

Esterification in the Presence of Anhydrous Salts¹

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The use of anhydrous salts as catalysts in the reaction between ethyl alcohol and acetic acid was first mentioned by Berthelot and Pean de St. Gilles² in 1862 when they made a study of the equilibrium percentages of ethyl acetate formed by the reaction of acetic acid with various concentrations of ethyl alcohol.

This work was followed by investigations of Bogojawlensky and Narbutt³ in 1905, Haberman and Berzina,⁴ in 1909, and Haberman and Kurtenacher⁵ in 1910, who found ferrous, nickel, copper, manganese, and zinc sulphates to be effective catalysts. N. G. Gajendrage⁶ studied the reaction between ethyl alcohol, methyl alcohol, and acetic acid at 230°C. in the presence of potassium-aluminum sulphate and silica and reported the equilibrium constant to be in good agreement with that obtained by other workers in the liquid phase at lower temperatures. Whitacre and Briscoe⁷ reported data obtained at 45°C. and 100°C. for the reaction between ethyl alcohol and acetic acid in the presence of various anhydrous salts. Some preliminary work in the gaseous state was also reported at this time.

This paper is a study of the reaction between the vapors of ethyl alcohol and acetic acid when passed over varied amounts of aluminum and copper sulphate.

Experimental Part

Apparatus. Much difficulty was encountered in designing and constructing a suitable apparatus for this problem. The apparatus shown in Figure 1 gave reproducible results. It was constructed entirely of Pyrex so that the liquid or gas came in contact with glass only.

Materials. The acetic acid used was glacial acetic having a gravity of not over 1.0510 at 20°C. Ethyl alcohol was prepared by the usual methods. No alcohol was used which had a gravity greater than 0.7900 at 20°C.

Alcoholic potassium hydroxide was used for titration because it was thought that in some cases it would be necessary to saponify the ester formed in order to obtain the required information concerning the progress of the reaction. The potassium hydroxide was standardized against weighed quantities of acetic acid and the standardization was checked with succinic acid.

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²Am. Chim. Phys. 65:385 (1862); 66:5 (1862); 68:225 (1863).

³Berichte 38:3344 (1905).

⁴Jour. Prakt. Chem. 80:349 (1909).

⁵Jour. Prakt. Chem. 83:541 (1910).

⁶Fifteenth Indian. Sci. Congr. Chem. Abstract.

⁷Proc. Ind. Acad. Sci 38:187 (1929).

