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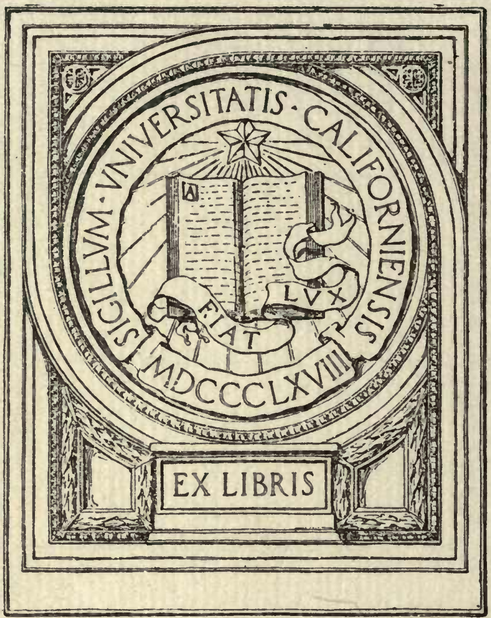
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BY
ADELBERT WILLIAM HARVEY

A DISSERTATION

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE
UNIVERSITY OF PITTSBURGH IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR CANDIDACY FOR THE DEGREE
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The Sulfonation of Benzene

The action of sulfuric acid on benzene has interested a number of investigators, principally because of the importance of the resulting product in the manufacture of picric acid during the war.

The authors were interested in a study of the sulfonation of benzene resulting from the passage of vaporized benzene through sulfuric acid, with the view toward finding the best conditions which would increase the efficiency of the sulfonation and reduce the possibility of certain undesirable side reactions to a minimum.

AN EXCELLENT paper by Peterkin[1] gives an idea of the various methods that have been devised for the production of benzene monosulfonic acid. The principal difficulty encountered in the process of refluxing benzene with sulfuric acid at about 100° to 110° C. is that a large part of the sulfuric acid is never converted into the sulfonic acid, because the reaction reaches an equilibrium when the sulfuric acid decreases to a concentration of 78 per cent calculated on the basis of the water present. The loss of acid and the necessity for its removal before using the sulfonic acid produced in subsequent operations have furnished the occasion for a study of conditions leading to a more complete utilization of the original sulfuric acid.

MATERIALS

The benzene was repeatedly washed with concentrated sulfuric acid and the treatment was continued until no color could be observed in the acid layer. After neutralization of the acid in the benzene with a dilute solution of alkali and separation of the hydrocarbon layer, the benzene was distilled. The fraction boiling between 79° and 82° C. was collected, dried over metallic sodium, and redistilled, the final product having a practically constant boiling point.

The sulfuric acid was of the ordinary C. P. variety, free from metallic salts, such as calcium, iron, and manganese, which might exert a catalytic effect. Analysis showed it to be 93.20 per cent sulfuric acid.

EXPERIMENTAL PROCEDURE

Fig. 1 illustrates the method employed for the sulfonation. The benzene was vaporized in the flask, *A*. The flask was heated by a water bath placed upon an electric heater, whereby the flow of benzene vapor was made as uniform as possible. *S* is the sulfonation chamber containing the sulfuric acid. An outer jacket, *O*, containing a solution of glycerol in water, boiling at the temperature desired for the sulfonation, served to control the temperature. The tube conducting the vapors of benzene into the acid terminated in a bulb having several holes of small diameter. A large number of small bubbles of benzene vapor were thus produced with a relatively large surface for contact with the acid. The rest of the apparatus is self explanatory.

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[1] *Ind. Eng. Chem.*, **10**, 738 (1918).

The glycerol-water solution in the outer jacket was heated to the desired temperature of sulfonation, after which the vapor of benzene was forced through the sulfuric acid contained in the inner jacket. The original quantity of acid was 50 cc. To permit the maximum amount of action and to minimize temperature changes, the flow of vapor was so adjusted that relatively little change in temperature was noticeable, and so that sufficient benzene vapor would escape from the acid and thus carry away the water formed in the reaction. By this procedure the acid was prevented from becoming too dilute to react with the benzene. The results obtained indicate that in this way practically all the acid becomes available for sulfonation. Samples were removed from the reaction chamber at regular intervals and analyzed to determine the progress of the reaction.

