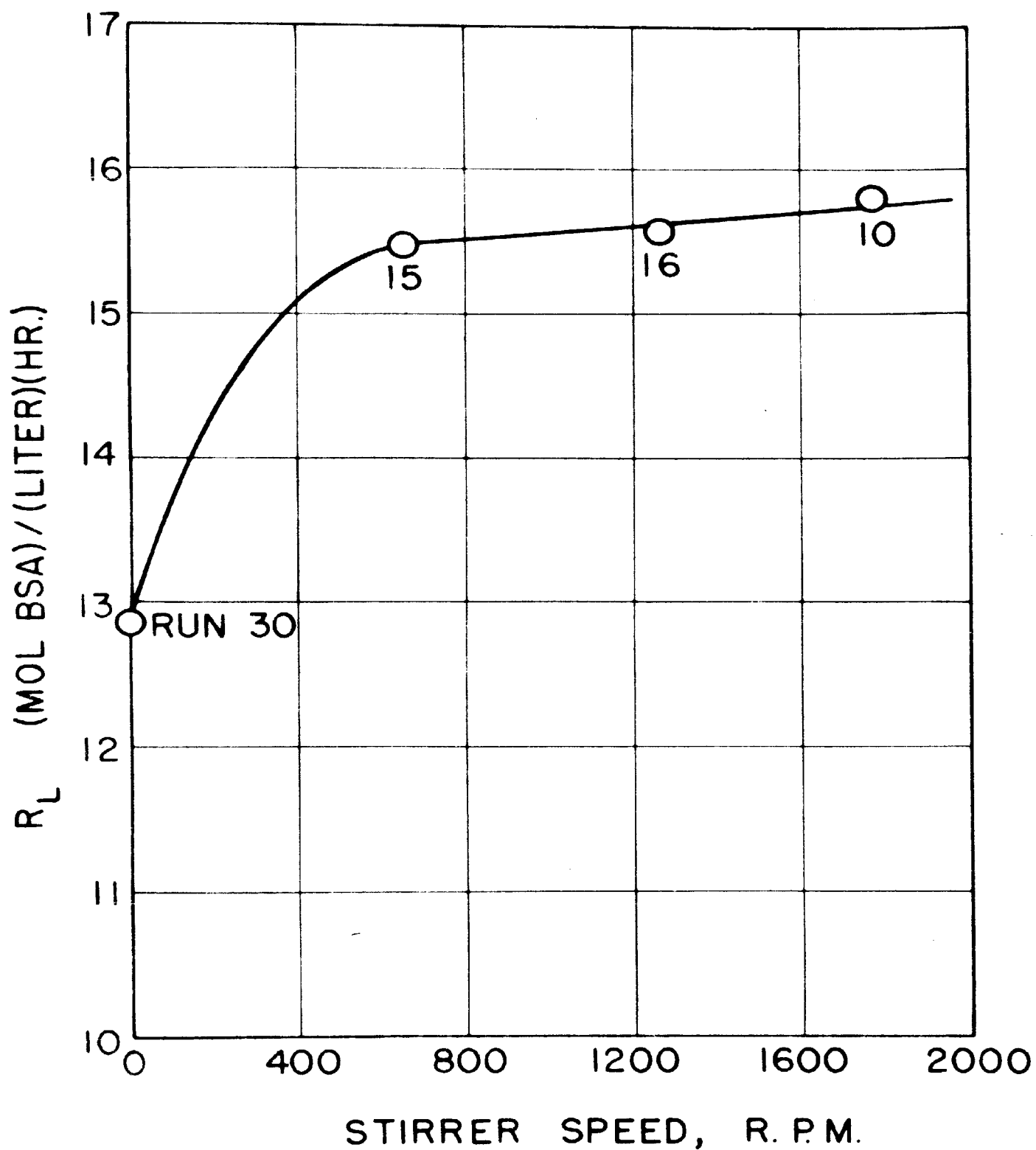


FIGURE 15. EFFECT OF AGITATION UPON RATE OF REACTION



employed, as shown by the rate of reaction in Run No. 30.

#### Distribution of Feed Liquid.

An additional test upon the effectiveness of the agitation was made by an observation on the rapidity by which the incoming acid reactant was distributed throughout the liquid system in the reaction cell. With the cell in operation at an agitation speed of 650 r.p.m. and at a temperature of 100°C., a methyl red dye solution was introduced into the acid reactant feed stream. The time required for the red color of the methyl red to reach the top and bottom portions of the liquid reaction system was approximately one second as measured by a stopwatch. The entering acid feed solution was thereby indicated to be distributed rapidly throughout the entire reaction liquid.

#### B. TESTS ON BY-PRODUCT FORMATION

##### Diphenyl Sulphone.

The reaction between benzene and sulfuric acid to produce benzenemonosulfonic acid was found to be quite free of by-product formation under the conditions employed in these experiments. The normal by-product, diphenyl sulphone, was shown by Harvey (8) to appear only when the reaction had proceeded nearly to completion and the benzenemonosulfonic acid concentration had exceeded values of about 80% by weight. The absence of sulfone formation in these experiments was indicated by the lack of precipitation when product samples were diluted with water; diphenyl sulfone is but very slightly soluble in water.

### Benzenedisulfonic Acid.

The presence of disulfonic acids was tested by preparing a barium salt of the sulfonic acid formed in Run No. 30, and analyzing the barium sulfonate salt for barium content. The barium content of the sulfonic acid salt preparation was determined to be 29.31% barium. This compares favorably with the barium content of the salt barium monosulfonate monohydrate. The barium content of the barium sulfonate formed from Run No. 30 product is compared in Table 7 with the calculated barium contents of other barium sulfonates.

T A B L E 7

#### BARIUM CONTENTS OF BARIUM SULFONATE SALTS

Salt	% Barium by weight
Sulfonic acids of Run No. 30	29.31
$\text{Ba}(\text{OSO}_2\text{C}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$	29.25
$\text{Ba}(\text{OSO}_2\text{C}_6\text{H}_5)_2$	30.41
$\text{Ba}(\text{OSO}_2)_2\text{C}_6\text{H}_4$	36.77

### C. CORRELATION OF BENZENE SULFONATION RATES

#### Composition Correlation.

The experimental rates of reaction between benzene and sulfuric acid in solutions saturated with respect to benzene correlate as a function of reaction system composition and temperature. Figure 16 shows values of  $\log R_L/C_A$  plotted against the corresponding values of  $\log (x_A - 1/2 x_W + 1/4 x_S)$ . In this plot, the values for the rates of reaction measured at a common

temperature lie close to a straight line, which may be used to express a functional relationship between the rate of reaction and the solution composition.

Each temperature line may be represented by the straight line equation

$$\log \frac{R_L}{C_A} = b \log (x_A - 1/2 x_W + 1/4 x_S) + \log I, \quad (14)$$

which reduces to the form

$$R_L = I (x_A - 1/2 x_W + 1/4 x_S)^b C_A, \quad (15)$$

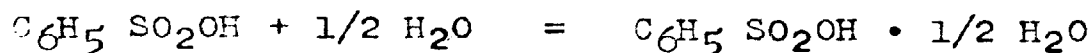
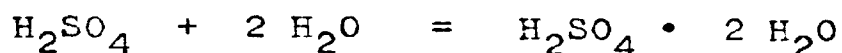
where  $\log I$  is the intercept at  $\log (x_A - 1/2 x_W + 1/4 x_S)$  equal to zero;  $b$  represents the slope and is a function of temperature.

Since the reaction rates were measured in solutions maintained saturated with respect to benzene at atmospheric pressure, the fugacity of the benzene component is maintained at a constant value of one atmosphere. The reaction rate for the system in which the benzene component is maintained at a constant fugacity may be written in a condensed form, and becomes

$$R_L = k C_A, \quad (16)$$

when taken on the basis of a first-order reaction with respect to sulfuric acid. From this equation it may be seen that the quantity  $R_L/C_A$  shown in Figure 16 is mathematically equivalent to the specific reaction rate coefficient  $k$ .