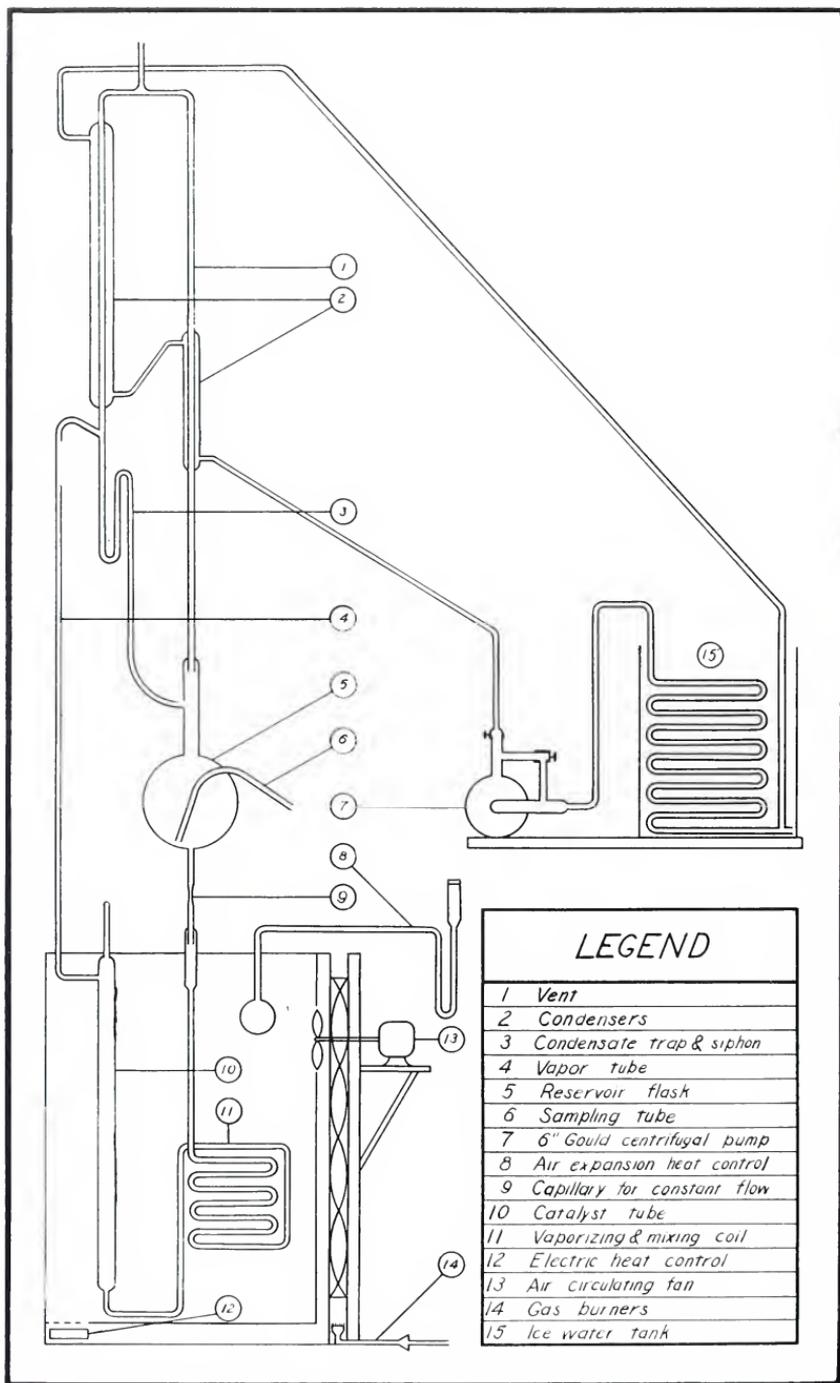


Fig. 1.

TABLE I. EXPERIMENTAL DATA

(a) (See Curve (A) Fig. II) Glass Wool		(d) (See Curve (D) Fig. II) 30.78 g. Al ₂ (SO ₄) ₃		
Time in Hours	Per Cent of Acid Converted	Time in Hours	Per Cent of Acid Converted	
5.0	2.10	1.25	14.30	
14.5	5.70	2.5	27.60	
24.0	9.00	5.25	56.40	
48.0	17.00	20.50	63.10	
72.0	23.00			
96.0	27.00	(e) (See Curve (E) and Fig. II) 26.4 g. Al ₂ (SO ₄) ₃		
(b) (See Curve (B) Fig. II) 3.42 g. Al ₂ (SO ₄) ₃		(a)	2.0	58.30
5.0	11.30	3.0	65.10	
17.0	33.20	(b)	1.25	20.80
24.0	47.90	4.25	68.92	
40.0	72.15	4.75	68.90	
48.0	79.05	(c)	1.25	25.60
72.25	81.75	4.0	71.00	
89.0	80.80	5.0	76.15	
(c) (See Curve (C) Fig. II) 17.1 g. Al ₂ (SO ₄) ₃		23.25	77.85	
5.5	30.80	(d)	0.75	32.70
10.5	58.60	1.50	54.90	
11.5	61.60	2.0	61.90	
22.0	67.90	4.0	63.60	
2.0	12.60	6.0	58.00	
5.0	29.40	(f) (See Curve (F) Fig. II) 68.1 g. Al ₂ (SO ₄) ₃		
10.0	56.20	(a)	0.5	38.60
8.0	47.50	1.0	52.15	
23.0	66.40	(b)	0.5	42.30
29.0	64.00	0.75	55.40	
(h) (See Curve (H) Fig. II) 34.2 g. Al ₂ (SO ₄) ₃		1.25	60.22	
2.0	42.00	(c)	0.166	14.80
3.0	53.20	2.75	61.18	
5.0	59.00	5.0	61.70	
(d') (See Curve (D') Fig. II) 10.25 g. Al ₂ (SO ₄) ₃		(g) (See Curve (G) Fig. II) 110.0 g. Al ₂ (SO ₄) ₃		
(a)	3.0	30.00	0.1	51.80
6.0	23.80	(z) (See Curve (Z) Fig. II) 30.78 g. Al ₂ (SO ₄) ₃		
9.0	6.40	The Reaction:		
(b)	2.0	21.00	2HAc + EtOEt → 2EtAc + H ₂ O	
5.0	46.25	5.0	C ₂ H ₅ -O-C ₂ H ₅ + 2CH ₃ COOH →	
17.0	61.10	17.0	2C ₂ H ₅ OOCCH ₃ + H ₂ O	
23.0	57.10	23.0	Ether, 103.9 c.c. Acid, 114.6 c.c.	
(d'') (See Curve (D'') Fig. II) 20.52 g. Al ₂ (SO ₄) ₃		20.52 g. Al ₂ (SO ₄) ₃		
1.75	25.20	7.25	1.75	
4.0	50.10	19.25	5.80	
5.0	53.50	29.0	12.25	
9.5	65.20	42.25	23.80	
		51.5	26.20	
		67.0	26.80	
		71.5	4.50	

