PART II—EQUILIBRIUM IN THE REACTION,

$$2\,C_2H_5{\cdot}OH \rightleftarrows (C_2H_5)_2\,O + H_2\,O.$$

INTRODUCTION.

Erlenmeyer (*Annalen*, 1872, **162**, 373) was the first to show that alcohol could be produced from ether and water. He mixed alcohol-free ether with four times its volume of water and a little sulphuric acid in a sealed tube and after measuring the ether layer heated the tube to different temperatures. The initial depth of the ether was 88 mm., after heating at 120° for 6 hours there was a slight diminution, after heating to 150–180° the depth was 20 mm. and after heating to 220–250° it was 34 mm. At first sight it might seem that about 75 per cent. of the ether was converted into alcohol and that the conversion was less at the higher temperature. More than a qualitative significance must not however be attached to these results as the equilibrium is probably displaced owing to formation of ethylsulphuric acid and, in presence of alcohol, the depth of the ether layer is not a true measure of the quantity of ether present.

Ipatieff (*Ber.*, 1904, **37**, 2996) also showed that alcohol could be formed from ether by heating under pressure in presence of alumina at 300–350°.

While the present experiments were in progress, Reid and Yung (*J. Amer. Chem. Soc.*, 1924, **46**, 390 and 2397) published two papers in which they claimed to have been the first to have prepared alcohol from ether and water. They obtained values of 0·66 and 8·0 for the equilibruim constants at 275° and 130° corresponding with conversions of alcohol to ether of 62 and 85 per cent. respectively. The latter figure is probably incorrect since the equilibrium point was approached from one side only and there is no evidence to show that true equilibrium was reached. The result approximates to the value we have obtained at 222° both by decomposition and formation of alcohol and is in all probability, low.

While going to press another paper by Clark, Graham and Winter (*J. Amer. Chem. Soc.*, 1925, **47**, 2748) has appeared in which a conversion of 80·8 per cent. at 250° is claimed and the equilibrium constant found to be 8·0 at 250°. These results are probably vitiated by the formation of ethylene which was produced in all the experiments.

It will be seen that the results we have obtained both by direct measurement and by calculation lie between those of the above authors.

CALCULATION OF THE EQUILIBRIUM CONSTANT.

An attempt has been made to calculate the equilibrium constant for the reaction by means of Nernst's heat theorem.

$$\log K_p = \frac{Qo}{4{\cdot}57T} - \frac{\Sigma \nu \alpha}{R} \log T - \frac{\Sigma \nu \beta}{4{\cdot}57} T - \frac{\Sigma \nu \gamma}{9{\cdot}14} T^2 - \Sigma \nu c$$

where $K_p = C_{ether} \ C_{water} \ / \ C^2_{alcohol}$ at constant pressure p, Q_o is the heat of reaction at 0°K., $\alpha \beta \gamma$ are the constants in the molecular heat formula

$$C_p^T = \alpha + 2\beta T + 3\gamma T^2$$

$\Sigma \nu$ refers to the algebraic sum (reactants positive, resultants negative) of the number of molecules of each substance multiplied by the corresponding constant, and $\Sigma \nu c$ is the algebraic sum of Nernst's 'Chemical Constants'.

The data available for the calculation are as follows :—

Heat of Reaction.—The most accurate determination of the heat of combustion of alcohol appears to be that of T. W. Richards (*J. Amer. Chem. Soc.*, 1920, **42**, 1599), viz., 328,000 cals. for the liquid at 18°. Adding Young's value (*Proc. Roy. Dublin Soc.*, 1910, **12**, 374) 10,100 for the molecular heat of vaporisation, we have for two molecules

$$2\ C_2H_5{\cdot}OH_{vap.} + 6O_2 = 4\ CO_2 + 6\ H_2O_{liq.} + 676{,}200 \text{ cals.}$$

The mean of Thomsen's and Stohmann's (*J. pr. Chem.*, 1887, (2) **35**, 140) values for ether gives

$$(C_2H_5)_2O_{vap.} + 6O_2 = 4\ CO_2 + 5\ H_2O_{liq.} + 659{,}900 \text{ cals.}$$

Hence $2\ C_2H_5{\cdot}OH = (C_2H_5)_2O + H_2O_{liq} + 16{,}300$ cals.