The composition function  $(x_A - 1/2 x_W + 1/4 x_S)$  may be regarded as "anhydrous"  $H_2SO_4$  on the basis of the hydration reactions

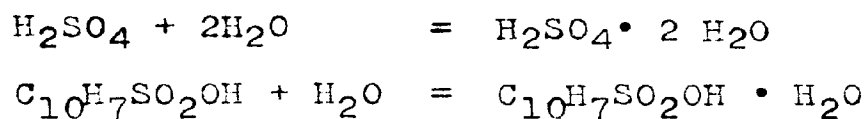


All water present is assumed to enter into hydration reactions. In these reactions, the benzenesulfonic acid is regarded as a dehydrating reagent, reacting with water to form the hemihydrate. The remaining water is regarded as combined with the sulfuric acid to form the double hydrate. The remaining sulfuric acid may then be viewed as being in the anhydrous form, and its mol fraction represented by the function  $(x_A - [1/2]x_W + [1/4]x_S)$ .

In product-free solutions, the dependence of the reaction rate upon the composition function  $(x_A - 1/2 x_W + 1/4 x_S)$  is in agreement with the "pi-value" concept defined by Guyot (7), and evaluated more extensively by others (6). In the case of benzene sulfonation, the limiting value of sulfuric acid concentration, below which the reaction will not proceed, has been evaluated at approximately 74% by weight of sulfuric acid. This value corresponds stoichiometrically to the dihydrate  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , and is equivalent to a zero value for the composition function  $(x_A - 1/2 x_W + 1/4 x_S)$  in product-free solutions. From the correlation chart, Figure 16, it is evident that as the composition function  $(x_A - 1/2 x_W + 1/4 x_S)$  approaches zero, the specific reaction rate likewise extrapolates to a zero value.

The presence of the benzenesulfonic acid product favors the rate of reaction by combining with some of the water present in the system, thus increasing the effective concentration of sulfuric acid reactant. This is in agreement with Spryskov's

observations (15) on the monosulfonation of naphthalene with sulfuric acid. He sulfonated naphthalene with sulfuric acid to give spent acid concentrations as low as 40.3% at 100°C. and 25% at 162°C., which are far below the "pi-values" of 65% and 63.7%, respectively, previously established. Spryskov concluded that hydration reactions occurred between water and the sulfuric and sulfonic acids, as



The naphthalene sulfonic acid apparently increased the effective concentration of sulfuric acid by combining with water to form a hydrate.

#### Composition-Temperature Correlation.

In a sulfonation system of constant composition, the reaction velocity coefficient was found to follow the Arrhenius temperature relationship

$$\log K = \frac{A}{T} + B. \quad (17)$$

Figure 17 shows the experimental specific reaction rates plotted against a combined function of temperature and reaction mixture composition. The straight line drawn through the experimental points on this figure is mathematically equivalent to the four temperature lines shown on Figure 16. This line is represented by the equation

$$\log \frac{R_L}{C_A} = \left( -9.239 + \frac{5349}{T} \right) \log(x_A - 1/2 x_W + 1/4 x_X) + 2.07 \quad (18)$$

$$\text{or } R_L = 118 (x_A - 1/2 x_W + 1/4 x_S)^{-9.239 + \frac{5349}{T}} \cdot C_A \quad (19)$$

$$\text{or } R_L = 118 e^{(-9.239 + \frac{5349}{T})} \ln(x_A - 1/2 x_W + 1/4 x_S) \cdot C_A \quad (20)$$

A comparison of the calculated and the observed values for  $R_L/C_A$  are listed in Table 6. The mean deviation for the thirty runs (not including Run 30) is 8.5% between the calculated and observed values.

Equation (20) is presented in a form employing the natural logarithmic base to facilitate comparison with an equation based upon theoretical considerations. By comparison with Equation (13) values for the basic reaction factors  $k^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  can be obtained from the empirical correlation equation. By comparison of Equations (20) and (13), it is seen that

$$k^\ddagger = 118,$$

$$\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} = (-9.239 + \frac{5349}{T}) \ln(x_A - 1/2 x_W + 1/4 x_S) \quad (21)$$

Values for the quantities  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  then become

$$\Delta S^\ddagger = -9.239 R \ln(x_A - 1/2 x_W + 1/4 x_S) \quad (22)$$

$$\Delta H^\ddagger = -5349 R \ln(x_A - 1/2 x_W + 1/4 x_S) \quad (23)$$

The entropy and enthalpy factors are here shown to be a function of the solvent medium of the reaction. Over the range of this experimental data, as represented by Runs Nos. 12 and 25, the calculated values for  $\Delta S^\ddagger$  vary from +16.5 to +36.7 cal./mol/°C., and the values for  $\Delta H^\ddagger$  vary from +9,500 to +21,200 cal./mol.

### Harvey's Sulfonation Data.

The data of this experimental work cover a space velocity range of 0.76 to 3.99 reciprocal hours. The data of Harvey (8) are on batch sulfonations of benzene by sulfuric acid for periods ranging from three to twelve hours, representing space velocities which can be conservatively estimated as equivalent to 0.08 to 0.33 reciprocal hours. The batch data therefore represents conditions of reaction as are present in the higher degrees of conversion. Although the rates of reaction computed from these batch experiments have large uncertainties, they are useful for order-of-magnitude investigation of some factors in the kinetics of the sulfonation reaction. Table 8 shows the rates of reaction and reaction mixture composition values as computed from Harvey's data. The degrees of conversion were computed from the batch sulfonation data, and graphically smoothed, and graphically differentiated, to obtain the specific reaction rate values shown in Table 8.

T A B L E 8

BATCH SULFONATION DATA (HARVEY)

Temp. °C.	Reaction Time, Min.	Mol Fraction				Sulfone x <sub>p</sub>	$\frac{RL}{CA}$	$\frac{RL}{CA^2}$
		H <sub>2</sub> SO <sub>4</sub> x <sub>A</sub>	H <sub>2</sub> O x <sub>w</sub>	BSA x <sub>s</sub>				
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
All	0	.715	.285	0	0	--	--	
130	270	.304	.371	.325	0	.160	.0357	
	420	.255	.332	.413	0	.167	.0483	
	570	.157	.251	.592	0	.175	.0975	
	690	.110	.172	.717	.001	.184	.1622	
	825	.087	.140	.768	.005	.194	.226	
140	180	.326	.345	.329	0	.225	.0481	
	280	.220	.267	.513	0	.249	.0934	
	400	.155	.248	.597	0	.277	.1560	
	520	.0968	.155	.747	.001	.317	.334	
	700	.0364	.0786	.878	.007	.480	1.469	
150	240	.152	.255	.593	0	.775	.444	
	305	.0946	.159	.746	0	.665	.705	
	375	.0672	.115	.815	.0026	.545	.861	
	465	.0194	.0095*	.951	.0196	.415	2.58	
	710	.0182	.0094	.919	.0530	.225	1.52	
160	150	.232	.388	.379	.0005	.497	.148	
	210	.138	.238	.621	.0026	.640	.416	
	274	.0868	.152	.756	.0052	.846	.587	
	360	.0176	.084*	.869	.0294	3.37	21.2	
	467	.0147	.087*	.791	.1072	2.92	23.0	
170	180	.108	.199	.690	.0033	.885	.782	
	300	.0120	.009*	.919	.060	5.70	59.1	
	360	.0103	.009*	.822	.159	5.72	70.0	
	450	.0119	.010*	.772	.207	4.25	46.4	
	540	.0116	.010*	.703	.275	3.33	38.1	

\* H<sub>2</sub>O weight percentage values were reported as < 0.20%.



### Test of the Effect of Benzenesulfonic Acid on Correlation.

Figures 18 and 19 illustrate the effect of benzenesulfonic acid on the reaction rate correlation. It can be seen in Figure 18 that when the benzenesulfonic acid concentration  $x_s$  is not included in the composition function,  $(x_A - 1/2 x_s)$ , the batch-sulfonation points lie far to the left of the line which correlates the flow data of this investigation. When the sulfonic acid concentration term is included in the composition function, as  $(x_A - 1/2 x_w + 1/4 x_s)$ , the batch-sulfonation points straddle the flow-data points as shown in Figure 19. The batch data, representing the higher concentrations of benzenesulfonic acid, indicate that the sulfonic acid has a significant effect upon the rate of reaction.

The correlation function,

$$\log R_L/C_A = (-10.180 + \frac{5877}{T}) \log(x_A - 1/2 x_w) + 2.50, \quad (24)$$

represented by the straight line drawn on Figure 18, was derived from a large-scale plot of the flow sulfonation data, similar to that of Figure 16.