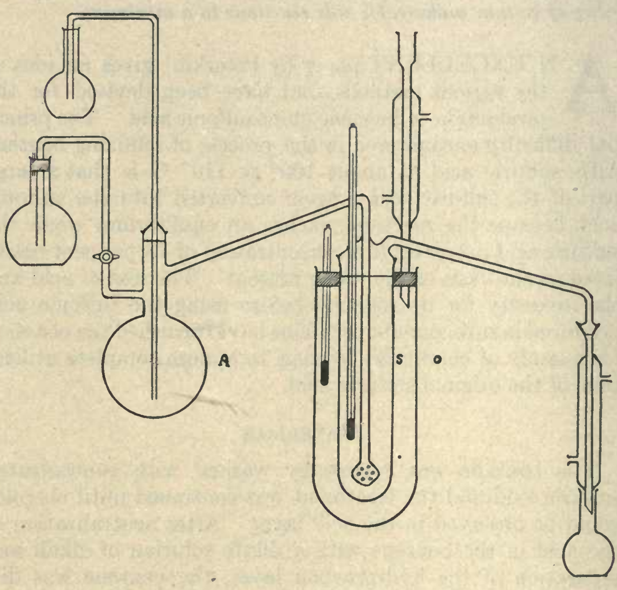

FIG. 1

ANALYSIS OF REACTION PRODUCTS

SULFURIC ACID—Sulfuric acid was estimated as barium sulfate. The required sample was diluted with distilled water, insoluble substances were filtered off, and the acid precipitated as barium sulfate. The addition of some picric acid to the solution aids materially in the production of a coarse-grained precipitate.

BENZENE MONOSULFONIC ACID—The monosulfonic acid was estimated indirectly. The total acidity was measured by means of 0.1 *N* sodium carbonate solution, using methyl orange as indicator. The sulfuric acid present having been estimated as mentioned, the monosulfonic acid was estimated by difference.

DIPHENYL SULFONE—On account of the appreciable solubility of diphenylsulfone in water, the following method was employed to estimate the quantity of this product. The sample was diluted with 200 cc. of water and neutralized with dry sodium carbonate, as light excess being used. The solution was then evaporated to dryness and heated at 110° C. for several hours. The residue was next extracted with petroleum ether in a Soxhlet extraction thimble which had previously been treated with this same solvent to remove all soluble material. Twelve to fourteen hours of extraction were necessary to remove all the sulfone, but the results were completely satisfactory.

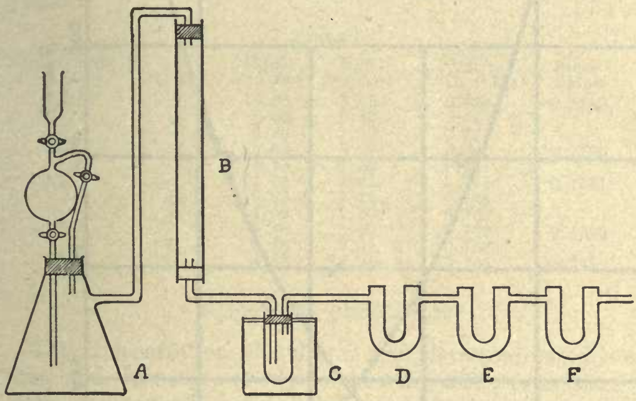

FIG. 2

UNSULFONATED BENZENE—The amount of unsulfonated benzene was found to be so small that it was not estimated.

WATER—For reasons mentioned later it was necessary to estimate the water content of the samples directly. The usual method, calculating this quantity by difference, was not applicable on account of the small amount present in some samples and because a certain quantity of charred products was always present, being formed especially at the higher temperatures. The calculation was, therefore,