The catalyst used here has been referred to in the discussion of Curve (Z).

The anhydrous copper sulphate was prepared by dehydrating the pentahydrate at 200°C. in the oven of the apparatus.

The aluminum sulphate was prepared in two ways. *Method I:* The hydrated salt was placed directly in the oven of the apparatus (200°C.). This produced a spongy easily pulverized mass. *Method II:* The hydrated salt was heated at 100°C. for 10 to 12 hours and then placed in the oven at 200°C. until needed. This produced a hard sintered mass which was broken up in a mortar. The particles used as the catalyst were those that passed through a ten-mesh screen and were retained by a twenty-mesh.

Experimental Procedure.—Acid and alcohol were removed from stock bottles, which were kept in a water bath at 25°C., and placed in separate burettes. Fifty ml. each of acid and alcohol was run from the burettes into a 250 ml. flask. This operation was carried out quickly in order to prevent any more than the unavoidable amount of air coming in contact with the reactants and to prevent the temperature from changing appreciably. The 250 ml. flask was tightly stoppered, and the mixture was violently shaken. A sample of this mixture was transferred to a small, accurately calibrated, water-jacketed 10 ml. burette. This sample was titrated with potassium hydroxide and recorded as "zero per cent acetic acid converted." The remainder of the mixture was placed in the storage bulb of the apparatus. The velocity of flow was adjusted so that the entire reaction mixture would pass over the catalyst in a certain time, say one hour. This velocity was kept constant at 1.66 ml. per minute during the entire investigation with noted exceptions. The temperature of the oven was maintained at 200°±5°C. during the entire investigation. The data are given in Table I.

Discussion of Data

These data are presented graphically in Figure 2 on log-log paper, which proves to be a convenient way of following the course of a reaction of this type.

In Curve A practically equimolecular quantities of alcohol and acid were passed through the apparatus with a plug of glass wool in the catalyst space. If this is compared with Curve 1 it will be seen that the reaction follows practically the same line in the gaseous phase at 200°C. as it does in the liquid phase at 45°C. The slope of this line between 2.5% and 15% acid converted is 0.35.

Curve B graphically represents the data obtained when a 3.42 g. portion of aluminum sulphate prepared by Method I is used. It will be seen that the equilibrium percentage is above 80%. This was caused by improper combustion in one of the gas burners which caused the temperature of the oven to fall to 170°C. after 30 hours of the run had been followed. The slope of this curve between the 10% and 40% points is 1.92.

Curve C presents the results of two runs after 13.68 g. of aluminum sulphate prepared by Method I was added to the original 3.42 g. in Curve B. The total weight of catalyst is 17.1 g. The slope between the 10% and 40% points is 5.54.