### Tests on Order of Reaction.

Tests for first and second orders of reaction with respect to the sulfuric acid component may also be applied to the data. The first and second order reactions may be expressed as,

$$\text{First order: } R_L = k C_A \quad (16)$$

$$\text{Second order: } R_L = k C_A^2 \quad (25)$$

Figure 20 shows the experimental points for the specific reaction rates and the composition function,  $(x_A - [1/2]x_W + [1/4]x_S)$ , on the basis of a second-order reaction. It is seen that the batch-reaction points lie definitely above the flow-reaction points, and that the two sets of data are not in agreement when compared on the basis of a second-order reaction. However, the two sets of data do fall together when plotted upon a first-order reaction basis, as shown in Figure 19, indicating that the sulfonation of benzene proceeds by a reaction of the first order.

The temperature-composition correlation function shown in Figure 20 for the second-order reaction is

$$\text{Log } \frac{kL}{C_A^2} = \left( -10.160 + \frac{5979}{T} \right) \log(x_A - [1/2]x_W + [1/4]x_S) + 1.38 \quad (26)$$

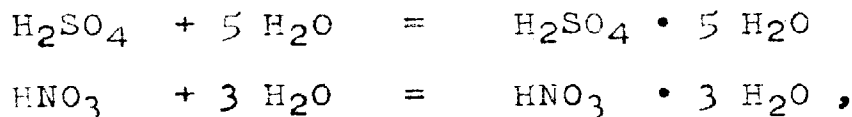
This equation was derived from a large-scale plot of the flow sulfonation data, similar to that of Figure 16. It is represented by the straight line drawn on Figure 20.

#### D. APPLICATION OF CORRELATION METHOD TO THE TOLUENE NITRATION REACTION

As a test of the method by which the benzene sulfonation rates of reaction were correlated, a similar viewpoint was applied to a similar type of reaction: the mononitration of toluene by a solution mixture of nitric acid, sulfuric acid and water. McKinley and White's (10) experimental data on toluene mononitration at 95°F. was employed for this test.

The reaction rate of toluene nitration is sensitive to comparatively small changes in concentrations of sulfuric acid

and water as well as in the prime reactant, nitric acid. Since the action of sulfuric acid is regarded as that of a dehydrating agent, the rate of reaction was considered upon the basis of the effect of hydration reactions upon the solution environment. It was found that when the hydration reactions were assumed as



a composition function  $(x_N + [5/3]x_A - [1/3]x_W)$  was obtained by which the specific reaction rate could be correlated. If it be assumed that all the sulfuric acid enters into the hydration reaction, and that the remainder of the water reacts with nitric acid, the quantity  $(x_N + [5/3]x_A - [1/3]x_W)$  might be viewed as representing "anhydrous"  $\text{HNO}_3$ .

In the nitration of toluene, the specific reaction rate  $R_N/x_T C_N$  plots very nearly as a straight line against the quantity  $(x_N + [5/3]x_A - [1/3]x_W)$  on a log-log plot, as shown in Figure 21. At the higher and lower values for the specific rates of reaction, the points fall above a line which represents the data over the major portion of the chart. These particular values represent measurements made at the lowest and highest concentrations of nitric acid employed. The points lying above  $\log (x_N + [5/3]x_A - [1/3]x_W)$  equal to  $-0.51$  represent reactions in solutions having  $\text{HNO}_3$  concentrations below 0.30% by weight. The fact that they lie above the line might be found in the difficulty of accurately determining small quantities of nitric acid. The points lying below  $\log (x_N + [5/3]x_A - [1/3]x_W)$  equal to  $-0.95$  represent the reactions conducted at high concentrations of nitric acid and low concentrations of sulfuric acid.

From Figure 21, the rate of mononitration of toluene at 95°F. may be expressed as

$$\text{Log } \frac{R_N}{x_T C_N} = 8.08 \log (x_N + [5/3]x_A - [1/3]x_W) + 6.40 \quad (27)$$

$$\text{or } R_N = 2,520,000 (x_N + [5/3]x_A - [1/3]x_W)^{8.08} x_T C_N \quad (28)$$

This equation represents the nitration data over a range corresponding to a ratio of 2500 to one in the value of the specific reaction rate  $R_N/x_T C_N$ .

#### E. SENSITIVITY OF REACTION RATES TO COMPOSITIONS

##### Quantitative Factors.

Since the correlations express the rates of reactions as large exponential powers of the composition functions, the individual rates of reaction are greatly changed by comparatively small variations in compositions of the reaction solutions. The effect of the large exponential powers is augmented by two additional factors: (1) The comparatively low molecular weight of water, and (2) the composition functions,  $(x_A - [1/2]x_W + [1/4]x_S)$  and  $(x_N + [5/3]x_A - [1/3]x_W)$ , both comprise differences between mol fraction quantities having the same order of magnitude.

##### Rates of Benzene Sulfonation.

In the sulfonation of benzene, it is seen from Equation 19 that an increase of sulfuric acid concentration from 85% to 86% by weight at 100°C. will result in an increase of 76% in the specific rate of reaction  $R_L/C_A$ .

Rates of Toluene Nitration.

In the mononitration of toluene at 95°F., it is seen from Equation 28 that small changes in concentrations will result in comparatively large changes in the specific reaction rate. A reaction mixture having a composition 9.91%  $\text{HNO}_3$ , 54.28%  $\text{H}_2\text{SO}_4$ , 35.49%  $\text{H}_2\text{O}$ , and 0.32%  $\text{HNO}_2$  is taken for example. In this case, if the concentrations of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  be respectively increased and decreased by 1% in weight, the predicted specific rate of reaction is increased by 215%. Likewise, if the concentrations of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  be respectively increased and decreased by 1% in weight, the specific rate of reaction is increased by 309%.