Deducting Smith's value (*Physical Rev.*, 1907, **25**, 145) 10,600 for the molecular heat of vaporisation of water, the heat of the reaction at 18° is 5,700 cals.

It may be pointed out that this figure is very uncertain. If Thomsen's values for both equations are adopted the result is 10,900 cals. for the heat of reaction.

Molecular Heats.—Not many determinations of the specific heat of alcohol vapour appear to have been made. The following figures are available:—

Ethyl Alcohol Vapour.

Temperature °C.	C_p	Observer
90	18·72	Dixon ... 1922
180–220	20·9	Regnault ... 1862
350	28·2	Thibault ... 1911

The figures for ether vapour are more numerous, but they are not at all concordant as may be seen from the following:—

Ethyl Ether Vapour.

Temperature °C.	C_p	Observer
25–110	31·7	Wiedmann ... 1897
27–189	34·2	Do.
69–224	35·6	Regnault ... 1862
80	27·8	Dixon 1922
100	34·2	...
185	40·5	De Heen ... 1888
300	43·7	...
350	44·5	Thibault ... 1911

The values at 100° and 300° are calculated from the values for C_v given by Rideal (*Proc. Roy. Soc.*, 1921, **99A**, 156).

The specific heat of water varies comparatively slightly within the temperature region we are considering, for example, Pier (*Z. Electrochem.*, 1909, **15**, 536) gives the values 8·2 and 8·5 at 100° and 400° c.

As the data in the case of ether and alcohol are not sufficiently accurate for expression by means of the usual type of equation, it has been assumed that $C^\circ_p = 3{\cdot}5 + 1{\cdot}5n$ where n is the number of atoms in the molecule of the substance. The experimental values have then been plotted and equations found for the most probable curve with the following results :—

$$\text{Alcohol}\quad C_p^T = 17 - 0{\cdot}0073\ T + 4{\cdot}0 \times 10^{-5}\ T^2$$
$$\text{Ether}\quad C_p^T = 26 + 0{\cdot}0025\ T + 4{\cdot}7 \times 10^{-5}T^2$$
$$\text{Water}\quad C_p^T = 8 + 0{\cdot}0006\ T$$

T being the absolute temperature.

By doubling the co-efficients for alcohol and subtracting those for ether and water, the following values are obtained :—

$\Sigma\nu a = 0,\ \ 2\,\Sigma\nu\beta = -0{\cdot}0176,\ \ 3\,\Sigma\nu\gamma = 3{\cdot}3 \times 10^{-5}$
Since $Q_T = Q_0 + \Sigma\nu a\ T + \Sigma\nu\beta\ T^2 + \Sigma\nu\gamma\ T^3$ and $Q_{291} = 5{,}700$, it follows that $Q_0 = 5{,}200$ which is sensibly the same as Q_{291} when the magnitude of the experimental error is considered.

The formula for the equilibrium constant now becomes $\log K_p = 1140/T + 0{\cdot}0019\ T - 1{\cdot}2 \times 10^{-6}\ T^2 - \Sigma\nu c$

At 500° K, the value of $\log K_p + \Sigma\nu c$, is 2·93 whereas the value of $\log K_p$ experimentally determined (p. 106) is 0·86 from which it follows that the value of the integration constant $\Sigma\nu c$ should be 2·07. It is well known that the available methods of evaluating this constant are unreliable. In the present case, using the values for alcohol, ether and water given by Nernst (*Applications of Thermodynamics to Chemistry*, 1907, p. 75) the result is 1·3, while if they are calculated by the Nernst-Trouton expression $C = 0{\cdot}14\ L/T$ where L is the molecular heat of vaporisation at the boiling point T° the figure is 1·9. The corresponding values of K_p are 40 and 10 so that it is evident that the Nernst equation is of little value for determining the absolute value of the equilibrium constant.

If, however, the integration constant is chosen so as to give a correct value at any one temperature, the equation is of use for indicating the manner in which the equilibrium constant varies with temperature. The results obtained when giving the constant the value 2·07 are shown in Table XVII.

The percentage conversion given is that which would be obtained with absolute alcohol. As calculated, it does not vary very greatly with the temperature.

