

PART I.—THE CONVERSION OF ETHYL ALCOHOL INTO ETHER.

INTRODUCTION.

The manufacture of ether is of considerable importance since ether functions as a solvent in many technical processes, more especially those connected with organic chemical industries and the manufacture of explosives. Recently there has been a growing demand for ether in preparing motor fuels of the Natalite type which may contain as much as 45 per cent. of this ingredient.

The production of ether by the sulphuric acid process has reached a very high state of efficiency. On a laboratory scale, if the acid is maintained at the usual temperature of 130–140°, considerable quantities of sulphur dioxide and ethylene are evolved; the conversion is only about 40 per cent. and when the weight of ether produced reaches some 16 times that of the sulphuric acid used, the conversion falls still lower. The acid mixture has then to be discarded owing to the charring which takes place (Cf. Evans and Sutton, *J. Amer. Chem. Soc.*, 1913, 35, 794).

On the manufacturing scale, it is possible to work at lower temperatures with the result that the side reactions are almost eliminated. Very little sulphur dioxide and practically no ethylene are produced and a given weight of acid will convert much more alcohol than it will in the laboratory. As the spent acid can be recovered, it is possible to reduce the actual consumption to a very low figure. At the Merebank factory in Natal the consumption of acid and caustic soda was 3 and 14 lbs. respectively per 100 lbs. of ether, while at Gretna, where the production was very large, these were reduced to the remarkably low figures 0.59 and 0.65 (*Second Report of Costs and Efficiencies, Department of Explosives Supply*, 1918, 99).

It is thus evident that any method of production intended to displace the sulphuric acid process would have to present remarkable advantages before there could be any question of its adoption. There are, however, certain disadvantages attending the use of sulphuric acid, particularly where, as in India, it is expensive, and where the size of

an ether-factory would not warrant the erection of an acid plant. It was considered of interest, therefore, to examine some of the solid catalysts which have been used for dehydrating alcohol and to ascertain whether they would compare at all favourably with sulphuric acid.

HISTORICAL.

The greater part of the work which has been conducted upon these lines is due to French chemists, especially Sabatier and his co-workers. Senderens (*Compt. rend.*, 1909, **227**, 229) discovered the catalytic method of making ether in his work upon metallic oxides as dehydrating catalysts. His method consists in passing alcohol vapour over precipitated alumina heated to $240-260^{\circ}$, the products being ether, unchanged alcohol and water. Sabatier and Mailhe (*Ann. Chim. Phys.*, 1910, viii, **20**, 346), showed that anhydrous aluminium sulphate is a good catalyst for preparing ether, but gave no experimental details. No satisfactory yield of ether was obtained by using thoria, titania and blue oxide of tungsten, although these are very efficient catalysts for the preparation of ethylene at higher temperatures. Mailhe and Godon (*Bull. Soc. Chim.*, 1919, **25**, 565) extended the idea to the use of the cheaper and more easily available potash alum. The alum was heated to $190-195^{\circ}$, i.e., slightly higher than the temperature required for complete dehydration. Using 170 grams of the catalyst in a series of four tubes, each 60 cm. long and 13 mm. in diameter and kept heated over a grating by a series of well regulated burners, so that the internal temperature was $190-195^{\circ}$ while the external temperature was $250-260^{\circ}$, a yield of ether equivalent to 71 per cent. of the theoretical was obtained when using 95 per cent. alcohol at 25 c.c. an hour. The yield depended on the weight of the catalyst and on the concentration of alcohol.

Reynose (*Ann. Chim. Phys.*, 1856, (3) **48**, 385) has used magnesium sulphate and chrome alum as catalysts, but no details of the method are available.

APPARATUS AND METHOD.

It was thought desirable to make preliminary tests with a number of catalysts under fairly uniform conditions in order to find out which was the most suitable.

The general plan of procedure was to pass the heated vapours over the hot catalyst and collect the resulting products by suitable devices. The alcohol was measured from a graduated separating

funnel and was allowed to flow through a pinch-cock and a capillary dropper which served to keep the rate of flow uniform, into a spiral copper tube vaporiser which was heated by means of a burner. The alcohol was vaporised completely, and after being super-heated in the hotter portion of the spiral was led through the reaction tube in which were placed about 100 grams of the granular catalyst. On emerging from the tube the vapours were either fractionally condensed, or collected as a whole in a receiver kept in a freezing mixture of ice and salt and subsequently fractionated with a Young's evaporator column. Samples of ether obtained were occasionally redistilled with the column and left no residue.

The specific gravity of the ether obtained was always higher (Sp. G.₂₅²⁵ = 0.715) than that of pure anhydrous ether (Sp. G.₂₅²⁵ = 0.710 Perkins, *J. Ind. Eng. Chem.*, 1917, 9, 521) indicating that the product obtained is probably the constant boiling mixture of ether and water containing 1.3 per cent. of water (Wade and Finnemore, *J. Chem. Soc.*, 1909, 95, 1842). Except when the vaporiser leaked, the total weight of the distillate (to the nearest 0.1 gram) almost agreed with the weight of alcohol admitted to the apparatus. The results were occasionally checked by determining the amount of unchanged alcohol in the clear residue after distilling the ether.

The reaction-tube consisted of a galvanised iron pipe 80 cm. long and 13 mm. in diameter fitted with a T at the exit end. A brass tube 20 cm. × 6 mm. closed at one end was inserted into the end of the tube to protect the mercury thermometer which recorded the inside temperature and the issuing vapours passed through the side branch. The iron pipe was covered with a layer of sheet asbestos and 60 ft. of No. 20 nichrome wire (resistance = 30 ohms) were wound on it with a pitch of 8 turns to the inch, the portion of the tube at the ends being wound closer to balance the heat loss owing to exposure.

A 100-volt circuit was used for heating and the temperature was controlled within a range of 5° by means of an adjustable resistance, a current of 1.2 amps, being sufficient to maintain the temperature at 210°. The temperature of the surface of the iron pipe was measured by a thermo-couple hard soldered to the pipe at its centre. The whole of the tube was packed with asbestos powder and contained in a wooden box. The temperature in the inside of the reaction tube for a length of 60 cm. and that of the surface of the tube were the same and uniform within 5°. The catalyst was confined to this region, the vacant space at the ends being packed with glass beads or pieces of pumice which were found to be inert.

Considerable care was necessary in designing the winding and in adjusting the quantity of lagging so as to obtain this uniformity. In a preliminary set of experiments these precautions were not taken and a difference of over 100° was found between the middle and ends of the catalyst.

EXPERIMENTS WITH DIFFERENT CATALYSTS.

These experiments were carried out in apparatus No. 1 at temperatures up to 300° . In each case an equal volume (60 cm. \times 13 mm.) of the catalyst was used because, from a technical point of view, the yield obtained from a given volume of catalyst in a given time is the main criterion of the efficiency. The alcohol used was a commercial product containing 88 per cent. of alcohol by weight, and this was admitted to the catalyst tube at the rate of about 50 cc. per hour.

(a) ALUMINA.

(1) *Senderens' Method.*—One kilogram of potassium alum was dissolved in 6 litres of water and the aluminium hydroxide, precipitated by ammonia, was washed with hot water until the filtrate gave only a faint test for sulphate. The hydroxide was dissolved in caustic soda solution and precipitated again with dilute sulphuric acid and washed for two weeks until free from sulphate. The hydroxide was then filtered by suction, dried at 200° and broken up into small granules; 48 grams of the substance between 10 and 20 mesh were used. The results of the experiments are given in Table I.

TABLE I.

*Catalyst Alumina prepared by Senderens' method. Weight, 48 grams.
Alcohol, 88 per cent. Rate 50 cc. per hour.*

| Experiment No. | Temperature in degrees centigrade | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|-------------------------|----------------------------|-----------------------|-----------------------|
| 303 | 240 | 90.2 | 86.0 | ... | ... |
| 304 | 250 | 82.2 | 81.0 | ... | ... |
| 305 | 265 | 86.0 | 85.0 | 6 | 10 |
| 306 | 290 | 82.0 | 77.0 | 7 | 13 |
| 307 | 300 | 81.6 | 78.0 | 11.0 | 20 |
| 308 | 320 | 86.0 | 86.0 | 17.0 | 28 |
| 309 | 240 | 82.0 | 82.0 | ... | ... |
| 310 | 260 | 81.6 | 80.0 | 17.0 | 30 |
| 311 | 260 | 75.5 | 75.0 | 12.0 | 27 |
| 312 | 260 | 82.0 | 83.5 | 12.5 | 21 |
| 313 | 300 | 65.6 | 66.5 | 19.0 | 40.4 |

After Experiment No. 309 the catalyst was heated at 450° for half-an-hour.