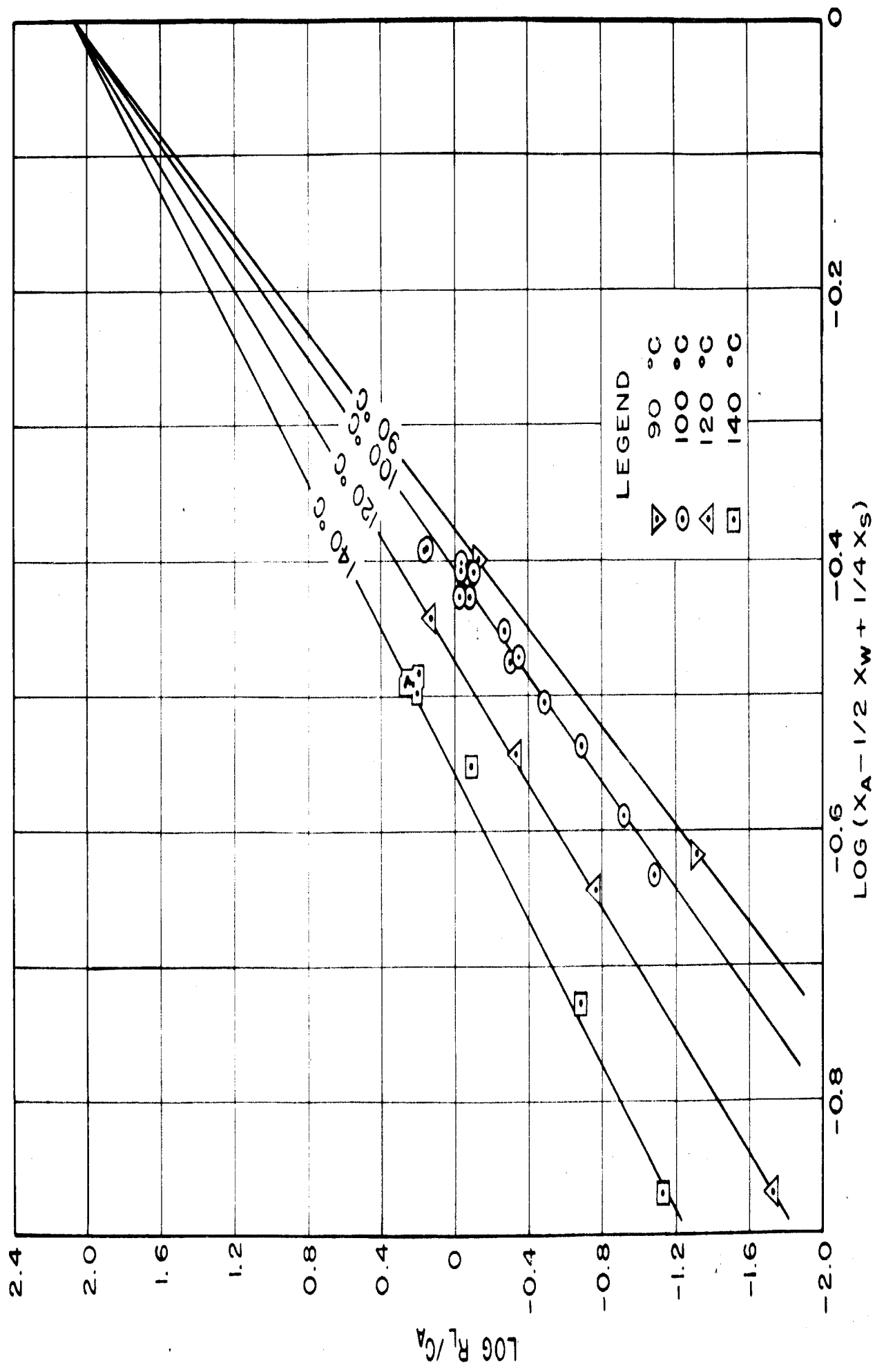


FIGURE 16. REACTION RATE - COMPOSITION CORRELATION

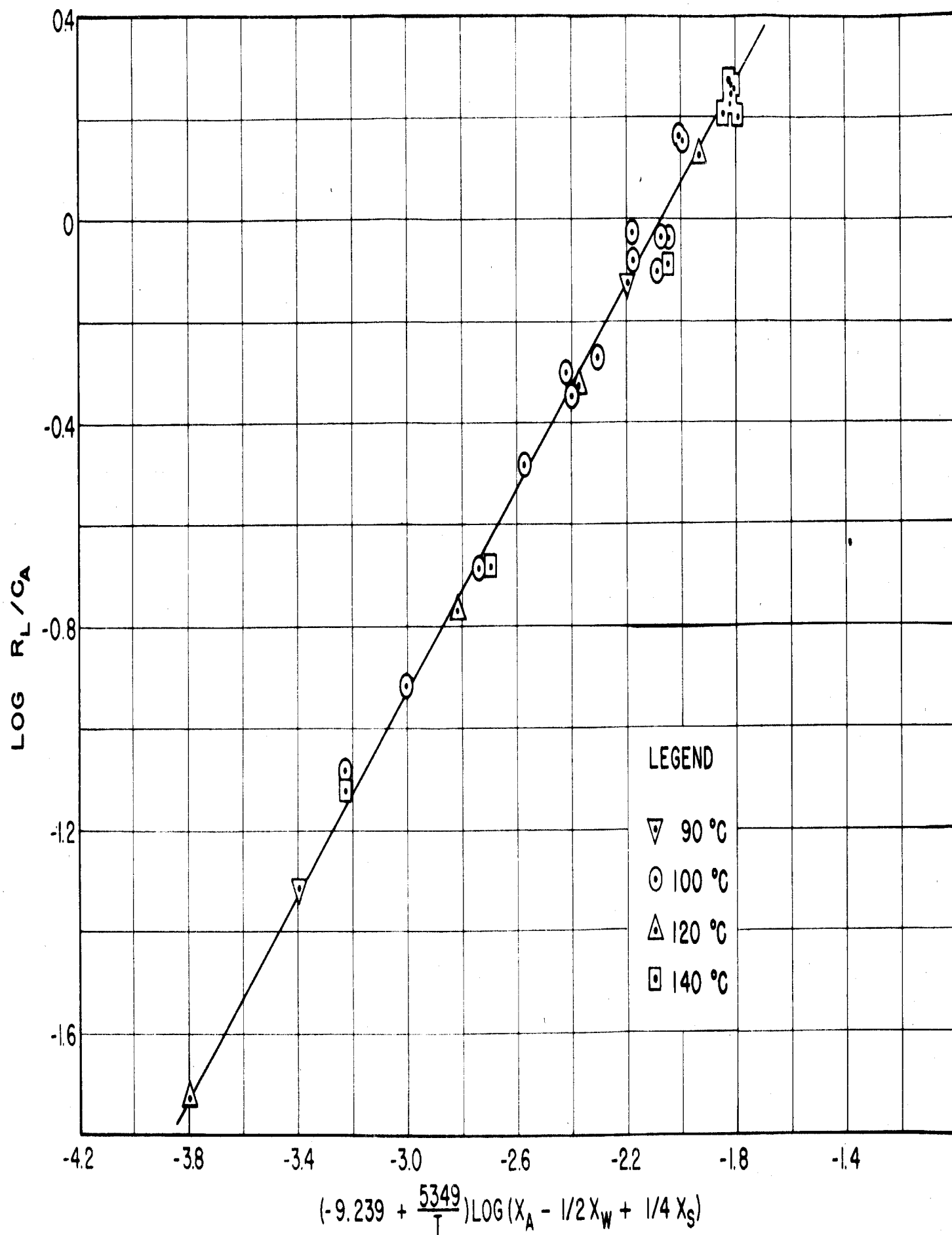