Our object in reproducing the above calculation has been mainly to emphasise the large errors which may be easily introduced into the results. Numerous calculations have been made (Cf. W. M. Lewis, *Physical Chemistry*, vol. 2, 388; Saunders, *J. Physical Chem.*, 1924, 28, 1151.) in which values of the equilibrium constant calculated by the Nernst heat theorem agree exceedingly closely with experimental results. To obtain these it appears almost essential that the chemical constants must have been chosen to fit the particular reaction under consideration. Unfortunately the number of reactions available for testing the theorem is far too small to lead to definite results.

TABLE XVII.

Values of the equilibrium constant.

Temperature		K_p	Percentage conversion
°K.	°C.		
400	127	22	90
450	177	12	87
500	227	7·3	84
550	277	4·9	81
600	327	3·5	79

In the present case it has been pointed out that the data for the specific heats and heat of reaction are very unreliable and attempts are now being made to redetermine these quantities.

EXPERIMENTAL.

DESCRIPTION OF APPARATUS.

The method adopted for determining the equilibrium constant was a dynamic one. A suitable quantity of the reacting substances was passed over the catalyst in which the temperature was maintained as constant as possible and the products collected and analysed. Numerous experiments in which alcohol was passed over the alum catalyst have already been detailed. The present section deals more particularly with the somewhat more difficult operation of the conversion of a mixture of ether and water into alcohol.

The apparatus used is shown in Fig. 6. Ether was contained in a separating funnel B and pressure applied by admitting water to a bottle A. The rate of flow was controlled by a capillary tap and the ether passed into a glass spiral C immersed in a water bath, the temperature of which was kept constant to 0·5° by means of a thermoregulator. The ether was volatilised in the spiral and the vapour passed through two wash bottles D and E also immersed in the bath and containing 50 c.c. of water each. The proportion of water to ether in the vapour could thus be adjusted by altering the temperature of the bath. The mixed vapours were passed to the copper superheater F and their temperature raised to about 200°. They then entered the outer jacket of the catalyst tube. The latter consisted of three concentric copper tubes 1½ in., 1 in. and ⅜ in. in diameter. The outer tube G was insulated with mica and asbestos paper and heated electrically. The heating wire consisted of 80 ft. of 20 S.W. G. nichrome wire and about 60 watts were required to keep the temperature at 225°. The temperature at the surface of this tube was measured by means of the thermo-couples 1, 2 and 3 and was maintained as uniform as possible by enclosing the whole in a box filled with asbestos the quantity of which was carefully adjusted in the same way as it was for apparatus No. 1. (p. 73). The second tube H contained 200 g. of catalyst extending over a length of 60 cm., the end being well within the uniform temperature region. The ends of the tube were packed with pumice. The catalyst and pumice were held in place by two perforated copper discs which also served to retain the tube I in a central position. The latter contained three thermo-couples 4, 5 and 6 for determining the temperature at the centre and the ends of the catalyst. They could be moved along the tube if necessary. The two central tubes passed through glands and could be removed when required.

The vapours passed from the space between tubes G and H through the catalyst and entered the condensing apparatus. The counter-current arrangement was intended to equalise the temperature as far as possible by avoiding direct heating of the catalyst by the heating wire and by carrying off the heat produced by the reaction in the case of alcohol decomposition or by supplying heat in the case of its synthesis. It was not however, entirely successful, probably owing to the comparatively large cross section of the catalyst tube and the low heat conductivity of the catalyst. It was found that when the temperatures at the beginning and in the centre of the catalyst were 225° the temperature where the vapour left the catalyst was only 210°.

The condensing apparatus consisted of a flask I fitted with a column K and the ether vapours were condensed in a flask L cooled in a freezing mixture. The outlet tube from L led to a test-tube M containing sulphuric acid to ascertain if any ether or ethylene was escaping. The whole apparatus was frequently tested to see that it was free from leaks.

ANALYSIS OF THE PRODUCTS.

Alcohol was determined by measuring the density of the residue lask J. This was kept in cold water during the experiments and n a sufficient quantity of reaction product had been collected least 100 c.c.) the temperature was raised and the ether distilled. temperature at the top of the column was not allowed to exceed (atmospheric pressure 680 mm.) and it was found that when no e ether distilled the residue had no smell of ether. This was a cate test as it was found quite easy to detect in this way 0·2 c.c. of r in 50 c.c. of 50 per cent. alcohol.

The liquid remaining in the fractionating column was assumed to the same composition as the original mixture. This was not e accurate since it contained very little water. As its total weight about 0·6 g. in comparison with the total amount of reaction lucts, the error could be neglected.