With this catalyst there is no conversion up to 260° . The percentage conversion increases from 10 to 28 as the temperature is raised to 320° , a remarkable fact being the absence of the formation of ethylene at $300\text{--}320^{\circ}$. This might be due to low catalytic activity, but it is nevertheless interesting because it indicates the possibility of preparing a catalyst which will catalyse the formation of ether and will not dehydrate the latter at comparatively high temperatures. In the case of most of the other catalysts studied, ethylene-formation was very evident at about 270° .

When the same catalyst was heated at 450° for half-an-hour in the tube and the reaction carried out at 260° , the conversion in the first run was 30 per cent. as against 10 per cent. in experiment No. 305, but it decreased on repeating the experiment. At 300° the conversion was 40 per cent. as against 20 per cent. in experiment No. 307, but the product was impure and had a peculiar smell. At 310° ethylene-formation was very rapid.

Senderens (*loc. cit.*) states that if the rate of passing alcohol is sufficiently slow, a quantitative conversion of alcohol into ether is obtained at $240\text{--}260^{\circ}$ with this catalyst. It is difficult to reconcile this statement with the results we have obtained.

(2) *Alumina by Baeyer's Method.*—A few experiments were made with a sample of alumina prepared from bauxite at the Institute on a moderately large scale by extraction with sodium hydrate solution under pressure at 140° and precipitation with alumina. It contained 0.1 per cent. free alkali. No conversion was obtained at any temperature from $200\text{--}300^{\circ}$. The substance was then heated to various temperatures from $300\text{--}500^{\circ}$ and the reactions carried out at $250\text{--}260^{\circ}$. In every case the alcohol was received unchanged after passing through the reaction chamber.

(3) *Modification of Engelder's Method.*—Engelder (*J. Physical Chem.*, 1917, 21, 676) has obtained a 75 per cent. conversion of alcohol into ether at 210° when passing absolute alcohol at 10 c.c. an hour over 1 gram of alumina prepared by precipitation from aluminium nitrate. As a variation we precipitated the hydroxide on pumice. 100 grams of pumice between 20 and 40 mesh were mixed with a concentrated solution of 35 grams of aluminium nitrate and the mass dried by heating with constant stirring. The pumice was then treated with aqueous ammonia and washed with hot water. The resulting product was drained and dried at 110° and subsequently heated to 250° to drive off the remaining ammonium nitrate. This substance, which contained about 10 per cent. alumina on the weight of pumice, gave no conversion at temperatures from $250\text{--}300^{\circ}$.

(b) BASIC ALUMINIUM SULPHATE.

This substance was prepared by adding a solution of 45 grams of caustic soda to a solution of 500 grams of potassium alum in 3 litres of water slowly at room-temperature with constant stirring. The precipitate was allowed to settle, washed by decantation, filtered and dried at 100–110°. The resulting substance has the formula $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{Al}_2\text{O}_3)_4 \cdot 15 \text{H}_2\text{O}$ and loses all water at 150° (Williamson, *J. Physical Chem.*, 1923, **27**, 284). It did not show any catalytic effect at temperatures from 150–250°.

(c) ALUMINIUM SULPHATE.

Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ when heated at 110° for 5 hours loses 14 molecules of water. When heated at 200° for 2 hours the substance retains 1 molecule of water which is expelled at 250°.

The finely powdered dehydrated substance was mixed with a boiling saturated solution of the compound with vigorous stirring to form a stiff paste and the whole was heated to 200–220° in the muffle furnace. The resulting hard mass was broken up and 80 grams of the portion between 20 and 40 mesh were used. The results are given in Table II. The conversion increases from 31 per cent. at 200° to 70 per cent. at 225° when 88 per cent. alcohol passes at 50 c.c. an hour. About 10 degrees higher the same conversion is obtained at double the rate. Further increase in the reaction-temperature reduces the conversion from 70 to 65 per cent. The optimum temperature is about 230–235°, at which the percentage conversion is 70 when the rate of alcohol is 100 c.c. an hour and 53 when running at 200 an c.c. hour.

When the catalyst was taken out of the tube it was found to be dark throughout the mass. This may be due to some free acid contained in the sulphate, because it is very difficult to prepare pure aluminium sulphate.

(d) CHROME ALUM.

The method of preparing this catalyst was similar to that used for aluminium sulphate. 100 grams of the catalyst between 20 and 40 mesh were used. The results are given in Table III. These show that chrome alum is more active than precipitated alumina at about 300°, but the activity is considerably less than that of aluminium sulphate.

TABLE II.

Aluminium Sulphate. Weight of catalyst 80 grams prepared at 200°. Alcohol 88 per cent.

| Experiment No. | Temperature in degrees centigrade | Rate cc. per hour | Weight of alcohol used grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|-------------------|------------------------------|----------------------------|-----------------------|-----------------------|
| 315 | 200 | 50 | 80.0 | 77.0 | 17.0 | 31 |
| 316 | 205 | 50 | 82.2 | 82.0 | 36.0 | 62 |
| 317 | 205 | 20 | 32.4 | 30.0 | 14.0 | 66 |
| 318 | 210 | 60 | 80.0 | 78.0 | 24 | 43 |
| 319 | 215 | 40 | 65.6 | 60.0 | 30 | 71 |
| 320 | 222 | 50 | 82.0 | 81.0 | 40 | 70 |
| 321 | 225 | 100 | 82.0 | 81.5 | 23.5 | 41 |
| 322 | 230 | 100 | 82.0 | 77.0 | 29.0 | 53 |
| 323 | 235 | 100 | 82.0 | 79.0 | 40.0 | 71 |
| 324 | 238 | 100 | 82.0 | 81.0 | 37.0 | 64.5 |
| 325 | 235 | 100 | 82.0 | 77 | 36 | 66 |
| 326 | 225 | 100 | 82.0 | 80 | 34 | 61 |
| 327 | 218 | 80 | 82.0 | 80 | 25 | 44 |
| 328 | 230 | 200 | 85 | 85 | 17.0 | 28 |
| 329 | 236 | 100 | 82 | 82 | 36 | 62 |
| 30 | 232 | 100 | 82 | 78.0 | 40 | 72 |
| 331 | 233 | 100 | 82 | 79.0 | 40 | 73 |
| 332 | 235 | 200 | 82 | 78.5 | 29 | 53 |
| 333 | 235 | 100 | 82 | 82 | 38 | 65 |

After Experiment No. 332 the catalyst was heated at 250° for 15 minutes.

TABLE III.

Chrome Alum 100 grams.

| Experiment No. | Temperature in degrees centigrade | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|-------------------------|----------------------------|-----------------------|-----------------------|
| 334 | 255 | 82.0 | 82.0 | 12.1 | 21 |
| 335 | 265 | 82.0 | 81.0 | 16.0 | 28 |
| 336 | 285 | 65.5 | 64.5 | 17.8 | 39 |
| 337 | 295 | 86.0 | 86.0 | 25 | 41 |

(e) MAGNESIUM SULPHATE.

The substance was granulated in the same way as the aluminium sulphate and about 100 grams between 20 and 40 mesh were used in the reaction-tube. No conversion was obtained up to 300°, at which temperature the distillate contained traces of ether.

EXPERIMENTS WITH POTASSIUM ALUM AS THE CATALYST.

PREPARATION OF THE CATALYST.

Most of our experiments have been carried out with this catalyst as the substance, in addition to being cheap and easily available, can be readily recovered in a state of purity. A number of different methods of preparing the catalyst so as to obtain maximum activity have been investigated.

The alum has to be dehydrated with some care as it melts at 80° in its water of crystallisation forming a sticky mass which is very difficult to render anhydrous even by heating to 400° in the muffle furnace. Experiments have shown that heating the catalyst above 250° partially destroys its activity and hence the water must be removed below this temperature.

Method A.—The first method adopted was to heat the alum crystals in a porcelain basin at 200–220° for two hours. After cooling, the swollen honeycomb-like mass was broken up and again heated at the same temperature for two hours. Contrary to the statement of Mailhe and Godon (*loc. cit.*) potassium alum was found to retain one molecule of water of crystallisation below 200° even on prolonged heating, but the state of hydration is not very important in the preparation of the catalyst because the final state undoubtedly depends upon the conditions of the experiment such as temperature, partial pressure of water, etc. The resulting substance is very friable and much goes to powder in the repeated heating and breaking of the sticky swollen masses. The granular portion between 20 and 60 mesh (weight 90 grams) was used in reaction tube No. I. The results are given in Table IV.