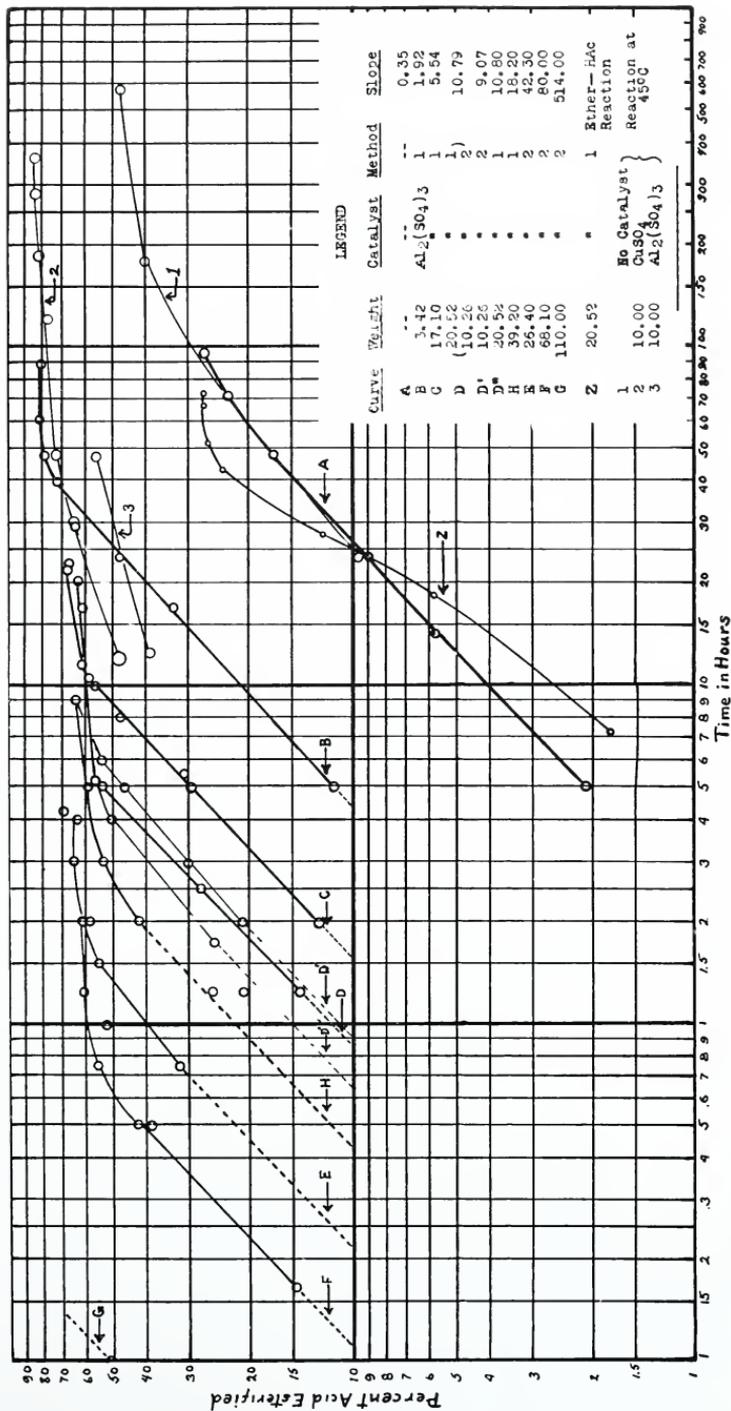


Fig. 2.

Curve H shows the points after 17.1 g. of aluminum sulphate prepared by Method I were added to the 17.1 g. used in obtaining Curve C. We have taken the liberty of projecting the curve parallel to other lines of this series. The slope of the projected line between the 10% and 40% points is 18.2.

Curve D' was obtained after the apparatus had been cleaned and refilled with 10.26 g. of aluminum sulphate prepared by Method II. The points indicated are the results of two consecutive runs. The slope of this line between the 10% and 40% points is 9.07.

The apparatus was cleaned again and Curve D'' was obtained with 20.52 g. of aluminum sulphate prepared by Method I. The slope of this line between the 10% and 40% points is 10.80.

The catalyst for Curve D'' was used to obtain the points on Curve Z for the reaction between diethyl ether and acetic acid. Curve D was obtained after 10.26 g. of aluminum sulphate prepared by Method II were added to this catalyst. The total weight of catalyst was 30.78 g. The slope of this line between the 10% and 40% points is 10.79.