The receiver in which the ether was condensed was not allowed to above −15°, and after expulsion of air from the apparatus no bles were observed in the test tube of sulphuric acid showing that loss of ether was negligible. The amounts of water and alcohol in ether were determined by measuring the specific gravity at 25° re and after treatment with anhydrous potassium carbonate and g the data given by Perkins (*J. Ind. Eng. Chem.*, 1917, **9**, 521). average content of water was 1·3 per cent. and of alcohol less than per cent. The water-content was checked by treatment with ium carbide and measuring the volume of acetylene evolved or nating it with silver nitrate as described by Walden (*J. Soc. m. Ind.*, 1924, **43**, 285 T). The alcohol-content was checked by ing with a saturated aqueous solution of ether and no diminution olume could be observed.

DISCUSSION OF RESULTS.

Table XVIII shows the results obtained. These are grouped rding to the temperature which is the temperature of the portion e catalyst with which the vapours were last in contact. Each group ranged with the experiments at the highest rate of flow first and e at the slowest rate last. Column 3 shows the molecular ratio vater to ether in the initial mixture and columns 5 and 6 the s of ether and water to alcohol in the distillate.

TABLE XVIII.

The reaction: $(C_2H_5)_2O + H_2O = 2\,C_2H_5\text{.-}OH$

Catalyst 200 grams.

1	2	3	4	5		6
Experiment No.	Final temperature °C.	Initial mixture Mols. water / Mol. ether	Rate of passing: grams per hour	Final Mixture		Kp.
				Mols. ether / Mol. alcohol	Mols. water / Mol. alcohol	
363	233	1·74	66	1·79	3·52	6·3
362	233	1·69	33	1·74	3·28	5·7
361	233	1·72	23	1·69	3·27	5·5
364	233	1·66	23	1·66	3·10	5·2
366	233	1·84	10	1·68	3·53	5·9
						5·6
342	228	2·25	57	1·74	4·35	7·8
343	228	1 95	55	1·84	4·11	7·5
368	228	1·79	40	1·91	3·81	7·3
375	228	1·67	40	1·94	3·58	7·0
345	228	2·27	30	1·57	4·2	6·7
344	228	2·00	28	1·73	3·96	6·8
353	228	1·41	27	2·05	3·02	6·1
367	228	1·77	23	1·84	3·65	6·8
372	228	1·41	23	2 10	3·14	6·6
370	228	1·41	15	2·25	3·4	7·7
369	228	1·43	13·5	2·2	3·26	7·3
371	228	1·36	13	2·33	3·32	7·7
						7·0
376	222	1·81	36	2·14	4·25	9.1
348	222	2·23	26	1·88	4·79	9 0
373	222	1·63	23	2·25	4·0	9·0
359	222	1·8	21	2·08	4·16	8·7
356	222	1·59	20	2·23	3 85	8·6
358	222	1·39	18	2·46	3·65	8·9
349	222	2·78	15	1·64	5·5	9·2
						8·9
378*a*	220	1·92	40	2·23	4·65	10·0
378*b*	220	2·6	40	2·05	4·9	9·8
346	220	1 62	36	2·55	4·43	10·6
350	220	1·54	36	2·43	4·0	9·7
352	220	1·44	22	2·5	3·8	9·5
360	220	1·65	18	2·3	4·33	10·0
						10·0
347	215	2·21	40	2·14	5·33	11·5
377	215	1·78	40	2·4	4·66	11·3
355	215	1·76	25	2·4	4·62	11·2
354	215	1·26	23	2·93	3·82	11·1
						11·1
383	225	0·37[1]	40	1·91	4·03	7·7
380	222	0·37	20	2·01	4·32	8·8
381	222	0·37	20	2·01	4·3	8·65
382	222	0·37	20	2·02	4·45	8·98
384	225	0 17	50	2·66	3·36	9·0
386	225	0·17	20	2·17	3·47	7·5[1]
387	225	0·17	20	2·21	3·42	7·5

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[1] Experiments 383 to the end are for the direct reaction and the ratio given is that of the number of mols. of water to mols. of alcohol.