At 200° a 49 per cent. conversion was obtained in the first run and only 29 per cent. in the second. After these experiments a run was carried out at 210° when the conversion was only 24 per cent. as against about 70 per cent. in experiment No. 167. The catalyst was taken out and heated in the muffle at 200–220° for an hour and used

in the reaction-tube at 210° when the conversion was 67 per cent. The results indicate that at 200° this catalyst takes up water from the reaction-mixture and its activity gradually diminishes. The activity is restored by taking out the catalyst and heating at 210°.

TABLE IV.
Potassium Alum (A) 90 grams.

| Experiment No. | Temperature in degrees centigrade | Rate cc. per hour | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|-------------------|-------------------------|----------------------------|-----------------------|-----------------------|
| 167 | 210 | 20 | 64.6 | 62.5 | 31.7 | 72 |
| 168 | 210 | 40 | 77.0 | 76.8 | 30.5 | 56 |
| 169 | 200 | 30 | 81.2 | 80.0 | 27.7 | 49 |
| 170 | 200 | 30 | 64.5 | 62.0 | 12.7 | 29 |
| 171 | 210 | 30 | 81.2 | 78.0 | 13.0 | 23.5 |
| 172 | 210 | 30 | 89.9 | 90.4 | 42.7 | 67.0 |

After Experiment No. 171 the catalyst was removed from the tube and heated at 210° for one hour.

Method B.—In order to utilise the fine powder remaining from the catalyst prepared by the first method it was mixed with an equal quantity of fused alum crystals with vigorous stirring so as to form a stiff paste and the whole mass was kept in the oven at 210° for one hour. The resulting hard, dense, pumice-like substance was broken up and sifted, the portion between 20 and 60 mesh being used in the reaction-tube where it was finally dehydrated at 210°. This method gave uniform samples of the catalyst which, in addition to being considerably less friable than that prepared by the first method, gave fairly constant yields at 200° under the same conditions as the first catalyst as may be seen from Table V. Most of the further work was done with catalyst prepared in this way.

Method C.—With the object of increasing the catalyst surface, pumice granules or kieselguhr were impregnated with various proportions of alum. Mr. Venkateswaram who made some experiments (unpublished) obtained results comparable with those given by Mailhe and Godon, but his catalyst was so fine that it was very difficult to pass vapours through it. (See Experiment 162, Table VI). We have conducted two sets of experiments with kieselguhr and alum mixtures:—(a) in which kieselguhr and alum were mechanically ground together and subsequently heated in the muffle furnace at 200–220° (Venkateswaram), (b) in which kieselguhr was added to the boiling

solution of alum and the resulting mass heated to 200–220°. In every case the granular portion between 20 and 60 mesh was used. The results in Table VI show that with a mixture containing 10 to 25 per cent. of alum in the case of pumice and 50 to 66 per cent. of alum in the case of kieselguhr no conversion is obtained. In the kieselguhr alum mixtures with increasing amount of alum the conversion increases up to 70 per cent. which occurs with mixtures containing 80 and 88 per cent. of alum indicating that kieselguhr does not promote the catalytic activity of the alum.

TABLE V.
Potassium Alum (B).
Alcohol 88 per cent.

| Experiment No. | Temperature in degrees centigrade | Rate cc. per hour | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|-------------------|-------------------------|----------------------------|-----------------------|-----------------------|
| 62 | 200 | 15 | 38.0 | 37.8 | 21.3 | 79 |
| 63 | 200 | 20 | 42.0 | 42.7 | 22.6 | 75 |
| 64 | 200 | 20 | 42.0 | 40.5 | 21.4 | 76 |
| 65 | 200 | 15 | 56.7 | 54.3 | 29.4 | 76 |
| 66 | 200 | 20 | 42.0 | 38.0 | 18.8 | 70 |
| 67 | 200 | 20 | 56.7 | 55.2 | 18.2 | 47 |
| 68 | 200 | 20 | 48.7 | 49.8 | 22.2 | 64 |
| 69 | 200 | 20 | 64.6 | 64.5 | 25.6 | 56 |
| 70 | 200 | 20 | 82.0 | 80.7 | 32.3 | 56 |
| 71 | 200 | 20 | 82.0 | 81.35 | 31.0 | 54.4 |
| 72 | 200 | 20 | 82.0 | 81.9 | 29.4 | 52 |
| 73 | 200 | 20 | 82.0 | 81.8 | 31.4 | 55 |
| 74 | 200 | 20 | 82.0 | 81.85 | 32.75 | 56.5 |
| 75 | 205 | 20 | 82.0 | 82.10 | 35.0 | 61 |
| 76 | 205 | 20 | 82.0 | 82.8 | 35.2 | 61 |
| 77 | 210 | 20 | 82.0 | 82.5 | 38.0 | 66 |
| 78 | 210 | 20 | 82.0 | 80.8 | 37.1 | 66 |
| 79 | 210 | 20 | 82.0 | 82.8 | 39.0 | 67 |
| 80 | 210 | 25 | 77.5 | 77.5 | 33.1 | 60 |
| 81 | 210 | 30 | 82.2 | 82.5 | 29.4 | 57 |
| 82 | 210 | 28 | 82.2 | 81.1 | 31.6 | 55 |
| 83 | 210 | 25 | 82.2 | 82.2 | 35.2 | 61 |
| 84 | 210 | 28 | 68.9 | 68.1 | 24.6 | 51 |
| 85 | 210 | 40 | 80.0 | 79.5 | 20.9 | 39 |
| 86 | 210 | 40 | 73.5 | 73.5 | 15.2 | 29 |
| 87 | 210 | 40 | 81.1 | 78.4 | 17.8 | 32 |
| 88 | 210 | 20 | 60.7 | 58.5 | 31.6 | 73 |
| 121 | 210 | 22.5 | 73.1 | 74.0 | 40.8 | 75 |
| 129 | 210 | 20 | 81.1 | 79.2 | 39.6 | 73 |
| 122 | 210 | 25 | 97.4 | 96.5 | 52.9 | 79 |
| 126 | 210 | 25 | 59.7 | 58.2 | 29.8 | 75 |
| 127 | 210 | 30 | 97.4 | 95.5 | 47.6 | 73 |

After Experiment No. 68 the catalyst was accidentally overheated to about 250° and the low results which follow show that the activity thus lost was not entirely recovered. A certain amount of shrinkage probably took place simultaneously. After Experiment No. 84 the shrinkage appears to have increased leaving channels in the catalyst, for when the catalyst was removed and replaced after Experiment No. 87 a higher conversion was obtained. The last five experiments were performed with fresh catalyst.

TABLE VI.

Results of experiments with catalysts prepared by impregnating pumice and kieselguhr with various proportions of potassium alum. Temperature 210-215°. Alkohol 88 per cent.

P = Pumice, K = Kieselguhr, A = Alum, (a) dry method, (b) wet method.

| Experiment No. | Catalyst | Rate c.c. per hour | Weight of alcohol added grms. | Weight of the distillate grms. | Weight of ether grms. | Per cent. conversion |
|----------------|---------------------|--------------------|-------------------------------|--------------------------------|-----------------------|----------------------|
| 61 | (a) P 90 + A 10 .. | 20 | 65.6 | 65.6 | 0 | 0 |
| 61a | (b) P 75 + A 25 ... | 20 | 81.6 | 80.0 | 0 | 0 |
| 154 | (a) K 50 + A 50 ... | 30 | 81.2 | 80.0 | 3.1 | 5 |
| 154a | (b) Do. ... | 40 | 65.8 | 65.4 | 0 | 0 |
| 155 | (a) K 33 + A 66 ... | 40 | ... | ... | 0 | 0 |
| 156 | (b) Do. ... | 40 | ... | ... | 0 | 0 |
| 157 | (a) K 19 + A 57 ... | 25 | 82.2 | 83.0 | 13.4 | 23 |
| 158 | Do. ... | 30 | 82.2 | 81.2 | 17.6 | 30.5 |
| 159 | Do. ... | 30 | 82.2 | 80.85 | 17.6 | 31 |
| 160 | (b) K 25 + A 75 ... | 40 | 82.0 | 81.8 | 29.6 | 50.5 |
| 160a | Do. ... | 30 | 81.2 | 79.8 | 33 | 58 |
| 161 | Do. ... | 30 | 82.0 | 81.35 | 32.7 | 57 |
| 163 | (b) K 20 + A 80 ... | 25 | 82.0 | 73.0 | 30 | 60 |
| 164 | Do. ... | 40 | 82.0 | 74.0 | 31 | 61 |
| 165 | Do. ... | 40 | 82.0 | 81 | 25.7 | 42 |
| 166 | Do. ... | 20 | 40.6 | 39.7 | 18.7 | 69 |
| 150 | (b) K 10 + A 70 ... | 40 | 82.15 | 82.15 | 40.4 | 69.5 |
| 150a | Do. ... | 40 | 80.75 | 80.75 | 39.8 | 69.5 |
| 151 | Do. ... | 60 | 96.0 | 96.0 | 39.0 | 57 |
| 151a | Do. ... | 80 | 131.2 | 127.2 | 38.5 | 43 |
| 152 | Do. ... | 30 | 82.0 | 80.0 | 36.8 | 65 |
| 153 | Do. ... | 35 | 81.2 | 80.15 | 37.9 | 67 |
| 162 | (a) K 25 + A 40 ... | 10 | ... | 20.5 | 3.9 | 27 |

The results obtained with various preparations of the same substance as the catalyst, especially the remarkable difference between the activity of A and B at 200° under identical conditions, and the entirely negative results obtained at $200-210^{\circ}$ with pumice and kieselguhr coated with moderate amounts of alum, cannot at present be explained.