FIGURE 17. REACTION RATE-COMPOSITION-TEMPERATURE CORRELATION

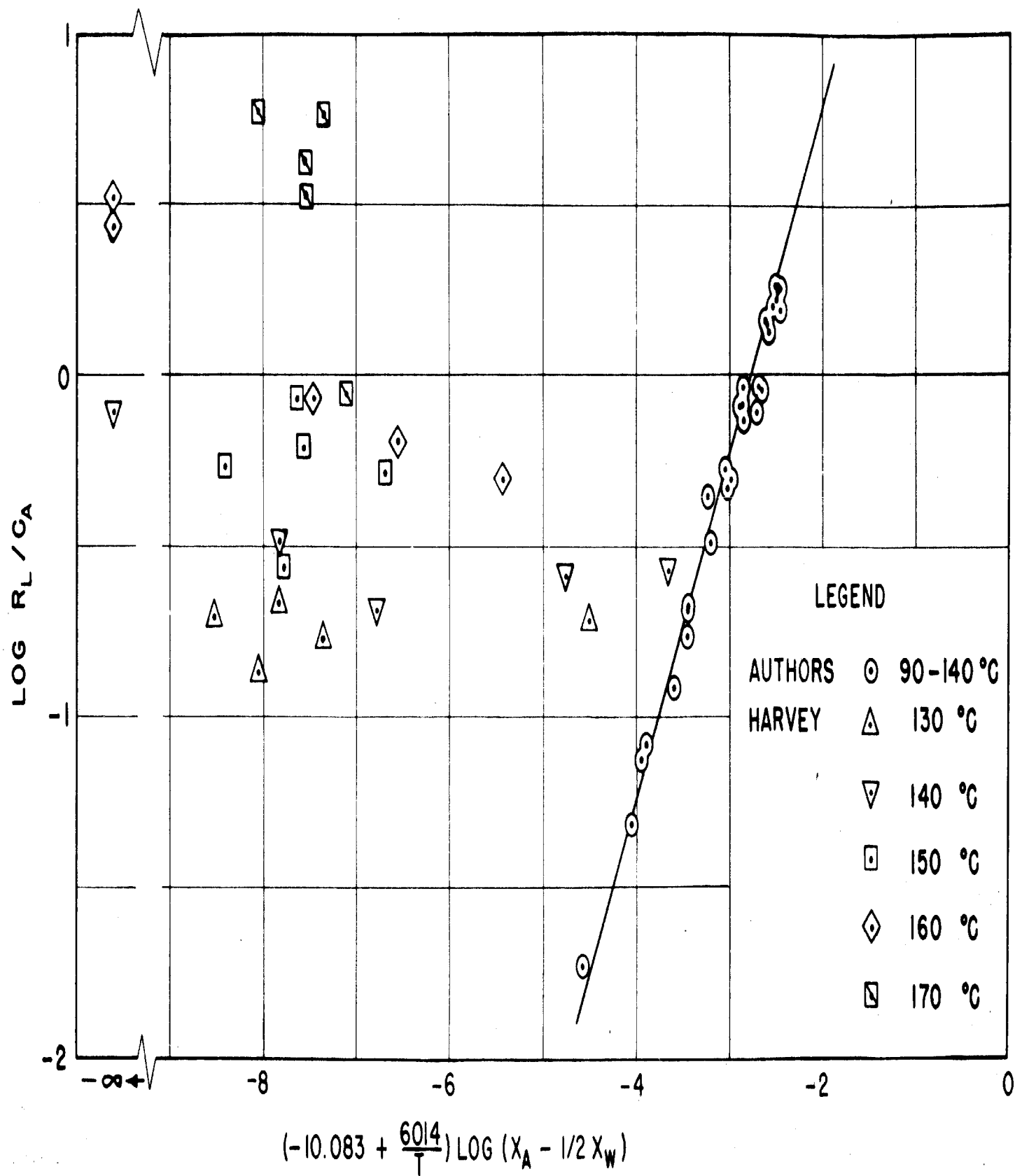
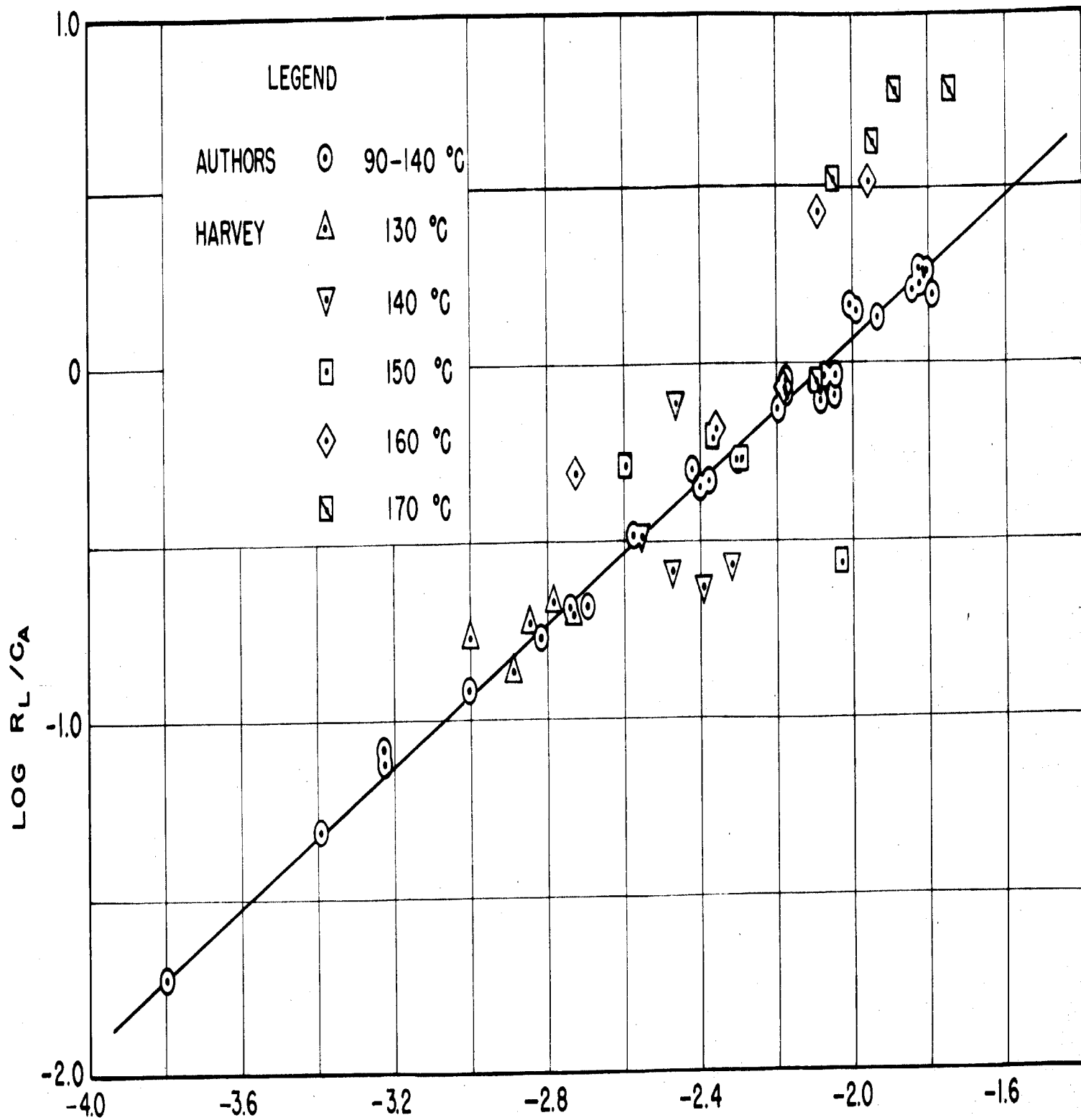