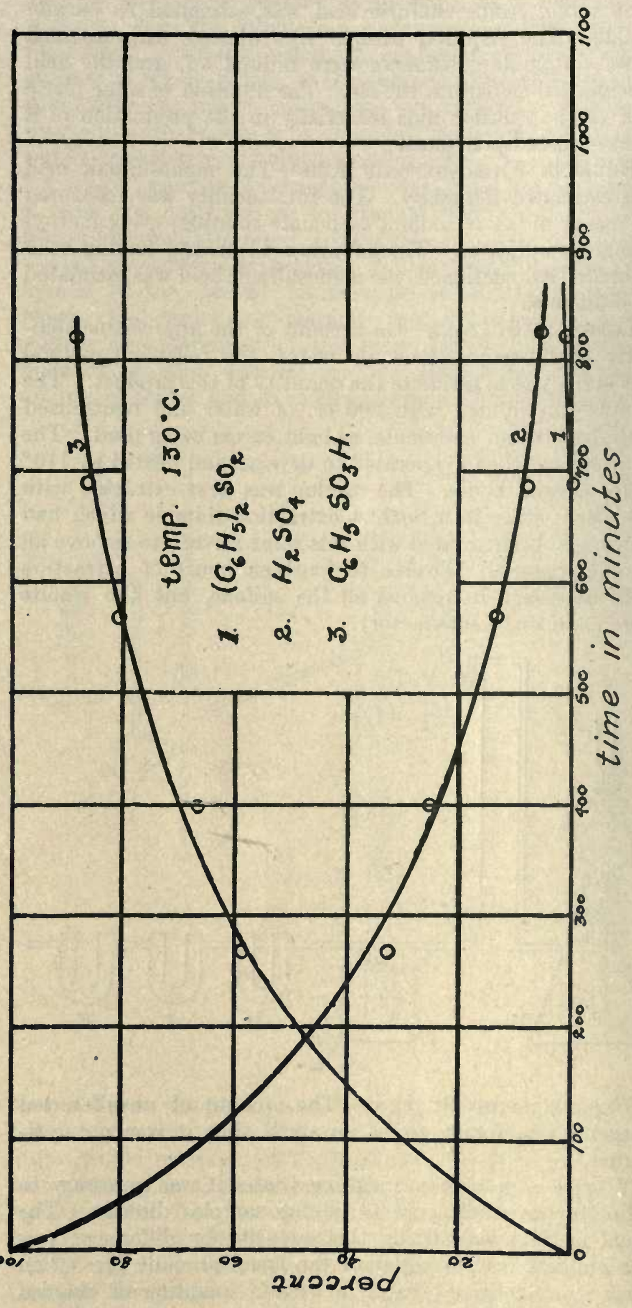
temp. 130°C.
1. $(C_6H_5)_2SO_2$
2. H_2SO_4
3. $C_6H_5SO_3H$
1
2
3
percent
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
1000
1100
time in minutes

FIG. 3

too inaccurate to have any significance. The apparatus shown in Fig. 2 illustrates the method employed in the estimation of the water content of the samples. *A* represents a carbon dioxide generator, the gas from which was dried by passage through the large tube, *B*, filled with calcium chloride. The gas then passed through the reaction chamber, *C* (a 4 × 20-cm. test tube), and out through the calcium chloride absorption tubes, *D* and *E*, and the protector tube, *F*. A weighed sample of the reaction products was placed in *C*, a known weight of distilled water added from a Lunge pipet, and the acid solution formed neutralized with an excess of anhydrous sodium carbonate which had been dried for several days at 180° C. The temperature of the oil bath surrounding *C* was then gradually raised to 180° C., while a stream of carbon dioxide was passed through the apparatus. The water collected in the absorption tubes, *D* and *E*, included the amount present in the sample, the amount added from the pipet, and that formed in the neutralization of the acids present. The concentration of the acids in the sample and also the amount of water added being known, the total amount of water originally present was obtained by difference.

RESULTS

The results obtained are shown in Figs. 3 to 7 and in Table I.

TABLE I

Temperature ° C.	Sample	H_2SO_4 Per cent	H_2O Per cent	$\frac{H_2SO_4}{H_2SO_4 + H_2O}$	Mean Value
130	3	13.15	3.85	0.775	0.7753
	4	8.06	2.30	0.778	
	5	6.20	1.82	0.773	
140	3	15.60	3.60	0.769	0.7700
	4	5.13	1.52	0.771	
150	1	12.74	3.92	0.765	0.7647
	2	6.92	2.14	0.764	
	3	4.60	1.40	0.765	
160	2	9.50	3.00	0.760	0.7590
	3	6.26	2.01	0.758	
170	1	8.57	2.91	0.746	0.746

DISCUSSION OF RESULTS

The concentration of sulfuric acid decreases rapidly at first, and then more slowly as the sulfonation proceeds. A value is eventually reached below which the concentration does not seem to fall. This is probably due to the regeneration of sulfuric acid, which is formed by the decomposition of the monosulfonic acid into sulfuric acid and diphenylsulfone. This is particularly noticeable at 170° C., where the sulfuric acid concentration becomes constant in the neighborhood of 0.60 per cent.