CATALYTIC ACTIVITY OF ALUM IN RELATION TO THE TEMPERATURE OF PREPARATION.

Experiments were made with the catalyst B heated to different temperatures in order to find the effect of preliminary heating on its activity. Two sets of experiments were made: (1) in which the same catalyst was heated to different temperatures in the tube itself and the reaction carried out at 210° , and (2) in which the substance was heated in a porcelain basin in an oven and then used in the reaction tube at 210° . The results are shown in Table VII. The conversion at corresponding temperatures in the latter case was higher than in the former. In Fig. 2 the percentage conversion at 210° has been plotted against the temperature of initial heating for various rates. To obtain a given percentage conversion a slower rate was required for the catalyst heated to a higher temperature. In both cases the catalytic activity decreased with increase of temperature in pre-treatment and is nil after heating to $450-500^{\circ}$.

This decrease in the activity can be explained by the assumption that on heating, owing to the sintering of the molecules at the surface, the capacity to form temporary absorption compounds with alcohol and water which the alum possesses in a marked degree when prepared at lower temperatures becomes lessened. The higher the heating-temperature, the slower is the rate at which it can absorb alcohol and water vapour.

Another important effect of heat on the catalyst is the possible progressive inactivation due to heating for prolonged periods at lower temperatures, viz., at the temperature of the experiment. The 'life' of the catalyst in a continuous process depends upon this factor. We have already shown that even after one hundred hours of intermittent working at $200-210^{\circ}$ the activity was found not to have decreased. In our later experiments in which the tube was not cooled below 200° for two and a half months the catalyst worked satisfactorily throughout, although found on removal to be darkened.

TABLE VII.

*Effect of preliminary heating on the activity of Potassium Alum.
Catalyst, weight 100 grams, prepared by method B.
Alcohol 88 per cent. Temperature 210°.*

| Experiment No. | Catalyst | Rate c.c. per hour | Weight of alcohol used grms. | Weight of distillate grms. | Weight of ether grms. | Percentage conversion |
|------------------|--|--------------------|------------------------------|----------------------------|-----------------------|-----------------------|
| 129 | Original catalyst ... | 20 | 73.08 | 73.85 | 37.8 | 72 |
| 128 | | 60 | 82.2 | 82.2 | 40.0 | 69 |
| 130 | | 80 | 97.4 | 95.8 | 39.9 | 59 |
| 131 | | 80 | 120.0 | 126.0 | 40.4 | 44 |
| 131 _a | | 30 | 65.9 | 64.4 | 33.9 | 73 |
| 132 | Original catalyst heated in tube 15 mins. at 250°. | 40 | 81.13 | 80.85 | 37.5 | 66 |
| 132 _a | | 60 | 81.13 | 80.2 | 25.3 | 45 |
| 133 | | 80 | 96.4 | 93.8 | 17.0 | 26 |
| 133 _a | | 30 | 81.2 | 80.8 | 36.9 | 65 |
| 134 | Original catalyst heated in tube 15 mins. at 300°. | 30 | 81.2 | 80.8 | 29.5 | 52 |
| 135 | | 40 | 81.2 | 79.9 | 22.9 | 40 |
| 136 | | 60 | 96.4 | 95.2 | 35.3 | 38 |
| 137 | | 30 | 81.2 | 80.0 | 29.8 | 53 |
| 138 | Original catalyst heated in tube 15 mins. at 350°. | 30 | 82.2 | 81.6 | 21.1 | 37 |
| 139 | | 40 | 80.0 | 78.75 | 13.8 | 25 |
| 139 _a | | 60 | 96.4 | 94.7 | 9.6 | 14 |
| 140 | | 30 | 80.0 | 78.2 | 19.7 | 36 |
| 141 | Original catalyst heated in tube 15 mins. at 400°. | 30 | 81.2 | 80.0 | 7.0 | 16 |
| 142 | | 30 | 81.2 | 80.8 | 8.3 | 15 |
| 96 | Original catalyst ... | 40 | ... | 76.2 | 38.3 | 72 |
| 97 | | 60 | 97.4 | 95.9 | 39.2 | 58 |
| 98 | | 80 | 129.9 | 128.2 | 42.0 | 46 |
| 99 | | 30 | 60.7 | 58.2 | 29.8 | 71 |
| 143 | | 30 | 81.2 | 81.05 | 34.7 | 61 |
| 144 | Original catalyst heated in oven 15 mins. at 300°. | 40 | 81.2 | 80.0 | 35.0 | 62 |
| 144 _a | | 50 | 81.2 | 78.0 | 31.1 | 56 |
| 145 | | 70 | 120.7 | 120.6 | 35 | 41 |
| 145 _a | | 30 | 80.0 | 78.3 | 35.3 | 64 |
| 147 | Original catalyst heated in oven 15 mins. at 350°. | 20 | 82.2 | 81.2 | 41.8 | 71 |
| 148 | | 30 | 81.2 | 80.0 | 29.5 | 52 |
| 149 | | 40 | 76.0 | 75.2 | 19.8 | 38 |

EFFECT OF REACTION-TEMPERATURE ON THE CONVERSION.

After finding a satisfactory method of preparing the catalyst, experiments were made to determine the optimum temperature for the reaction.

One hundred grams of the catalyst prepared according to the second method (catalyst B) were employed. The alcohol used was 88 per cent. The results are given in Table VIII.

TABLE VIII.

*Effect of Temperature. Weight of Catalyst 100 grams.
Alcohol 88 per cent.*

| Experiment No. | Temperature in degrees centigrade | Rate c.c. per hour | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Percentage conversion |
|----------------|-----------------------------------|--------------------|-------------------------|----------------------------|-----------------------|-----------------------|
| 73 | 200 | 20 | 57.4 | 57.4 | 23.5 | 58 |
| 74 | 200 | 20 | 82.2 | 80.7 | 32.5 | 57 |
| 75 | 205 | 20 | 82.2 | 82.8 | 35.2 | 60 |
| 76 | 205 | 20 | 82.2 | 82.1 | 35.0 | 60 |
| 128 | 210 | 40 | 82.2 | 79.3 | 39.6 | 71 |
| 130 | 210 | 60 | 97.4 | 95.8 | 39.9 | 59 |
| 131 | 210 | 80 | 120.0 | 126.0 | 40.4 | 45 |
| 207 α | 215 | 25 | 60.2 | 60.7 | 31.1 | 72 |
| 207 β | 225 | 20 | 78.0 | 77.5 | 43.5 | 79 |
| 208 | 225 | 50 | 81.6 | 79.0 | 42.0 | 75 |
| 209 | 225 | 40 | 81.0 | 83.0 | 36.4 | 76 |
| 209 α | 225 | 60 | 49.2 | 51.1 | 27.0 | 75 |
| 210 α | 225 | 80 | 98.5 | 99.9 | 53.4 | 75 |
| 210 β | 225 | 80 | 163.0 | 158.5 | 83.5 | 75 |
| 211 | 225 | 100 | 163.2 | 162.3 | 84.6 | 74 |
| 223 | 235 | 80 | 163.2 | 155.1 | 81.8 | 74 |
| 224 | 235 | 90 | 162.4 | 160.4 | 77.8 | 69 |
| 225 | 235 | 100 | 81.2 | 79.3 | 37.0 | 66 |
| 226 | 245 | 80 | 81.2 | 81.1 | 40.8 | 71 |
| 227 | 250 | 75 | 121.8 | 121.8 | 60.8 | 71 |
| 228 | 230 | 60 | ... | 84.6 | 40.6 | 68 |
| 229 | 230 | 80 | ... | 74.0 | 30.8 | 59 |
| 229 α | 225 | 100 | 121.8 | 114.0 | 40.3 | 50 |
| 230 | 225 | 80 | 129.8 | 127.5 | 43.1 | 48 |
| 231 | 225 | 75 | ... | 74.4 | 29.9 | 57 |
| 232 | 270 | 80 | ... | 99.9 | 49.8 | 71 |

The conversion increases with temperature from 200° to 230° especially at the higher rates, owing to the increase in the rate of reaction. A rough idea of the magnitude of this increase may be formed by comparing the total quantity of ether obtained at different temperatures for the higher rates of flow, that is to say before equilibrium is established. For example in experiment No. 131 at 210° at 80 c.c. per hour, the conversion was 45 per cent. A value interpolated between experiments Nos. 285 and 295 in Table IX shows that this conversion is obtained at 227° when the rate is about 220 c.c. per hour so that the increase in reaction-velocity is of the order of 2.7 for 17° .