FIGURE 18. CORRELATION NEGLECTING EFFECT OF BENZENE SULFONIC ACID





$$(-9.239 + \frac{5349}{T}) \text{LOG}(X_A - 1/2X_W + 1/4X_S)$$

FIGURE 19. CORRELATION INCLUDING EFFECT OF BENZENE SULFONIC ACID

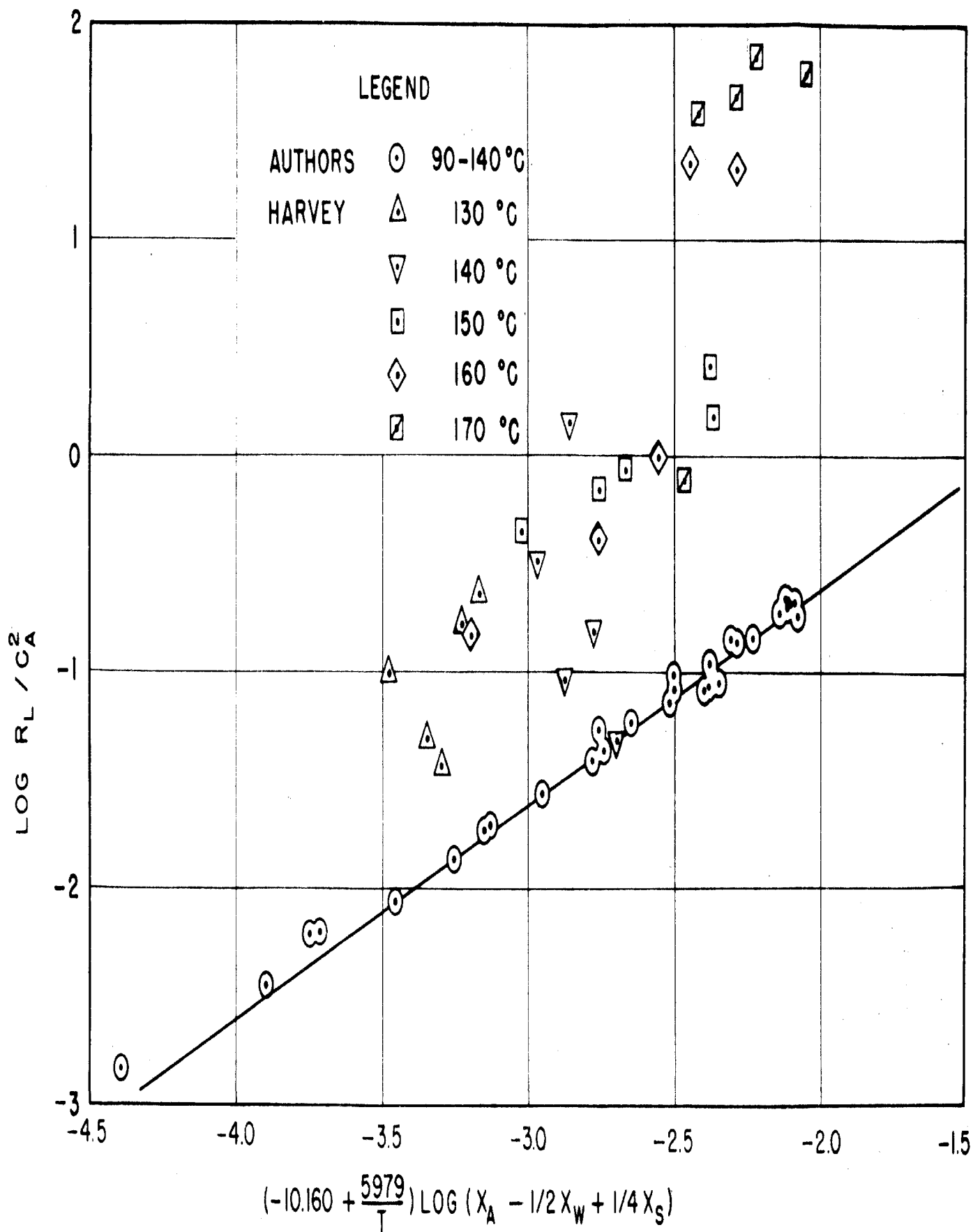


FIGURE 20. TEST OF SECOND-ORDER REACTION WITH RESPECT TO  $\text{H}_2\text{SO}_4$  CONCENTRATION

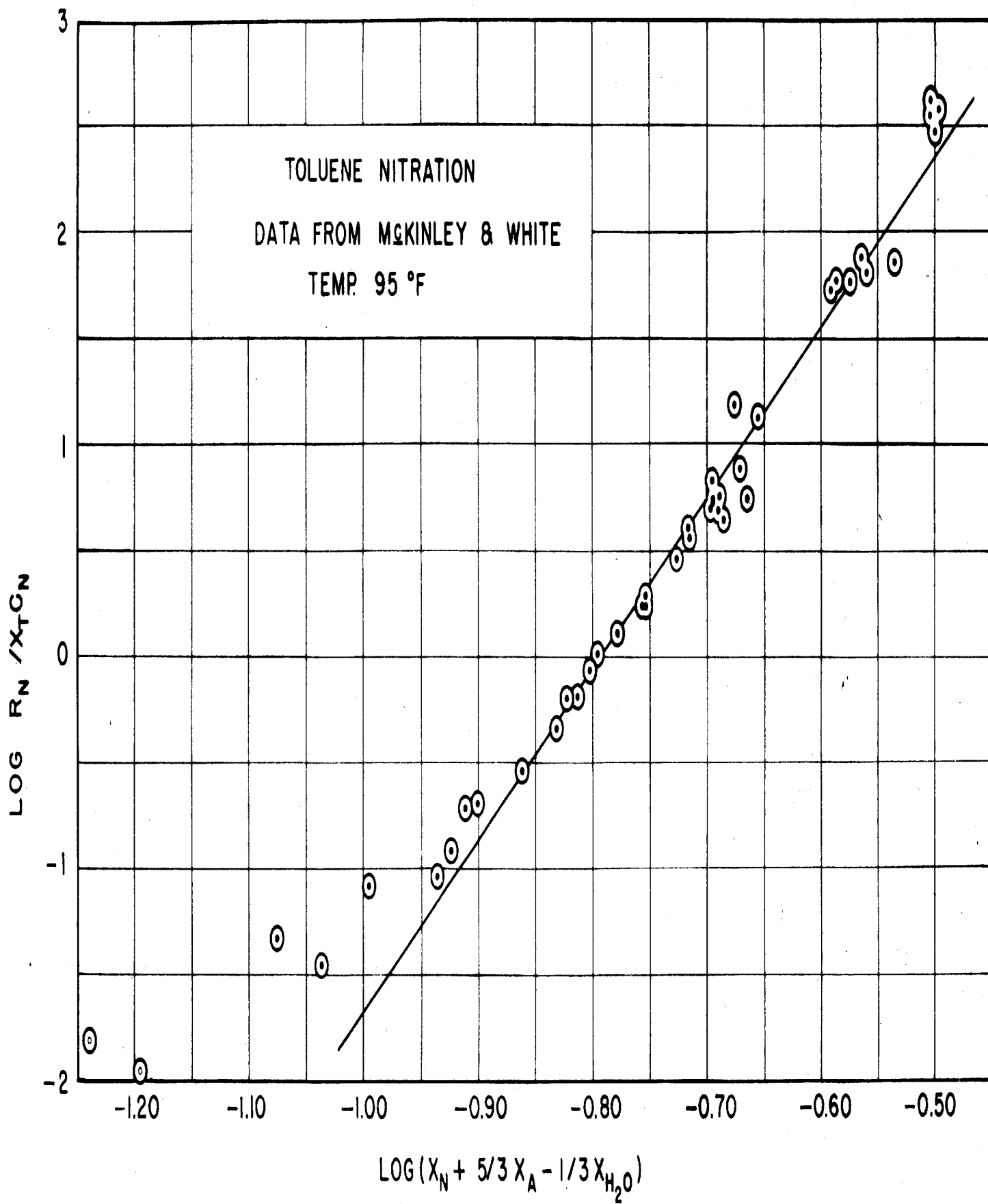


FIGURE 21. REACTION RATE - COMPOSITION CORRELATION OF TOLUENE MONONITRATION

## VI. C O N C L U S I O N S

1. The rate of sulfonation of benzene by benzene-saturated sulfuric acid solutions has been measured over a temperature range from 90°C. to 140°C. The reaction rates determined extend over the range from 0.239 to 15.81 moles of benzenemonosulfonic acid formed per hour per liter of solution.

2. The reaction cell employed maintained the reaction liquid saturated with respect to benzene at stirrer speeds of 650 r.p.m. and above.

3. The logarithm of the specific reaction rate coefficient is a linear function of the reciprocal absolute temperature,

$$\text{Log } k = \frac{A}{T} + B$$

where A and B are functions of the solution composition.

4. The specific reaction rate coefficient is an exponential function of the solution composition  $(x_A - [1/2]x_w + [1/4]x_s)$ .

5. The rate of sulfonation of benzene in benzene-saturated sulfuric acid solutions at atmospheric pressure can be expressed as a function of composition and temperature,

$$R_L = 118 (x_A - [1/2]x_w + [1/4]x_s)^{-9.239 + \frac{5349}{T}} \cdot C_A$$

6. The method employed to correlate rates of reaction in benzene sulfonation has been tested by application to the correlation of rates of reaction in the mononitration of toluene by mixed acid. Specific reaction rates in both systems correlate as exponential functions of the solution compositions.

7. The specific reaction rate of toluene mononitration by mixed acid at 95°F. may be represented by an exponential function of the solution composition, as

$$R_N = 2,520,000 (x_N + [5/3]x_A - [1/3]x_w)^{8.08} x_T C_N$$

N O M E N C L A T U R E

A	Component A
A	Coefficient in Arrhenius equation
a	Stoichiometric coefficient
B	Component B
B	Constant in Arrhenius equation
b	Stoichiometric coefficient
b	Slope
BSA	Benzenemonosulfonic acid
C	Component C
$C_A$	Concentration, mols component A/unit volume
$C_A$	Concentration of $H_2SO_4$ , mol/liter
$C_B$	Concentration, mols component B/unit volume
$C_C$	Concentration, mols component C/unit volume
$C_D$	Concentration, mols component D/unit volume
$C_N$	Concentration of $HNO_3$ , mols $HNO_3$ /liter acid phase
c	Stoichiometric coefficient
D	Component D
$E_A$	Experimental activation energy
e	Base of natural logarithms
F	Free energy
H	Enthalpy
h	Flowmeter differential height, cm.
I	Constant
K	Thermodynamic equilibrium constant
K	Flowmeter constant, ml./hr.(cm.)

$k$	Specific reaction rate coefficient
MNT	Mononitrotoluene
$R_L$	Rate of benzene sulfonation, mol BSA/(hr)(liter)
$R_N$	Rate of toluene nitration, mol MNT/(hr)(liter of acid phase)
$r$	Reaction rate, mol/(unit vol.)(unit time)
$T$	Absolute temperature, deg. Kelvin
$t$	Temperature, deg. Centigrade
$X^\ddagger$	Activated complex component
$x_A$	Mol fraction $H_2SO_4$ , benzene-free basis in sulfonation
$x_A$	Mol fraction $H_2SO_4$ , acid phase, in nitration
$x_N$	Mol fraction $HNO_3$ in acid phase
$x_F$	Mol fraction diphenyl sulfone, benzene-free basis
$x_S$	Mol fraction benzenesulfonic acid, benzene-free basis
$x_T$	Mol fraction toluene in organic phase, on acid-free basis
$x_W$	Mol fraction water

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A P P E N D I X ASAMPLE RUN DATA AND CALCULATIONSRun No. 20

The procedures followed in obtaining the data of this investigation are illustrated herein by a detailed treatment of Run No. 20. This run employed an acid feed concentration of 89.98%  $H_2SO_4$ , an acid feed space velocity of  $3.92 \text{ hr.}^{-1}$ , and was conducted at a temperature of  $100^\circ C$ .

Operating Conditions.

Acid feed: 89.98%  $H_2SO_4$ , 10.02%  $H_2O$ .