The equilibrium constants in column 6 appear somewhat irregular but it must be remembered that in this reaction a small experimental error in estimating the constituents of distillate has a large effect on the value of the constant, particularly if the error is in determining the alcohol. For example, in the first experiment, the composition of the distillate was found to be :—Ether 54·8, water 26·2, alcohol 19·0 per cent. by weight. If these were changed to :—Ether 55·3, water 26·7, alcohol 18·0, K_p would become 7·2 instead of 6·3.

Fortunately the determination of alcohol is in all probability fairly accurate, while the ether, losses of which in the form of vapour are most likely to occur, was in all these experiments present in quantities of 50 grams or more so that small losses would have little effect on the value of K_p.

The mean value of K_p at each temperature has been estimated, neglecting the results for the higher velocities.

It will be observed that there is a marked tendency of K_p to rise as the temperature is diminished even within the small range under consideration. To some extent this might be expected from theoretical considerations (p. 103) but it must be remembered that incomplete attainment of equilibrium would also lead to high values of K_p.

It is probable that at the lower temperatures equilibrium is not complete, particularly in view of the comparatively large proportion of water, and the method of extrapolating to zero velocity does not give correct results. It is necessary therefore to regard the values of K_p as being of the nature of an upper limit.

This view is confirmed by a consideration of some of the results obtained in the first part of the paper. For example, the highest conversion obtained with 88 per cent. alcohol at 210° is 79 per cent. as may be seen from Table VI (p. 81). Even this value is probably due to an experimental error, as 75 per cent. is the maximum figure obtained in all the other experiments. The equilibrium constant corresponding with 79 per cent. conversion is 6·8, so that 11 is almost certainly too high a value.

At 225–227° there is a fair agreement between the equilibrium constants obtained by the two methods although it is remarkable that those obtained by the synthesis of alcohol appear to be, in general, distinctly lower than those obtained by its decomposition.

The low value obtained at 233° is particularly remarkable since it is scarcely likely that the equilibrium constant would change from 7·0 to 5·5 for a temperature change of 5°. In the experiments on the decomposition of alcohol at 235° (Table IX) the maximum conversion of 74 per cent. was obtained with a rapid flow of alcohol so that the value of K_p 3·9 deduced is very probably low.

In view of the experimental difficulties connected with the problem, further discussion does not seem advisable at this stage although there are numerous points of interest. An oil-heated apparatus in which a very uniform temperature can be maintained has been constructed and it is hoped by means of it to obtain rather more reliable results with a greater variety of mixtures than those which have so far been described.

SUMMARY.

1. Experiments have been made using different solid catalytic agents for the production of ether from alcohol, and potassium alum has been found the most suitable.

2. Methods of preparing the catalyst so as to obtain maximum activity have been investigated. A catalyst prepared at low temperatures in the form of hard and dense granules shows greater activity than any which have previously been described. Poor yields were obtained using pumice or kieselguhr as supports.

3. A study of the effect of heat on the catalyst shows that a temperature of 250° or higher reduces its activity, the effect being irreversible.

4. At lower temperatures (190–195°) the catalyst is temporarily affected by water vapour, but the activity is restored by raising the temperature to 210°.

5. The optimum temperature is 225–230° at which the conversion is 75 per cent. of the theoretical when using 88 per cent. alcohol.

6. The quantity of ether produced by a given weight of catalyst increases to a maximum as the rate at which alcohol vapour is supplied increases, and then decreases. The maximum weight of ether obtained per hour from 100 grams of catalyst is 64 grams using 88 per cent. alcohol. With more concentrated alcohol the maximum yield is increased.

7. The effect of dilution of the alcohol with water has been studied. It has been found that the conversion with very dilute

alcohol is less than would be expected on theoretical grounds owing to the great retardation in velocity produced by water vapour.

8. Experiments have been made with a reaction vessel 45 cm. × 7·5 cm. in diameter containing about 2 kilos of the catalyst. A 72 per cent. conversion was obtained when passing 2 litres of alcohol per hour. Only 1–2 c.c. of gas consisting of ether vapour and ethylene was evolved per minute. The ether was free from appreciable quantities of impurities except alcohol and water.

9. Experiments have been made using still larger apparatus holding about 10 kg. of the catalyst. It was found possible to obtain 5 litres of ether per hour when passing 10 litres of 88 per cent. alcohol an hour, the percentage conversion varying from 52 to 70.