The concentration of the monosulfonic acid increases rapidly at first, then more slowly as the reaction proceeds, the rate being greater at the higher temperatures. The concentration reaches a maximum and then decreases, owing to the formation of diphenylsulfone. The maximum concentra-

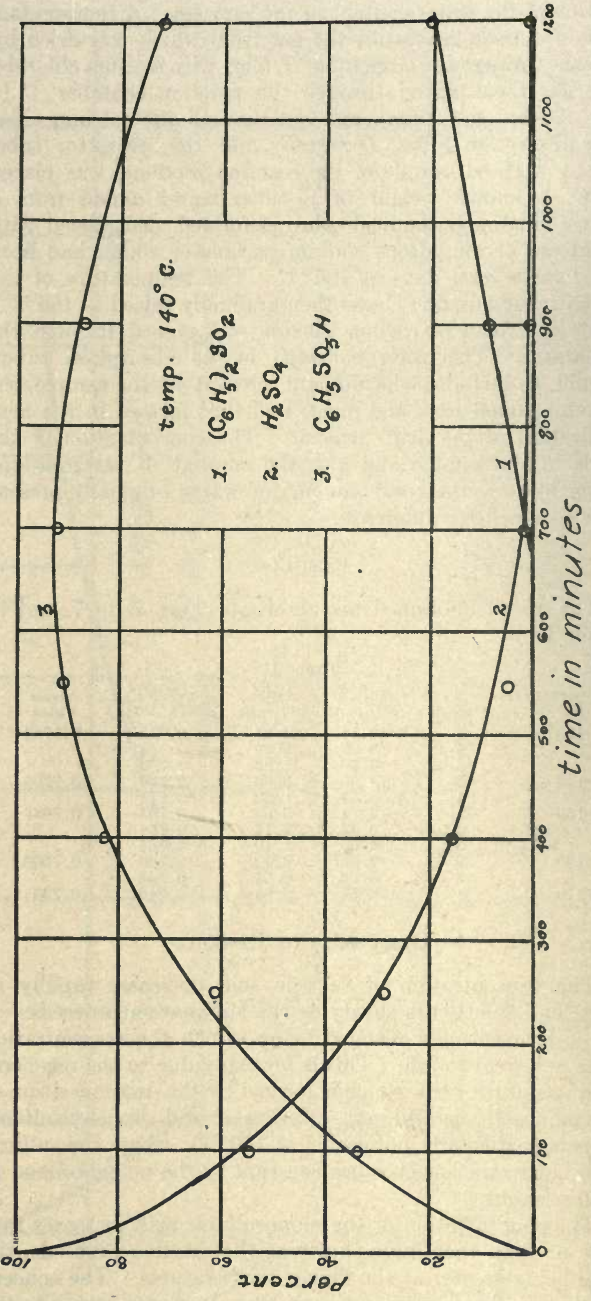
temp. 140° C.
1. $(C_6H_5)_2SO_2$
2. H_2SO_4
3. $C_6H_5SO_3H$
percent
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
time in minutes
1
2
3