It will be noted that at 235° there are distinct signs of a diminution in efficiency of the catalyst. This is still more marked at 250° , and on subsequently repeating the experiments at 230° and 225° , much lower yields were obtained than before the heating, showing definitely that the catalyst had deteriorated. These experiments indicate that $225-230^{\circ}$ is the most suitable temperature for the reaction and at this temperature a conversion of 75 per cent. can be obtained with 100 c.c. of alcohol per hour per 100 grams of catalyst.

No appreciable decomposition into ethylene takes place up to 270° . At 275° , ethylene is evolved at the rate of 20 c.c. per minute, at 300° 100 c.c. per minute and very rapidly at higher temperatures; at 360° alum is decomposed by alcohol vapour giving sulphur and its compounds in the distillate. The latter on fractionation gave a liquid boiling at $25-29^{\circ}$ having a pungent and disagreeable odour resembling that of mercaptan.

POISONING OF THE CATALYST BY WATER VAPOUR.

Mailhe and Godon (*loc. cit.*) have shown that at $160-165^{\circ}$ water is taken up by the catalyst and prohibits the exercise of its activity. Under our experimental conditions this occurs even at 200° in the case of the catalyst A, which can be activated only after removal from the tube and heating at $200-220^{\circ}$. In the case of catalyst B, hydration takes place at $190-195^{\circ}$, but the activity can be more easily restored by raising the temperature of the reaction-tube to $200-210^{\circ}$. In both cases the 'poisoning' which is reversible can be more easily remedied than the more serious heat effect which is irreversible and necessitates the dissolving, crystallising and drying of the whole catalyst in order to effect its recovery.

EFFECT OF CONCENTRATION OF ALCOHOL ON THE
CONVERSION.

Mailhe and Godon have pointed out that one advantage of their method is that even 50 per cent. alcohol can be used for making ether. It was therefore of some interest to study the effect of the initial concentration of alcohol on the conversion.

In the following experiments the weight of the catalyst was 100 grams (catalyst B) and the temperature $225-230^{\circ}$. The results are given in Table IX. At lower velocities the conversion with 95, 88, 80 and even 70 per cent. alcohol is not appreciably different. At higher velocities the conversion falls, but the product of the velocity and the percentage conversion increases. This product is proportional to the total yield of ether in a given time as shown in column 8. The results are shown in the form of curves in Fig. 3.

In the curve for 88 per cent. alcohol at all velocities from 20 to 130 c.c. per hour the conversion is about 75 per cent. and therefore the total yield of ether is proportional to the velocity. With velocities from 130 to 200 c.c. per hour the percentage conversion falls gradually, but the total yield of ether increases with the increase of the rate. With further increase in the rate the conversion diminishes rapidly and the total yield also decreases. The maximum weight of ether we have obtained with 88 per cent. alcohol in an hour is 64 g. for 100 g. of catalyst.

The results in Table IX show that water vapour reduces the rate of conversion which falls from 83 per cent. in the case of 99.5 per cent. alcohol to 4 per cent. in the case of 30 per cent. alcohol at the rate of 100 c.c. per hour. The lower conversion is not entirely due to establishment of equilibrium since the results indicate that if the time of contact is prolonged, higher values for conversion are obtained. It will be shown (p. 103) that the average value for the equilibrium constant is 7.3 and in Fig. 1 are given curves for the theoretical conversions and those actually obtained.

The lower rate of conversion in the case of dilute alcohol is not due to the 'poisoning' of the catalyst by water vapour because consecutive runs gave practically the same conversion and in the subsequent run the catalyst gave the same conversion with 88 per cent. alcohol as it did before,

TABLE IX.

Effect of Concentration of Alcohol. Temperature 227°.

| Experiment No | Concentration of alcohol | Rate c.c. per hour | Weight of alcohol | Weight of distillate | Weight of ether | Per cent. conversion | Hourly output |
|---------------|--------------------------|--------------------|-------------------|----------------------|-----------------|----------------------|---------------|
| 294 | 99.5 | 20 | 78.5 | 79.0 | 53.0 | 84 | 10.7 |
| 281 | 99.5 | 100 | 79.5 | 79.0 | 52.0 | 82 | 53.0 |
| 241 | 94.5 | 70 | 114.0 | 113.3 | 70.2 | 81.4 | 35.1 |
| 242 | 94.5 | 100 | 147.3 | 147.3 | 86.0 | 77.0 | 48.5 |
| 243 | 94.5 | 120 | 92.0 | 91.7 | 51.6 | 75 | 54.7 |
| 244 | 94.5 | 120 | ... | 149.8 | 84.8 | 75 | 54.7 |
| 245 | 94.5 | 130 | ... | 71.2 | 40.0 | 73 | 59.0 |
| 245a | 94.5 | 150 | 140 | 140.0 | 80.0 | 75 | 69.5 |
| 293 | 88.0 | 20 | 78.0 | 77.5 | 43.5 | 79 | 9.3 |
| 285 | 88.0 | 50 | 81.6 | 79.0 | 42.0 | 75 | 21.9 |
| 264 | 88.0 | 50 | 82.0 | 92.5 | 48.0 | 73.4 | 21.5 |
| 298 | 88.0 | 60 | ... | 74.1 | 38.4 | 75 | 25.5 |
| 299 | 88.0 | 60 | 51.0 | 51.1 | 27.0 | 75 | 25.5 |
| 223a | 88.0 | 80 | 163.2 | 152.1 | 81.8 | 76 | 35.4 |
| 223b | 88.0 | 80 | 162.0 | 158.5 | 83.5 | 74.5 | 34.8 |
| 265 | 88.0 | 100 | 164.0 | 164.0 | 87.0 | 75 | 43.5 |
| 266 | 88.0 | 120 | 162 | 152.0 | 80.5 | 75 | 52.5 |
| 267 | 88.0 | 130 | 162 | 152.0 | 80.0 | 74.4 | 57.0 |
| 287 | 88.0 | 200 | 162 | 159.5 | 61.5 | 54 | 64.0 |
| 295 | 88.0 | 250 | 206 | 206 | 49.0 | 33.5 | 49.0 |
| 297 | 80.0 | 20 | 83.7 | 83.5 | 41.0 | 75 | 8.2 |
| 288 | 81.0 | 50 | 83.7 | 84 | 41.0 | 74 | 20.5 |
| 292 | 80.0 | 75 | 56.4 | 55.5 | 23.5 | 66 | 26.7 |
| 273a | 81.1 | 100 | 83.7 | 84.0 | 38.0 | 69 | 38.0 |
| 273 | 81.1 | 120 | 108.8 | 108.0 | 38.0 | 54 | 34.5 |
| 298 | 70.0 | 20 | 87.0 | 86.0 | 36.0 | 73 | 7.1 |
| 298a | 70.4 | 50 | 88.0 | 88.0 | 35.0 | 70 | 17.0 |
| 291 | 70.4 | 50 | 88.0 | 88.0 | 35.0 | 70 | 17.0 |
| 274 | 70.5 | 80 | 68 | 66.0 | 22 | 60 | 23.3 |
| 274a | 70.5 | 100 | 103 | 97.0 | 32 | 60 | 29.0 |
| 290 | 61.2 | 20 | 87.0 | 87.0 | 27.0 | 64 | 5.5 |
| 275 | 60.0 | 100 | 71.0 | 71.0 | 16.0 | 46 | 19.7 |
| 275a | 60.0 | 100 | 94.0 | 93.0 | 22.0 | 46 | 19.7 |
| 283a | 51 | 50 | 50 | 94.0 | 17.0 | 43 | 8.0 |
| 284 | 50 | 100 | ... | 94.0 | 11.0 | 28 | 10.4 |
| 279 | 49 | 100 | ... | 94.5 | 8.5 | 23 | ... |
| 279a | 49 | 100 | ... | 92.0 | 9.0 | 25.4 | ... |
| 279b | 49 | 100 | ... | 91.0 | 9.0 | 25 | ... |
| 278 | 40.5 | 100 | 93.0 | 93.5 | 6.5 | 19 | ... |
| 278a | 40.5 | 100 | 93.0 | 92.5 | 5.5 | 18 | ... |
| 277 | 31 | 100 | 94.0 | 91.0 | 1.0 | 4 | ... |
| 277a | 31 | 20 | ... | 107.0 | 7.0 | 26 | ... |
| 276 | 20 | 100 | 96.5 | 96.1 | 0.1 | 2 | ... |
| 296 | 20 | 20 | 96.5 | 92.0 | 1.0 | 6 | ... |