10. Attempts to calculate the equilibrium constant of the reaction by means of the Nernst heat theorem do not give satisfactory results partly owing to lack of data.

11. Measurements of the equilibrium constant have been made by determining the quantity of alcohol formed when mixtures of ether and water are passed over the catalyst. The results are of the same order as those obtained by decomposition of alcohol, although certain anomalies have not been explained. The most probable value of the equilibrium constant is 7·3 at 500° K.

In conclusion we wish to express our best thanks to Dr. J. J. Sudborough for advice and assistance during the course of the work.

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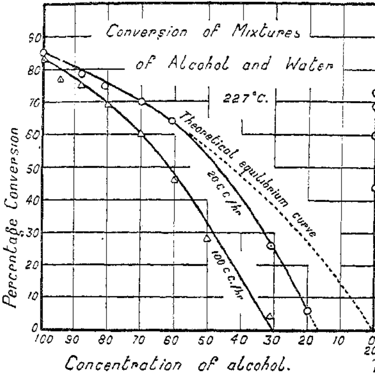
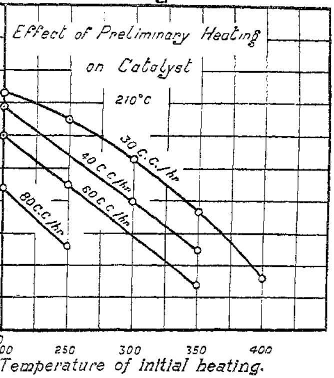
Fig 1.


Conversion of Mixtures of Alcohol and Water

227°C.

Fig 2.


Effect of Preliminary Heating on Catalyst

210°C

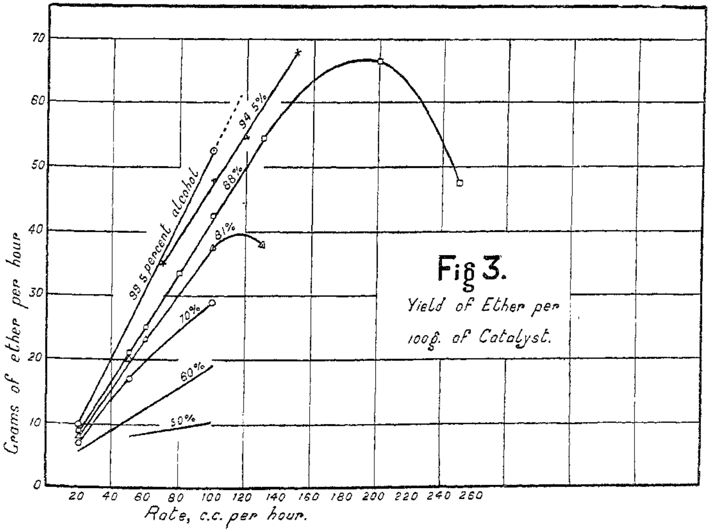


Fig 3.

Yield of Ether per 100g. of Catalyst.

Fig 4.

Apparatus No. 3.