Stirrer speed: 650 r.p.m.

Barometer: 731.8 mm. at  $25^\circ C$ .

Ambient temperature:  $25^\circ C$ .

Constant temperature bath heater control,

High: 5.8 amp. through "1250" watt heater.

Low : 3.7 amp. through "750" watt heater.

Acid flowmeter zero: 1.9 cm.

Benzene flowmeter zero: Left, 25.4 cm.; Right, 25.6 cm.

Reaction Liquid Volume.

#1. Liquid level at 1.28 in. below baffle = 357 ml.

#2. Liquid level at 1.26 in. below baffle = 359 ml.

Av. = 358 ml.

Correction for liquid in tubing = 8 ml.

Liquid volume in cell = 366 ml.

T A B L E 9

OPERATING LOG OF RUN NO. 20

Time	Benz. Res. CM.	Benzene FM		Acid Feed		Product		Benz. Rec. CM.	Cell Temp. Mv.	Bath Temp. °C.
		Left CM.	Right CM.	Res. CM.	FM CM.	Rec. CM.	Outage			
3:45	62.64	15.6	34.5	66.68	35.1	6.60		0.0	4.095	97.1
3:52:30	61.37	15.6	34.5	64.04	35.1	9.88	OS-1	1.4	4.109	98.4
4:00	60.09	15.6	34.5	61.42	34.95	14.70		2.7	4.223	99.9
4:07:30	58.85	15.6	34.5	58.84	34.95	19.40		3.95	4.200	99.4
4:15	57.58	15.6	34.5	56.24	34.95	24.20		5.25	4.215	99.7
4:25	55.90	15.7	34.4	52.75	34.95	30.50		7.00	4.232	100.1
4:35	54.22	15.7	34.4	49.34	34.94	35.5	OS-2	8.70	4.225	100.0
4:45	52.55	15.7	34.4	45.86	34.95	41.95		10.68	4.228	100.0
4:55	50.90	15.7	34.4	42.38	34.90	48.24		11.45	4.228	100.0
5:05	49.24	15.7	34.4	38.84	34.90	12.15	Drain*	11.45	4.231	100.05
5:15	47.54	15.7	34.4	35.42	34.90	17.22	OS-3	11.55	4.227	100.0
5:25	45.85	15.6	34.5	31.98	34.86	22.20	OS-4	13.28	4.228	100.0
5:36	44.00	15.6	34.5	28.20	34.90	26.75	**	15.18	4.227	100.0

\*. Volume drained equivalent to 42.20 cm. height in receiver.

\*\* Overflow sample and cell sample taken.

Samples Taken.Overflow Samples for Density Measurements

Sample	Temp.	Density	Density at 25°C.	Weights, Gm.		
				Gross	Tare	Net
OS-1	27.0	1.7091	1.7108	162.7	.66.0	96.7
OS-2	26.9	1.7085	1.7101	161.5	67.3	94.2
OS-3	26.9	1.7086	1.7100	162.1	67.1-	95.0
OS-4	27.0	1.7086	1.7101	164.4	66.0	98.4

## Cell Sample:

Sample + 10 ml. H <sub>2</sub> O + flask	= 144.379 g.
Flask	= <u>59.551 g.</u>
Sample + 10 ml. H <sub>2</sub> O	= 85.828 g.
Wt. 10 ml. H <sub>2</sub> O	= <u>9.971 g.</u>
Weight cell sample	= 74.857 g.
Dilution factor, 84.828/74.857	= 1.1332

## Benzene Condensate Samples:

#1.	4:25:30 to 5:04:30 pm.	<u>Gross</u> 137.47	<u>Tare</u> 57.10	<u>Net</u> 80.37 g.
#2.	5:04:30 to 5:16:00 pm.	130.98	53.86	<u>77.12 g.</u>
		Total		157.49 g.

Product Receiver Levels Adjusted for Outage.

Time	Rec. Level Cm.	Equivalent Samples Cm.	Level Out* Drain Cm.	Adjusted Rec. Level Cm.
3:45	6.60	—		6.60
3:52:30	9.88	1.30		11.18
4:00	14.70	1.30		16.00
4:07:30	19.40	1.30		20.70**
4:15	24.20	1.30		25.50
4:25	30.50	1.30		31.80
4:35	35.50	2.57		38.07
4:45	41.95	2.57		44.52
4:55	48.24	2.57		50.81
5:05	12.15	2.57	42.20	56.92
5:15	17.22	3.85		63.27
5:25	22.20	5.17		69.57**

\* 43.9 ml. is equivalent to 1 cm. difference in receiver level.

\*\* Values used in subsequent flow rate computation.

Flow Rates.

Flow rates were obtained from timed observations of the liquid levels in the reservoirs and receivers:

$$\text{Acid feed rate} = (49.34 - 28.20) \frac{60}{61} (69.1) = 1437 \text{ ml/hr.}$$

$$\text{Benzene feed rate} = (54.22 - 44.00) \frac{60}{61} (68.2) = 685 \text{ ml/hr.}$$

$$\text{Product rate} = (69.57 - 20.70) \frac{60}{77.5} (43.9) = 1661 \text{ ml/hr.}$$

Condensate rate =

$$\left[ (13.28 - 5.25) 44.5 + \frac{157.5}{.880} \right] \frac{60}{70} = 460 \text{ ml/hr.}$$

Acid Feed Analysis.

Sample = 89.4909 - 82.4648 = 7.0261 gm. Diluted to 250 ml. and 25 ml. aliquot portions taken.

#1. NaOH = 47.20 ml.

#2. NaOH = 47.16 ml. Av. 47.18 ml. NaOH.

$$\frac{(47.18)(.27346)(49.04)}{(.70261)(1000)} \times 100 = 89.98\% \text{ H}_2\text{SO}_4.$$

### Cell Product Analysis.

Sample = 153.8630-144.7308 = 9.1322 g.

Diluted to 250 ml. and 25 ml. aliquot portions taken.

Free Sulfuric Acid:

#1. BaSO<sub>4</sub> ppt. = 16.9248-15.4682 = 1.4566 gm.

#2. BaSO<sub>4</sub> ppt. = 17.8984-16.4430 = 1.4554 gm.

Av. = 1.4560 gm.

$$\frac{(1.4560)(0.42017)}{0.91322} \times 100 = 66.99\% \text{ H}_2\text{SO}_4$$

Dilution correction, (66.99)(1.1332) = 75.92% H<sub>2</sub>SO<sub>4</sub>

Total Acidity:

#1. NaOH = 48.12 ml.

#2. NaOH = 48.10 ml. Av. 48.11 ml. NaOH

$$\frac{(48.11)(0.27346)(49.04)}{(0.91322)(1000)} \times 100 = 70.60\% \text{ H}_2\text{SO}_4 \text{ acidity}$$

Dilution correction, (70.60)(1.1332) = 80.00% H<sub>2</sub>SO<sub>4</sub> acidity

Benzene Sulfonic Acid:

$$(80.00-75.92) \frac{158.17}{49.04} = 13.16\% \text{ BSA.}$$

### Overflow Product Analysis.

Sample = 135.3562-127.4295 = 7.9267 gm.

Diluted to 250 ml. and 25 ml. aliquot portions taken.

Free Sulfuric Acid:

#1. BaSO<sub>4</sub> ppt. = 16.7196-15.2977 = 1.4219 gm.

#2. BaSO<sub>4</sub> ppt. = 15.7655 - 14.3436 = 1.4219 gm.

Av. = 1.4219 gm.

$$\frac{(1.4219)(0.42017)}{0.79267} \times 100 = 75.37\% \text{ H}_2\text{SO}_4$$

Total Acidity:

#1. NaOH = 47.14 ml.

#2. NaOH = 47.16 ml. Av. = 47.15 ml.

$$\frac{(47.15)(0.27346)(49.04)}{(0.79267)(1000)} \times 100 = 79.70\% \text{ H}_2\text{SO}_4 \text{ acidity}$$

Benzene Sulfonic Acid:

$$(79.70 - 75.37) \frac{158.17}{49.04} = 13.96\% \text{ BSA.}$$

### Water Analysis.

Fischer Reagent Blank:

#1. 15.00 ml. Fischer reagent = 11.56 ml. alcohol soln.

#2. 15.00 ml. Fischer reagent = 11.59 ml. alcohol soln.

Av. = 11.58 ml.