The similarity of the results obtained with three distinctly different weights of catalyst shows that there was some influence of the method of preparation upon the rate of the reaction. Curve D indicates that the original two-thirds of the total catalyst used was very likely poisoned by the ethyl alcohol acetic acid reaction. That the 10.26 g. of added catalyst carried the burden of the reaction is supported by the similarity of the slope of D and D'.

Curve E shows the results obtained with 26.4 g. of new aluminum sulphate prepared by Method II. The slope of Curve E is 42.3.

Curve F presents the results of two runs after 41.7 g. of aluminum sulphate prepared by Method II had been added to the 26.4 g. used in Curve E, making a total of 68.1 g. The slope of this curve between the 10% and 40% points is 80.0.

Curve G is the result of one pass after the total weight of catalyst

TABLE II.

Curve	Weight	Catalyst	Method of Preparation	Slope
A	0.0	Glass Wool	0.35
B	3.42	Al ₂ (SO ₄) ₃	1	1.92
C	17.1	"	1	5.54
H	34.2	"	1	18.20
D'	10.26	"	2	9.07
D''	20.52	"	1	10.80
D	30.78	"	1 and 2	10.79
E	26.4	"	2	42.30
F	68.1	"	2	80.00
G	110.0	"	2	514.00

had been increased to 110 g. by addition of aluminum sulphate prepared by Method II to that used in Curve F. The slope of this curve if projected parallel to other curves of this series is 514.0.

In Table II the weights of the catalyst are compared with the slopes of the respective curves. This slope represents the rate of the reaction in per cent conversion per hour. The letters accompanying the points refer to their respective curves in Figure 2.

No definite function of the rate of the conversion to the weight of the catalyst could be found. It was true however that where corresponding weights of the catalysts prepared by the two methods were compared, the velocity was greater with catalyst prepared by Method II.

Figure 3 shows the results obtained when similar runs were made on copper sulphate. The action was very erratic, and, since there was relatively little acceleration of the reaction, further discussion of copper sulphate has been omitted in this paper.

At the beginning of practically every run with aluminum sulphate a white fog appeared high in the condensers and persisted for about 15 minutes. On one occasion the water was removed from the condensers,

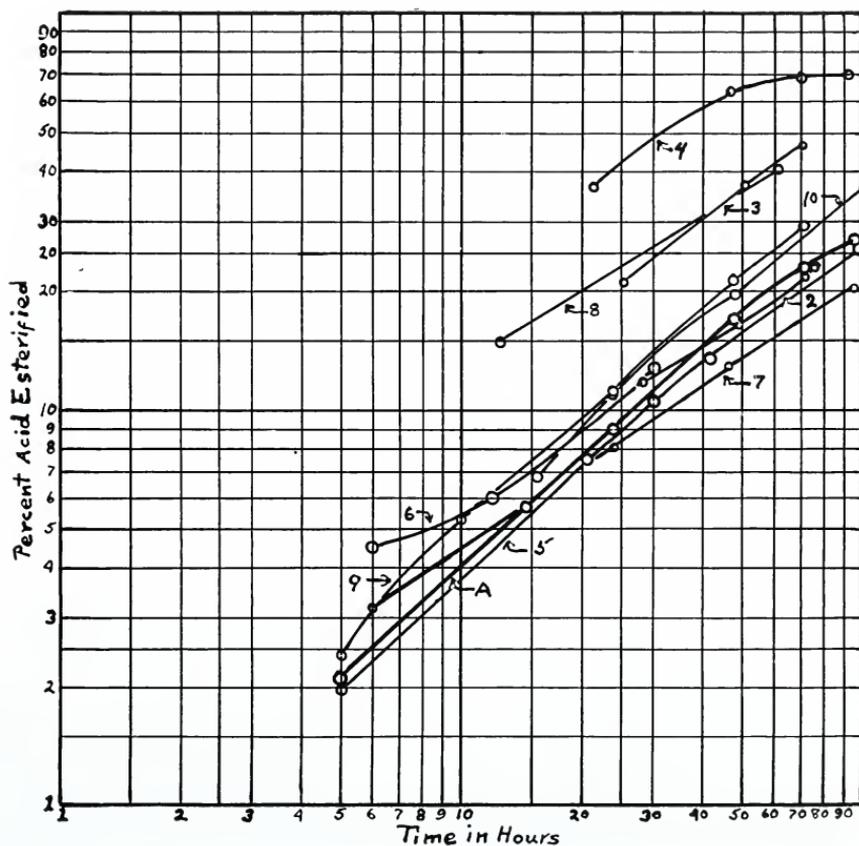


Fig. 3.