Dilution of the alcohol vapour by water vapour must have a considerable effect on the velocity, but there are indications that water has in addition some specific retarding effect, since dilution with ether vapour appears to act in a somewhat different manner. A few experiments have been conducted with mixtures of alcohol, ether and water with the results shown in Table X.

TABLE X.

*Conversion of Ternary Mixtures,
100g. catalyst. Rate 100 c.c. per hour at 227°.*

| Expt. No. | Initial mixture | | Final mixture | | Percentage Conversion | K _p |
|-----------|-----------------|-------------|---------------|-------------|-----------------------|----------------|
| | Mols. ether | Mols. water | Mols. ether | Mols. water | | |
| 276a | 0.08 | 0.30 | 2.12 | 3.24 | 78 | 6.9 |
| 282 | 0.38 | 3.00 | 0.75 | 4.45 | 29 | 3.3 |
| 279 | 0.00 | 2.43 | ... | ... | 26 | |
| 300 | 1.13 | 1.88 | 2.70 | 4.17 | 48 | 11.4 |
| 275 | 0.00 | 1.70 | ... | ... | 46 | |
| 283 | 0.46 | 0.07 | 5.60 | 2.92 | 83 | 16.3 |
| 273a | 0.00 | 0.59 | ... | ... | 69 | |

This gives the composition of the initial and final mixtures in terms of mols. of ether and of water to 1 mol. of alcohol. The results of two experiments from Table IX are also incorporated for comparison. The last column gives the value of $K_p = C_{\text{ether}} C_{\text{water}} / C_{\text{alcohol}}^2$. As equilibrium is not attained in most cases this is not the true equilibrium constant.

In No. 282, where the alcohol is considerably diluted with water and ether, the conversion is slightly greater than in No. 279 in which there is less water and no ether. A similar case is presented by Nos. 300 and 275. The mixture of almost anhydrous alcohol and ether in No. 283 gives a higher conversion than the similar mixture of alcohol and water in No. 273 a.

It will be noticed that the values for K_p in Nos. 283 and 300 are very high indicating an abnormally high conversion. The reason for this is not clear and further work on ternary mixtures might be of interest from this point of view.

COMPARISON WITH MAILHE AND GODON'S RESULTS.

Some of these results have been given in Table XI. Although the French chemists have not given figures for velocities higher than 20 c.c. per hour, the lower yields obtained even after prolonged contact show that their catalyst was very inferior to ours in activity. This has also been confirmed by the poor yields obtained in our preliminary experiments in which the catalyst was made according to the details given by them.

TABLE XI.
Comparative Results.

| — | M. and G. | | | | Authors | | | |
|---------------------------|---------------|----|----|----|--------------|----|----|----|
| Weight of catalyst, grms. | 102 | | | | 100 | | | |
| Size of tube ... | 180 X 1.3 cm. | | | | 60 X 1.3 cm. | | | |
| Mean temperature ... | 225° | | | | 225° | | | |
| Conc. of alcohol ... | 95 | 90 | 80 | 60 | 95 | 88 | 80 | 60 |
| Rate c.c. per hour ... | 20 | 20 | 20 | 20 | 70 | 20 | 20 | 20 |
| Percentage conversion... | 49 | 48 | 40 | 32 | 81 | 79 | 75 | 64 |

EXPERIMENTS WITH DIFFERENT TYPES OF APPARATUS.

APPARATUS NO. 2.

In all our preliminary work the rate of passing alcohol was frequently only 20 c.c. an hour which involved careful attention and temperature regulation for five hours continuously in order to obtain sufficient product for analysis. By increasing the dimensions of the catalyst-tube it should be possible to reduce the time required for each experiment. Mailhe and Godon used tubes from 60 cm. to 240 cm. in length, and following their example apparatus No. 2 was constructed similar to apparatus No. 1, but having the reaction-tube three times as long, viz., 210 cm. and 13 mm. in diameter charged with 300 grams of catalyst. In order to drive the gas from 60 c.c. of liquid per hour through this long tube, considerable pressure was necessary and this made the regulation a matter of some difficulty. At first the reservoir holding the alcohol was raised about six feet in order to obtain sufficient head, but later, pressure was applied to the alcohol by

connecting the top of the reservoir with a large closed bottle into which tap water was slowly run. Even this was not wholly satisfactory, and, moreover, it was difficult to maintain a uniform temperature in the long tube.

The result of a few experiments with this apparatus are given in Table XII. It is interesting to note that in experiment No. 104 the conversion is 76 per cent., while it has been shown (Table VIII) that under similar conditions the conversion in the shorter tube is 45 per cent., hence 45 per cent. of the alcohol is converted into ether in the first one-third of the tube and the remaining 31 per cent. in the latter two-thirds.

Since at about 10° higher, equally good results were obtained with apparatus No. 1 at more rapid velocities, work with apparatus No. 2 was abandoned.

TABLE XII.

Experiments with Apparatus No. 2. 88 per cent. alcohol.

| Expt. No. | Average Temp. °C. | Rate c.c. per hour | Weight of alcohol | Weight of distillate | Weight of ether | Percentage conversion |
|-----------|-------------------|--------------------|-------------------|----------------------|-----------------|-----------------------|
| 101 | 210 | 60 | 190.5 | 190.3 | 86.7 | 65 |
| 102 | 210 | 50 | 188.7 | 179.5 | 97.0 | 77 |
| 103 | 210 | 75 | 210.6 | 208.9 | 116.3 | 79 |
| 104 | 210 | 80 | 324 | 314.5 | 167.0 | 76 |

APPARATUS No. 3.

As a long narrow tube was found to be unsatisfactory, a comparatively short and wide tube was next used as a container for the catalyst.

A sketch of this apparatus is shown in Fig. 4. The alcohol was contained in a two-litre graduated Winchester A from which it was forced by compressed air through the pinch-cock and dropper B into the spiral copper tube boiler and super-heater C. The slightly superheated vapours passed through an auxiliary electrically heated super-heater D to which a T was fixed to admit the thermometer E into the reaction chamber F. This consisted of an iron tube 45 × 7.5 cm. in the centre of which was fixed a pipe (40 × 1 cm.) G, closed at the inside end, for the thermo-couple H which recorded the temperature of the centre of the tube. The tube was heated electrically and the temperature of the

heating surface was measured by means of a thermo-couple Γ soldered to it.

The emerging vapours were partially condensed by means of the condenser J and the residual vapours passed through fractionating columns K and L of which the first contained 32 hollowed baffle-plates and the other 12 bubbling cap-type plates. The first column was intended to condense water and the second alcohol. The ether vapours from the top of the second column were mostly condensed by a double-walled metal condenser M in which water at room-temperature ($22-25^{\circ}$) was used. The remaining vapours were passed through a helical coil N of lead tube kept in ice and the uncondensed gases and vapours, if any, were allowed to escape.

TEMPERATURE CONDITIONS IN THE REACTION VESSEL.

It is shown in Part II (p. 100) that the reaction is exothermic the heat of reaction for two molecules of alcohol being approximately 5,700 cal. If 88 per cent. alcohol is used and a 75 per cent. conversion is obtained the approximate temperature-rise of the gases assuming no loss of heat, would be 80° . This condition would be attained if a very wide tube were used and hence it is evident that in designing apparatus the reaction-tube must not be allowed to exceed a certain diameter unless some means of internal cooling are introduced.