Overflow Product Water Content:

	#1	#2
Gross	136.5176 g.	136.1991 g.
Tare	<u>136.1991</u>	<u>135.7966</u>
Sample	0.3185 g.	0.4025 g.
Ml. Fisher reagent added	15.00	15.00
Ml. alcohol solution required	3.91	1.89
Blank ml. alcohol	<u>11.58</u>	<u>11.58</u>
Ml. alcohol equivalent of sample	7.67	9.69

Alcohol factor = 0.00458 gm. H<sub>2</sub>O/ml. alcohol solution.

$$\#1. \frac{(7.67)(0.00458)}{(0.3185)} \times 100 = 11.03\% \text{ H}_2\text{O}$$

$$\#2. \frac{(9.69)(0.00458)}{(0.4025)} \times 100 = 11.03\% \text{ H}_2\text{O}$$

Av. = 11.03% H<sub>2</sub>O

## Benzene Condensate Water Content:

	#1	#2
(1) Flask, condensate, and MeOH, gm.	144.24	140.73
(2) Flask and condensate, gm.	137.47	130.98
(3) Flask tare, gm.	57.10	53.86
(4) Wt. condensate sample (2)-(3)	80.37	77.12
(5) Wt. MeOH added (1)-(2)	6.77	9.75
(6) Water content of MeOH added, %	1.51	1.51
(7) Aliquot portion titrated	25/101	50/101
(8) Ml. Fischer reagent added	15.00	15.00
(9) Ml. std. alcohol soln. req'd.	8.48	5.30
(10) Blank, ml. std. alcohol soln.	11.58	11.58
(11) Ml. alc. equiv. of sample (10)-(9)	3.10	6.28
(12) Gm. H <sub>2</sub> O titrated 0.00458 x (11)	.01420	.02876
(13) Gm. H <sub>2</sub> O in MeOH 0.00151 x (5)(7)	.00254	.00730
(14) Gm. H <sub>2</sub> O in Sample (12)-(13)	.01166	.02146

$$\#1. \frac{(0.01166)}{(80.37)} \times \frac{101}{25} \times 100 = 0.0585\% \text{ H}_2\text{O}$$

$$\#2. \frac{(0.02146)}{(77.12)} \times \frac{101}{50} \times 100 = 0.0563\% \text{ H}_2\text{O}$$

$$\text{Av.} = \underline{0.0574\% \text{ H}_2\text{O}}$$

Correction of Cell Analysis by a Sulfur Material Balance.

Basis: If no vaporization of benzene occurs during withdrawal of the cell sample, the sulfur contents of the cell and overflow samples should be equal.

	Factor	Cell Analysis	Overflow Analysis	Adjusted Cell Analysis
% H <sub>2</sub> SO <sub>4</sub>		75.92	75.37	75.87
% BSA		13.16	13.96	13.15
% H <sub>2</sub> O		—	11.03	10.94
% Total			99.36	99.96
%S in H <sub>2</sub> SO <sub>4</sub>	.32688	24.817	24.637	
%S in BSA	.20269	2.667	2.830	
% Total		27.484	27.467	



$$\text{Correction factor} = \frac{27.467}{27.484} = 0.9994$$

$$\text{Adjusted H}_2\text{SO}_4 = (75.92)(0.9994) = 75.87\%$$

$$\text{Adjusted BSA} = (13.16)(0.9994) = 13.15\%$$

After-Reaction Adjustment of H<sub>2</sub>O Concentration:

$$\text{After-reaction decrease in } \% \text{ H}_2\text{SO}_4 = 75.87 - 75.37 = -0.50\%$$

$$\text{Water formed} = 0.50 \times \frac{18.0}{98.1} = +0.09\%$$

$$\text{Adjusted H}_2\text{O} = 11.03 - 0.09 = 10.94\%$$

### Material Balances.

Total Material Balance:

$$\text{In: H}_2\text{SO}_4, \quad 1437 \times 1.8090 \quad = 2599 \text{ g./hr.}$$

$$\text{Benzene,} \quad 685 \times 0.874 \quad = \underline{599}$$

$$\text{Total} \quad 3198 \text{ g./hr.}$$

$$\text{Out: Product,} \quad 1661 \times 1.636 \quad = 2783 \text{ g./hr.}$$

$$\text{Condensate,} \quad 460 \times 0.874 \quad = \underline{402}$$

$$\text{Total} \quad = 3185 \text{ g./hr.}$$

Note: 1.636 = estimated product density at 50°C.

Product Rate by Difference:

$$\text{Total materials in} \quad = 3198 \text{ g./hr.}$$

$$\text{Condensate out} \quad = \underline{402}$$

$$\text{Product rate} \quad = 2796 \text{ g./hr.}$$

Sulfur Balance:

$$\text{In: By H}_2\text{SO}_4, \quad (2599)(.8998)(.3269) \quad = 764.4 \text{ g./hr.}$$

$$\text{Out: By H}_2\text{SO}_4, \quad (2796)(.7587)(.3269) \quad = 693.5 \text{ g./hr.}$$

$$\text{By BSA,} \quad (2796)(.1315)(.2027) \quad = \underline{74.5}$$

$$\text{Total} \quad 768.0 \text{ g./hr.}$$

## Oxygen Balance:

In:	By H <sub>2</sub> SO <sub>4</sub> ,	(2599)(.8998)(.6525)	= 1525.8 g./hr.
	By H <sub>2</sub> O	, (2599)(.1002)(.8884)	= <u>231.3</u>
		Total	= 1757.1 g./hr.
Out:	By H <sub>2</sub> SO <sub>4</sub> ,	(2796)(.7587)(.6525)	= 1384.1 g./hr.
	By BSA	, (2796)(.1315)(.3035)	= 111.6
	By H <sub>2</sub> O	, (2796)(.1094)(.8884)	= 271.8
	By Cond.,	(402)(.0006)	= <u>.2</u>
		Total	= 1767.7 g./hr.

## Benzene Balance:

In:	Benzene feed,	(599)(1.000)	= 599.0 g./hr.
Out:	By Cond.,	(401.8)(.9994)	= 401.6 g./hr.
	By BSA	, (2796)(.1315)(.4938)	= 181.6
	By Product,	(2796)(.0004)	= <u>1.1</u>
		Total	= 584.3 g./hr.

Rate of Benzene Sulfonation.

$$\text{Rate BSA formation} = (2796)(.1315) = 367.7 \text{ g./hr.}$$

$$\frac{367.7}{158.2} = 2.325 \text{ mols BSA/hr.}$$

$$\frac{2.325}{0.366} = 6.35 \text{ mols BSA/hr./liter}$$

A P P E N D I X BSTANDARD SOLUTIONS FOR THE DETERMINATION OF WATERPreparation of Fischer Iodine Reagent.

The Fischer reagent was prepared according to the method of Almy, Griffin and Wilcox (1). It is a dark brown solution of approximately the following composition.

Pyridine	31.3%
Methyl alcohol, anhydrous	48.7
Sulfur dioxide	6.4
Iodine	<u>12.6</u>
	100.0%

The solution was prepared in 2000 - gm. quantities by the following procedure: 626 g. pyridine was mixed with 700 ml. absolute methyl alcohol in a 2-liter flask. The flask was then tared on a laboratory scale and 128 g. of dry gaseous  $\text{SO}_2$  introduced into the pyridine-alcohol solution through a glass tube immersed in the liquid. After cooling the solution, an additional 550 ml. of methyl alcohol was added and the solution thoroughly mixed. Then 252 g. of iodine crystals was added. The iodine liberated considerable heat upon solution, and care was necessary to avoid overheating the mixture.

Standardization of Alcohol-Water Solution.

The trihydrate of sodium acetate,  $\text{Na Ac} \cdot 3\text{H}_2\text{O}$ , was used as a primary standard; the hydrate contains 39.73% by weight of water.

The alcohol-water solution was standardized by the following procedure: A blank was obtained by determining the

number of ml. of alcohol solution required to react with 20 ml. of iodine solution. Then 20 ml. of iodine solution were added to an accurately weighed portion of approximately 0.20 g.  $\text{Na Ac} \cdot 3\text{H}_2\text{O}$ , and followed by titration with the alcohol solution to react with the excess iodine reagent. The difference between the quantities of alcohol solution used in the two titrations was equivalent to the water present in the  $\text{Na Ac} \cdot 3\text{H}_2\text{O}$  standard.

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