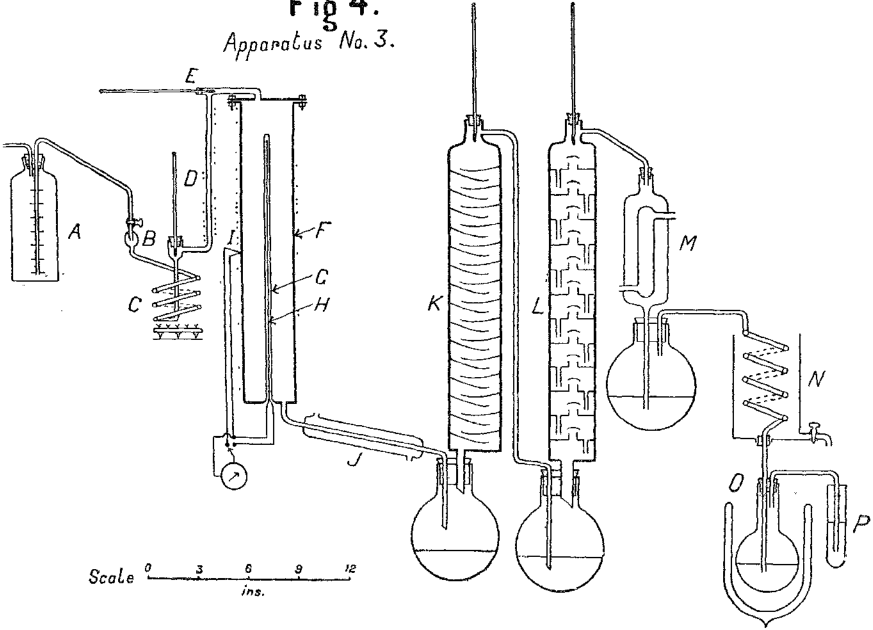
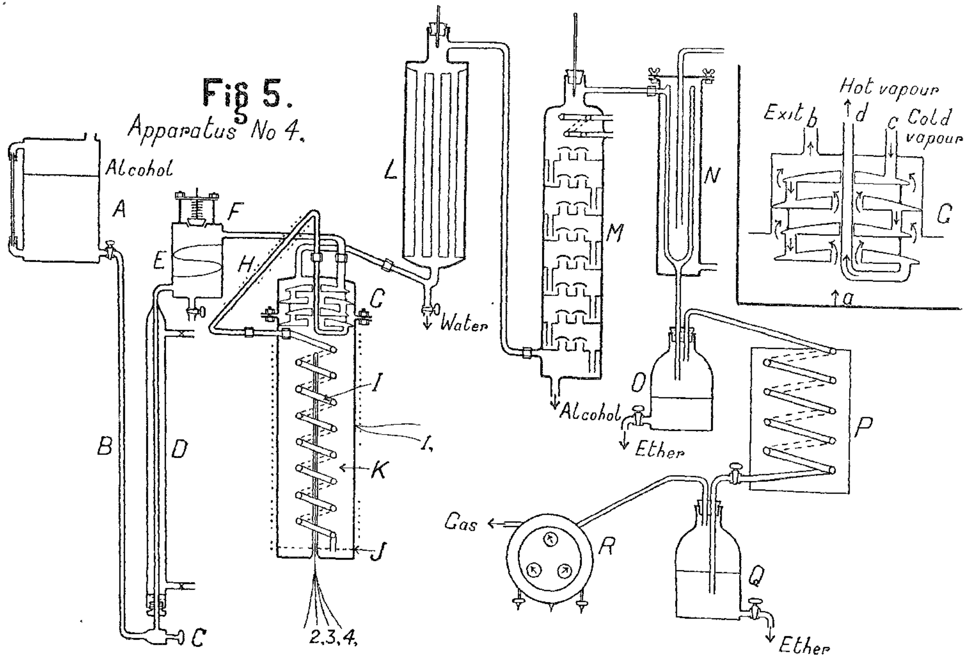
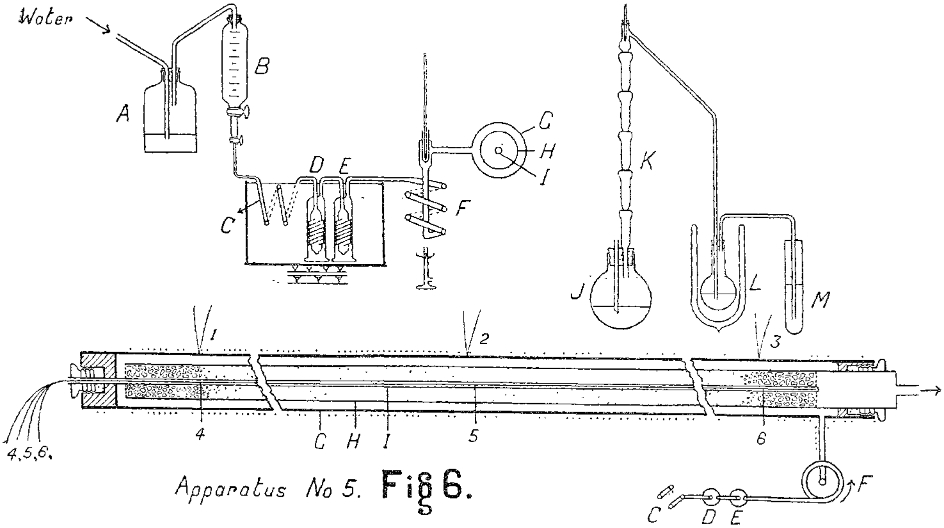


Fig 5.

Apparatus No 4.





Apparatus No 5. Fig 6.