FIG. 4

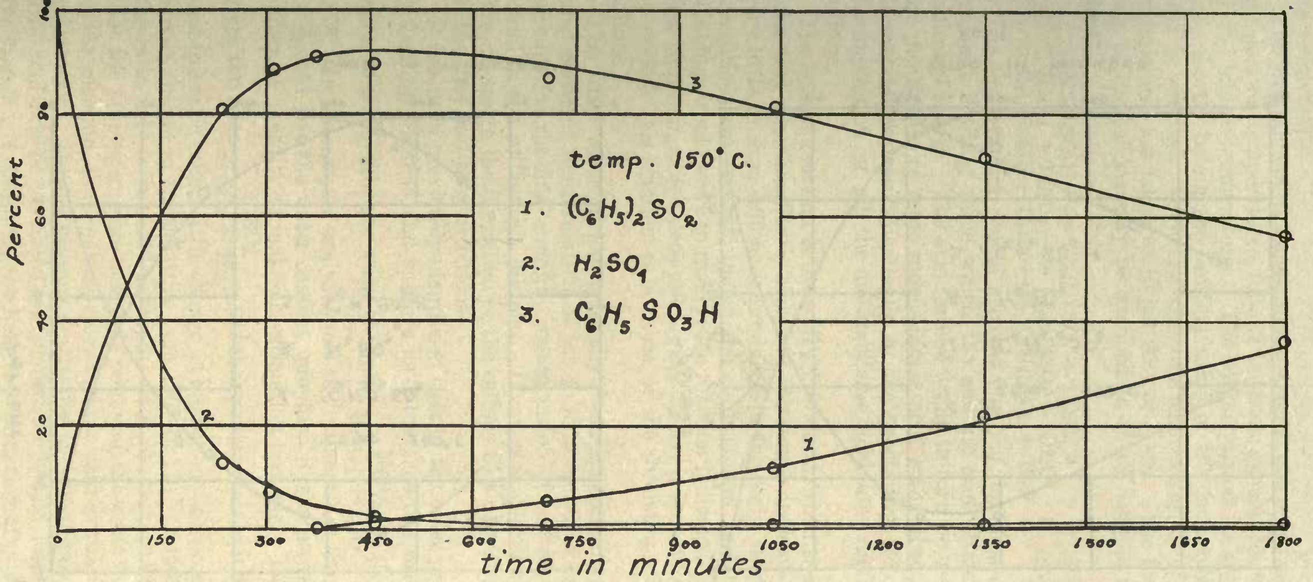
percent
100
80
60
40
20
0
150
300
450
600
750
900
1050
1200
1350
1500
1650
1800
time in minutes
temp. 150° C.
1. $(C_6H_5)_2SO_2$
2. H_2SO_4
3. $C_6H_5SO_3H$
1
2
3

FIG. 5

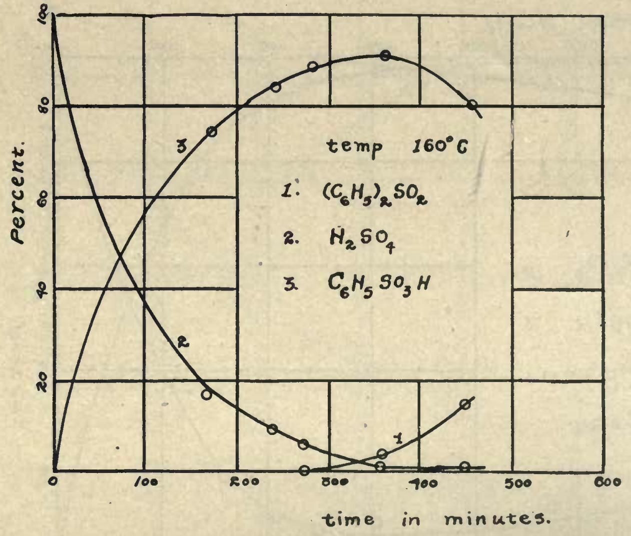
Percent.
100
80
60
40
20
0
100
200
300
400
500
600
time in minutes.
temp 160°C
1. $(C_6H_5)_2SO_2$
2. H_2SO_4
3. $C_6H_5SO_3H$
1
2
3

FIG. 6

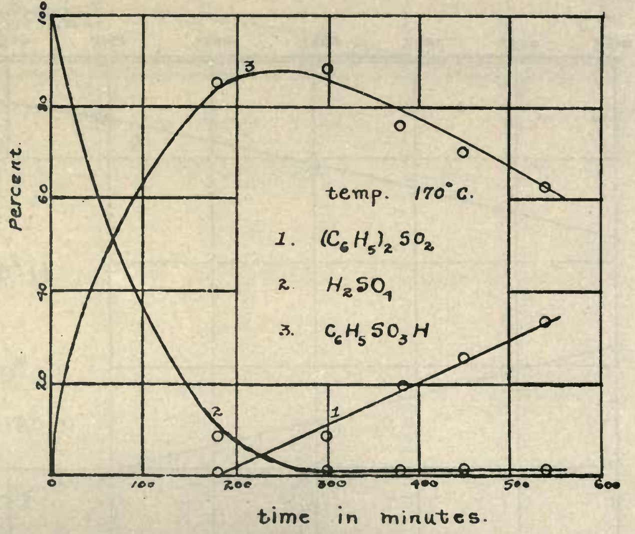
Percent.
100
80
60
40
20
0
100
200
300
400
500
600
time in minutes.
temp. 170°C.
1. $(C_6H_5)_2SO_2$
2. H_2SO_4
3. $C_6H_5SO_3H$
1
2
3

FIG. 7

tion appears to be between 88 and 92 per cent, depending on the temperature.