With the tube used in apparatus No. 3, which was 7.5 cm. in diameter there was a difference in temperature of $25-30^{\circ}$ between the hottest and coolest portions measured along the axis, the maximum temperature being in the centre when the rate was 1,400 c.c. per hour and somewhat nearer the outlet end with a rate of 2,000 c.c. per hour. When no gas was passing a heating current of 1.5 amps. was necessary to maintain the temperature at 230° , but this had to be reduced to 0.5 amp. when the reaction was in progress, the corresponding amounts of energy being 67 and 7 watts.

It will be seen that as the reaction is very slow below 200° it is necessary to heat the gases to this temperature initially unless a very long catalyst tube is used, a result which was confirmed in practice. If the maximum temperature is not to exceed 235° it is evident that it is not desirable to use a much wider tube than the one under consideration unless internal cooling is adopted.

In the earlier experiments the temperature of the surface of the tube was not measured and the catalyst-chamber was allowed to cool down in the evening and heated in the morning. The efficiency of the catalyst was very low as will be seen from Tables XIII and XIV.

TABLE XIII.

*Apparatus No. 3. Weight of catalyst 1,600 grams,
10-40 mesh. Alcohol 88 per cent.*

| Experiment No. | Inside temperature in degrees centigrade | Rate c.c. per hour | Weight of alcohol grams | Weight of distillate grams | Weight of ether grams | Conversion per cent. |
|----------------|--|--------------------|-------------------------|----------------------------|-----------------------|----------------------|
| 170 | 215 | 100 | 97.1 | 94.75 | 52.2 | 78 |
| 172 | 205 | 150 | 182 | 182 | 111 | 86 |
| 174 | 210 | 400 | ... | 280 | 121 | 61 |
| 175 | 210 | 400 | 818 | 803 | 385 | 68 |
| 176 | 210 | 400 | 818 | 769 | 357 | 75.7 |
| 177 | 210 | 400 | 818 | 813 | 323 | 56 |
| 178 | 210 | 500 | 410 | 420 | 210 | 71 |
| 178 α | 210 | 500 | 410 | 403 | 161 | 57 |
| 179 | 220 | 400 | 1258 | 1244 | 597 | 68 |
| 180 | 205 | 500 | 1215 | 1205 | 524 | 62 |
| 181 | 220 | 500 | 1640 | 1590 | 661 | 58 |
| 184 | 190 | 500 | 410 | 416 | 63 | 22 |
| 184 α | 200 | 500 | 373 | 373 | 149 | 58 |
| 185 | 205 | 500 | 818 | 806 | 386 | 68 |
| 186 | 205 | 500 | 410 | 396 | 156 | 68 |

TABLE XIV.

*Weight of catalyst 1,700 grams.
Alcohol 88 per cent.*

| Experiment No. | Inside temperature in degrees centigrade | Rate c.c. per hour | Weight of alcohol added grams | Weight of distillate grams | Weight of ether grams | Weight and composition of residue | Conversion per cent. |
|----------------|--|--------------------|-------------------------------|----------------------------|-----------------------|-----------------------------------|----------------------|
| 194 | 225 | 500 | 818 | 810 | 400 | 110 (95%) 300 (39%)* | 68 |
| 195 | 225 | 500 | 818 | 747 | 391 | 110 (95%) 245 (27%) | 74 |
| 196 | 225 | 500 | 818 | 822 | 415 | 140 (96%) 267 (24%) | 72 |
| 197 | 205 | 500 | ... | 776 | 296 | 160 (96%) 320 (50%) | 52 |
| 198 | 225 | 600 | ... | 709 | 358 | 177 (93%) 174 (21%) | 62 |
| 199 | 215 | 600 | ... | 694 | 321 | 183 (91%) 190 (40%) | 56 |
| 200 | 225 | 600 | 487.2 | 462 | 211 | 128 (94%) 113 (28%) | 62 |
| 201 | 225 | 500 | 412 | 391 | 107 | 102 (95%) 182 (48%) | 39 |
| 202 | 230 | 600 | 822 | 735 | 327 | 167 (96%) 241 (36%) | 63 |
| 203 | 230 | 500 | 822 | 767 | 361 | 171 (96%) 236 (31%) | 66.5 |
| 204 | 225 | 600 | 732 | 764 | 334 | 183 (94%) 247 () | 66 |
| 205* | 210 | 40 | 64.96 | 65.6 | 29.0 | 36.6 | 62.4 |
| 206* | 225 | 40 | 81.2 | 80.3 | 40.9 | 39.4 | 72.0 |
| 207* | 225 | 60 | 81.2 | 78.8 | 36.3 | 42.5 | 65.6 |

* Experiments with samples of the catalyst from above 100 grams used in Apparatus No. 1.

This was found to be due to the inactivation of the catalyst near the surface by over-heating. When the thermo-couple I was subsequently soldered to the surface of the tube and the initial heating conducted as usual, it was found that the outside of the tube sometimes attained a temperature of 280° and, as has already been shown, heating to this temperature permanently reduces the activity of the catalyst. This inactivation was confirmed by removing a portion of the catalyst and using it in apparatus No. 1 with the low results shown at the end of Table XV. In the following experiments the catalyst-chamber was very gradually heated, and the surface temperature did not rise above 225° . After the first heating it was not allowed to cool below 200° during the $2\frac{1}{2}$ months for which the experiments lasted. The results are given in Table XV. These show that with 2 litres of 88 per cent. alcohol per hour the percentage conversion is 70-72, the catalyst working consistently throughout. Some uncondensed vapour, possibly ethylene mixed with ether, escapes at the rate of 1 to 2 c.c. per minute. The density of the ether obtained was 0.715-0.720 at 20° . When the experiments were made at the rate of 500 c.c. of alcohol per hour it was found possible to recover 60-70 per cent. of the unchanged alcohol at a concentration of 94-96 per cent. from column L as shown in Table XIV. At higher rates it was only possible to recover 30-40 per cent. of the alcohol with a strength of 80-85 per cent. This indicated that the columns were rather small for the maximum quantities operated.

It will be noticed that in these experiments the real quantity of alcohol admitted does not agree very well with the amount of distillate. This is due to the large quantity of liquid retained by the columns and the difficulty of keeping its volume constant. The conversion results are consequently not as accurate as those with the smaller apparatus.

APPARATUS NO. 4.

As the apparatus described above gave satisfactory results it was decided to construct a still larger one which could be used for producing sufficient ether to supply the requirements of the laboratory. A sketch of this apparatus is given in Fig. 5.

Alcohol was contained in a five-gallon drum A fitted with a glass level indicator and a cock at the bottom. In order to obtain sufficient head this was raised about 8 ft. and the liquid was fed through metal tube B and a screw cock C for controlling the rate, into the evaporator D,

TABLE XV.

APPARATUS NO. 3.

*Weight of catalyst 1,850 grams (prepared at 220°C).**Alcohol 88 per cent.*

| Experiment No. | Average Temperature in degrees C | Rate c.c. per hour | Weight of ether | Weight of residue | Conversion per cent. |
|------------------|----------------------------------|--------------------|-----------------|-------------------|----------------------|
| 240 | 220 | 1,000 | 427 | 318 | 75 |
| 250 | 230 | 1,600 | 371 | 216 | 80 |
| 251 | 225 | 1,400 | 607 | 269 | 75 |
| 252 | 220 | 1,600 | 262 | 335 | 62 |
| 253 | 225 | 1,800 | 388 | 346 | 75 |
| 254 | 225 | 2,000 | 403 | 307 | 70 |
| 255 | 235 | 1,500 | 615 | 586 | 72 |
| 256 | 235 | 1,300 | 583 | 575 | 75 |
| 257 | 235 | 1,400 | 421 | 446 | 69 |
| 258 | 230 | 1,400 | 775 | 702 | 75 |
| 259 | 230 | 1,400 | 782 | 701 | 75 |
| 260 | 225 | 1,400 | 439 | 330 | 80 |
| 261 | 225 | 2,000 | 771 | 773 | 71 |
| 262 | 225 | 2,000 | 798 | 757 | 72.5 |
| 263 | 230 | 2,000 | 373 | 420 | 67 |
| 267 _a | 225 | 2,000 | 821 | 777 | 72.6 |
| 268 | 225 | 1,800 | 764 | 694 | 74 |
| 269 | 220 | 2,000 | 852 | 888 | 69 |
| 270 | 225 | 2,000 | 1,129 | 1,255 | 67 |
| 272 | 225 | 2,000 | 277 | 262 | 72.6 |

This consisted of a copper tube 7 ft. \times $\frac{5}{8}$ in. fixed inside a steam jacket into which steam at 40 lbs. pressure was admitted. It was fitted at the top with a spray separator E to guard against accidental passage of liquid into the rest of the apparatus, and a safety valve F.