and this fog was allowed to rise over the top of the condensers. The odor indicated a fairly high concentration of ether. It was also noted that when the catalyst mass was flushed with alcohol for some time, a considerable quantity of ether was produced. On several occasions the ether appeared in sufficient quantities to be separated as a double layer when the contents of the apparatus were removed and diluted with water. It was decided that perhaps the ether might be an intermediate in the reaction between acetic acid and alcohol under these conditions. As a result, a few preliminary runs were made with ordinary stock ether and acetic acid. After some ethyl acetate was obtained in this manner, a complete run was made using 103.9 ml. absolute ether and 114.6 ml. of acetic acid. The data obtained from this reaction are presented by Curve Z, Figure 2.

Theoretical Discussion

The production of ethyl ether and the reaction between ethyl ether and acetic acid leads the authors to believe that the alcohol may be absorbed by the catalyst where it may react with other molecules of alcohol to form ether, with acetic acid to form ethyl acetate, or with itself and acetic acid simultaneously to produce ether and ethyl acetate. The suggestion of Adkins, Adkins and Nissen⁸ that alcohol and ether are stable alike toward alumina at 350°C., 400°C., and 465°C. leads us to the further suggestion that in the course of the reaction between ethyl alcohol and acetic acid at 200°C., ethyl alcohol and the ethyl ether are both attached to the catalyst and react collectively with the acetic acid to form ethyl acetate.

Although we have made no precise attempts in the work reported here to obtain the location of the equilibrium point, the curves show that most of the points are between 60% and 70% of acid converted. The points outside of this range have been explained.

The data given here concerning the equilibrium point do not agree with Berthelot and St. Giles,⁹ Edgar and Schuyler,¹⁰ nor Milligan, Chapell, and Reid,¹¹ that the equilibrium point is far above that in the liquid state.

The reaction between ethyl ether and acetic acid is being studied at the present time and will be presented in a later paper.¹²

The theoretical kinetics of the reaction show that it should take place, and sizable yields of ethyl acetate have been prepared by the reaction. It has also been found that considerable dehydration of the ether to form ethylene takes place.

Conclusions

Ethyl alcohol and acetic acid were allowed to react in an apparatus designed to permit repeated passages of the reactants and the products through varied amounts of copper and aluminum sulphates. The following observations were made:

1. Copper sulphate did not produce results of sufficient importance to warrant extensive study.

⁸ Jour. Amer. Chem. Soc., 44:2175 (1922). Ibid 46:1301 (1924)

⁹ loc. cit.

¹⁰ Jour. Amer. Chem. Soc., 46:64 (1924).

¹¹ Jour. Phys. Chem. 28:872 (1924)

¹² Ruff and Whitacre. Unpublished Thesis. Case School of Applied Science, 1936.

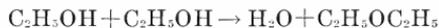
2. Aluminum sulphate will dehydrate ethyl alcohol without the formation of appreciable amounts of decomposition products.

3. Aluminum sulphate will greatly increase the velocity of the reaction.

4. The method of preparing the aluminum sulphate affects the velocity of the reaction.

5. The average equilibrium percentage in all runs was 69% which agrees fairly well with the percentages found in liquid-phase esterification. These results are not in keeping with the predictions of Milligan, Chappel, and Reid.¹³

6. Ethyl ether and acetic acid were passed through aluminum sulphate with the formation of ethyl acetate. This leads the authors to believe that the gaseous reaction in the presence of aluminum sulphate may involve, under certain conditions, three reactions which run concurrently. These reactions are:



If this be the case, the disagreement between the results of various investigators of vapor phase esterification may be explained on this basis.

¹³Jour. Phys. Chem. 28:872, 1924.