The formation of diphenylsulfone, though not very evident at the lower temperatures, follows the same general course as at the higher temperatures. The sulfone makes its appearance shortly before the limiting value of the monosulfonic acid is reached. In every case the concentration of the sulfuric acid has fallen to 10 per cent or lower. The formation of the sulfone may be ascribed to three possible reactions:

$$2C_6H_5SO_3H \longrightarrow (C_6H_5)_2SO_2 + H_2SO_4 \qquad (1)$$
$$2C_6H_6 + H_2SO_4 \longrightarrow (C_6H_5)_2SO_2 + 2H_2O \qquad (2)$$
$$C_6H_5SO_3H + C_6H_6 \longrightarrow (C_6H_5)_2SO_2 + H_2O \qquad (3)$$

The first reaction would account best for the apparently constant limiting value which the sulfuric acid attains, as indicated before. The acid formed would in turn be used in the production of more monosulfonic acid with subsequent decomposition, resulting finally in the practically complete decomposition of all the monosulfonic acid into diphenyl sulfone.

The second reaction is more likely to occur when the sulfuric acid concentration is high, but the results indicate that very little, if any, sulfone is produced in the early stages of the sulfonation, so that, unless the sulfuric acid present at this stage would serve to reverse the reaction indicated in the first equation, which does not appear likely, it seems logical to exclude this reaction as a cause of the formation of the sulfone.

The third reaction has generally been accepted[2] as the chief cause of the formation of the sulfone, but it does not account for the final uniform concentration of sulfuric acid found in the sulfonation samples. It appears logical, therefore, to assign the formation of the sulfone to a combination of the first and third reactions.

It has been previously mentioned that in the older process of heating benzene and sulfuric acid together the reaction came to an equilibrium when the ratio $\frac{H_2SO_4}{H_2SO_4 + H_2O}$ became 0.78. In the samples analyzed one of the quantities that was estimated was the water content, provided it was present in sufficient quantity to make an estimation possible. Table I gives the ratio $\frac{H_2SO_4}{H_2SO_4 + H_2O}$, and the results obtained indicate that this ratio suffers little change as the sulfonation proceeds, even a change in temperature from 130° to 170° C. reducing the ratio only from 0.773 to 0.746. It is obvious, therefore, that the process consists in simply removing the water formed in the reaction, thus making more sulfuric acid available for sulfonation. In this manner practically all the original sulfuric acid may be converted into monosulfonic acid, and if the reaction is not continued too long the formation of diphenyl sulfone will be negligible.

[2] Guyot, *Chimie & Industrie*, **2**, 879 (1919).

From the standpoint of time consumed and energy required to vaporize the benzene used, the process can best be carried out at 160° to 170° C. At this temperature the formation of diphenyl sulfone is no more noticeable than at the lower temperatures, as in all cases only traces of the sulfone were observed while the concentration of the sulfonic acid was rising to its well-defined maximum. The higher temperature might appear to be ideal for the formation of a black charred residue so often found in organic reactions, but even this is scarcely more noticeable than at the lower temperatures at which observations were made. The quantity of charred products rarelv exceeded 2 or 3 per cent of the total reaction product.

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VITA

Adelbert William Harvey was born in Central Square, New York, March 8, 1894. His elementary and high school training were received there. After teaching one year in public school, he entered Colgate University and at the end of the Freshman Year transferred to Syracuse University. He was graduated in 1917 with the degree of Bachelor of Science in Chemistry. He took up graduate work at the University of Pittsburgh in September, 1917, and received the degree of Master of Science in 1919. During this time and while continuing his studies toward the degree of Doctor of Philosophy, he served as instructor in inorganic chemistry.

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