The vapour was passed to the heat interchanger G which was assembled in the lid of the catalyst chamber. As first constructed this consisted of 20 ft. \times $\frac{1}{4}$ in. copper tubing wound in flat

spirals but the pressure required to drive the vapour through it was found to be excessive and it was replaced by the arrangement shown in the diagram.

It consisted of four hollow discs, two the same diameter as the lid and two smaller, each being fitted with suitable baffles inside to ensure good circulation of the vapours. The discs were connected alternately one above the other by pipes as shown in the diagram in separate detail. The whole was silver-soldered together and fixed inside the lid of the catalyst-chamber so that it could be removed in order to obtain access to the catalyst.

After leaving the heat interchanger, the vapours passed through the superheater H consisting of a copper tube 18 in. long and $\frac{3}{8}$ in. diameter covered with mica and asbestos paper and wound with 25 ft. of 28 S.W.G. nichrome wire (resistance 70 ohms). They were then led to the bottom of the catalyst-chamber through the $\frac{1}{2}$ in. helical copper pipe I. The object of this pipe was to assist in equalising the temperature throughout the mass of the catalyst.

The catalyst-chamber itself was made of copper sheet and was 2 ft. long and 8 in. in diameter. It was heated electrically by 60 ft. of 20 S.W.G. nichrome wire wound round it and insulated from it by mica and asbestos. It contained 10 kilos of the catalyst resting on a perforated false bottom J. The vapours passed up through this false bottom into the catalyst, the inside temperature of which was measured by means of thermo-couples 2, 3 and 4 in a central copper pipe. The temperature of the surface of the chamber was measured by the thermo-couple (7). The vapours issuing from the top of the catalyst passed over the heat interchanger and then entered the condenser L which condensed water. The uncondensed vapours were led to the bottom of the fractionating column M and the ether vapour issuing from the top was condensed by the condenser N through which water at room-temperature was run. The remaining vapours were passed through a tin worm P cooled in ice which condensed nearly all the ether, and the uncondensed vapours were measured by the gas-meter R.

PREPARATION OF ALUM CATALYST FOR THE LARGER-SCALE EXPERIMENTS.

The method of preparing the catalyst (B) already described (p. 79) was found somewhat tedious when larger quantities were required but it was used for making the first charge of catalyst for the large apparatus. The alum spread on trays in thin layers was partially

dehydrated by heating to 80° in a well ventilated chamber until eighteen molecules of water were lost. The temperature was then gradually raised to 200°, the friable mass so obtained mixed with fused alum and the resulting stiff paste heated at 200–220° for two hours. Batches of about 1 kg. could be prepared in this way.

Attempts were made to dehydrate the catalyst by passing hot air over it when in the catalyst chamber, but the results were not satisfactory.

The method finally adopted was partially to dry the finely powdered crystals on trays as before. When the loss in weight amounted to 30 per cent. (16 H₂O) the powder was heated to 100°. The resulting mass consisted of a mixture of hydrated and dehydrated alum which was transferred to a large enamelled basin and gradually heated to 160–180° the whole being turned over continuously. In this process the crystals fused and combined with the dehydrated powder to form hard granules which could be subsequently heated to 200°C. without fusion and crushed in a jaw-crusher. Portions between 10 and 20 mesh were used.

The results of some experiments with this apparatus are shown in Table XVI.

TABLE XVI.

APPARATUS NO. 4.

Weight of Catalyst 9 kg. Temperature 200–230°.

| Experiment No. | Concentration of alcohol per cent. | Rate litres per hour | Weight of alcohol kg. | Weight of distillate kg. | Weight of pure ether kg. | Weight of residue kg. | Percentage conversion |
|----------------|------------------------------------|----------------------|-----------------------|--------------------------|--------------------------|-----------------------|-----------------------|
| 401 | 88 | 10 | 5.1 | 4.95 | 2.53 | 2.42 | 72.2 |
| 402 | 88 | 10 | 4.5 | 4.37 | 2.02 | 2.35 | 65 |
| 403 | 88 | 10 | 17.0 | 16.66 | 8.10 | 8.55 | 63 |
| 404 | 88 | 10 | 21.0 | 20.66 | 10.33 | 10.33 | 70 |
| 405 | 88 | 10 | 14.2 | 13.83 | 6.48 | 7.35 | 63 |
| 406 | 85 | 10 | 18.0 | 17.76 | 7.16 | 10.60 | 60 |
| 407 | 85 | 10 | 18.5 | 18.14 | 7.49 | 10.65 | 57 |
| 408 | 88 | 6 | 24.4 | 24.4 | 13.16 | 11.24 | 74 |
| 409 | 88 | 10 | 34.5 | 34.5 | 13.88 | 20.62 | 57 |
| 410 | 88 | 10 | 32.7 | 32.66 | 14.16 | 18.5 | 61 |
| 411 | 85 | 10 | 37.0 | 36.75 | 12.9 | 23.85 | 52 |
| 412 | 88 | 10 | 32.0 | 31.75 | 12.47 | 19.28 | 56 |
| 413 | 88 | 10 | 37.0 | 36.75 | 15.88 | 20.87 | 61 |
| 414 | 88 | 10 | 37.0 | 36.75 | 14.5 | 22.25 | 56 |
| 415 | 85 | 10 | 37.0 | 36.75 | 12.9 | 23.85 | 52 |

Fresh catalyst was used after Experiment No. 407.

It will be noticed that at the rate of 10 litres an hour the conversion with 88 per cent. alcohol averages 66 per cent. for the first 5 experiments and 58 per cent. for those performed later. This is partly due to the fact that the catalyst used in experiment 407 was prepared by method B, while for the remaining experiments a fresh catalyst prepared by the modification described on p. 96 was employed. This was not quite as active as the other.

A rate of 10 litres per hour in this apparatus corresponds with a rate of 1.4 litre per hour in apparatus No. 3 for equal gas velocities. It will be seen from Table XVI that conversions of 75 per cent. were obtained at this velocity with the latter apparatus, so that the efficiency of the larger apparatus is not so great. One reason for this was that with a fine catalyst, bad channelling took place, due possibly to shrinkage in the wider tube or more probably to the facts that the gas passed upwards. Consequently it was decided to use a coarser catalyst. A few preliminary experiments with apparatus No. 1 had shown that the difference thus produced was quite appreciable. For instance, at 210° at a rate of 60 c.c. per hour, 60 per cent. conversion was obtained with a 20-40 mesh catalyst and only 50 per cent. with a coarser one from 10-20 mesh.

No great pains were taken in the design of the fractionating and condensing system as the technique of the separation of alcohol, ether and water mixtures is well known and moreover, a good separation is difficult on a small scale. With the apparatus described, however, if the temperature of the vapours emerging from L was kept at 60° and those from M at 33° , 40-50 per cent. alcohol was obtained from the former condenser and 85 per cent. alcohol practically free from ether from the latter. With cooling water at 25° , 75 per cent. of the ether was condensed in O and did not contain more than 3 per cent. of water and alcohol. The remaining ether in Q was practically pure.

In experiments 403 and 4, 120 and 250 litres of gas respectively were obtained. This was largely due to defective cooling, as on condensing the gas in liquid air and passing the gas evolved on boiling through the meter, under 40 per cent. was obtained, the rest being ether. If 40 per cent. is taken to be ethylene, the total weights in the two experiments are 60 and 125 grams or 0.35 and 0.60 per cent. on the original weight of alcohol. It is possible that the evolution of gas in these two cases was due to accidental overheating since no gas at all was obtained in the remaining experiments. This result is of considerable technical importance.

The operation of the apparatus was very simple and when once started practically no attention was required. The small superheater H was only used at the beginning of an experiment and it was cut off as soon as the input of alcohol reached its maximum. The outer heating current was simultaneously reduced until only one-tenth of the energy necessary to maintain the tube at 225° with no reaction taking place was supplied.

For work on a large scale the most suitable type of plant would probably consist of a battery of small tubes 4 in. in diameter by 2 ft. long with double walls through which oil could be circulated for heating or cooling. The great disadvantage would be the small output of each unit because of the limitation in size already mentioned and the consequent high cost of the plant and the complexity of piping. Alternatively it might be possible to design a larger vessel in the form of a cylinder about 2 ft. high cooled internally by a system of vertical tubes through which the alcohol vapour could be passed and superheated before coming in contact with the catalyst.