

# ESTERIFICATION EQUILIBRIA IN VAPOUR PHASE. EQUILIBRIUM BETWEEN METHYL ALCOHOL, ACETIC ACID, METHYL ACETATE AND WATER.

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## INTRODUCTION.

Although there are numerous papers on esterification equilibria in vapour phase, of ethyl alcohol and acetic acid, there has been no attempt so far, to find out the corresponding equilibrium constant in the reaction of methyl alcohol with acetic acid.

According to Menshutkin [*Ann. Chim. Phys.*, 1880, (5) 20, 302] the limit of esterification in the liquid phase of an equimolecular mixture of methyl alcohol and acetic acid is, at 69.9% esterification ( $K_p = 5.3$ ), and according to Berthelot [*Ibid.*, 1863, (3) 68, 235], 67.5%. It appears that in liquid phase, the equilibrium constants for the formation of esters from normal aliphatic acids and primary alcohols, are about the same order of magnitude.

It is now well known that the equilibrium constants for the reaction of ethyl alcohol with acetic acid in vapour phase, are very much higher than the values in liquid phase. In this paper it is shown that this holds good even for the vapour phase esterification of acetic acid by methyl alcohol, and that, curiously enough, the equilibrium constant is nearly the same as that for the vapour phase esterification of acetic acid by ethyl alcohol, at the same temperature.

It was shown by us (*Jour. Amer. Chem. Soc.*, 1937, 59, 798) that although potassium alum is far more active than silica gel for esterification, the lower limit with this catalyst is due to the simultaneous establishment of ether equilibrium. It was therefore interesting to find out if there was any formation of methyl ether, when vapours of methanol and acetic acid were passed over alum catalyst, and also to compare the relative activity of silica gel and alum for the vapour phase esterification. Both methanol and acetic acid can be made available in large quantities in Bhadravati.

## EXPERIMENTAL.

The apparatus used and the experimental procedure followed was the same as that described by Gajendragad, Jatkar and Watson (*This Journal*, 15A, 59-69).

The copper tube was not attacked by acetic acid at temperatures higher than 200°. The mixture of alcohol and acid was allowed to flow drop by drop into the copper tube vapouriser, superheated and then passed through the catalyst tube. The resulting products were condensed in a test tube kept in a freezing mixture.

*Analysis.*—A large number of preliminary experiments were made to find out if there were side reactions, such as the dehydration of alcohol to ethers and decarboxylation of the acid to carbon dioxide, water and acetone. The latter could not be detected. The dehydration of methyl alcohol to methyl ether, did not occur even at low space velocities, owing to the lower activity of the alum catalyst for this reaction than for the decomposition of ethyl alcohol, and, to the general preference of the esterification to etherification over dehydrating catalysts.

The absence of any side reaction such as etherification was easily proved, as the corresponding ether is a gas which could be estimated by absorbing in sulphuric acid.

Optimum temperature for the silica catalyst was determined by passing, at the rate of 10 c.c. per hour, an equimolar mixture of methyl alcohol and acetic acid, at various temperatures from 200°–270° and finding out the percentage of acid esterified. The results are given in the following table. Experiment No. 8 was done with the rate of 12 c.c. an hour.

Catalyst: 66 grams of silica.

Expt. No.	Temp.	% conversion	Expt. No.	Temp.	% conversion
1	205	42.0	6	270	76.4
2	230	62.5	7	270	77.9
3	230	66.0	8	230	59.3
4	250	76.4	9	230	66.0
5	250	72.7			

These results show that the optimum temperature was in the region 230°–270°. Heating the catalyst to 270° did not appreciably change the activity of the same at lower temperatures. Thus experiments 3 and 9 gave the same result.

Study of the reverse reaction  $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$  over *silica* catalyst at 260° was taken up. Pure methyl acetate was taken in the burette and the ester vapours saturated

with water vapour were passed into the reaction chamber through the superheater.

The ester vapours thus saturated with steam were initially condensed and analysed for free acid. It was found that under these circumstances the ester was not hydrolysed. Thus the initial mixture contained the vapours of the ester and the water only, the relative proportion being controlled by the temperature of the humidifier.

According to the equation  $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$  equivalent quantities of acetic acid and alcohol are produced. In these runs the total acid and free acid per gram of product are determined, the quantity of the alcohol is assumed to be equivalent to the free acid, and the water is estimated by difference. The results obtained are summarised in the following table. The composition of the product in mols %, is given in columns 4, 5 and 6, and the apparent value of

$$K_p = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{HAC}} \times C_{\text{EtOH}}}$$

calculated from the composition of the product is given in column 7.

Expt. No.	Initial mixt. Ester : Water	Rate	Composition of the product in mols %			K <sub>p</sub>	% Conversion
			Ester	Water	Alcohol = Acid		
171	62 : 38	11.3	51.2	27.9	10.45	13.1	78.4
172	64 : 36	9.1	51.6	18.5	9.9	9.8	75.9
173	81 : 19	5.6	72.1	9.2	9.4	8.0	74.0
174	83 : 17	5.5	75.5	8.4	8.1	9.7	75.9

In the last column the apparent equilibrium constants are translated in terms of percentage conversion of equimolecular mixture.

It appears from these results that the equilibrium constant in the vapour phase esterification of acetic acid by methyl alcohol corresponds to 76% conversion of the equimolecular mixtures at 260°, which is the optimum temperature for the silica gel catalyst.

*Esterification of Methyl Alcohol and Acetic Acid over Potassium Alum Catalyst at 230°.*—The same apparatus and materials were used as in our experiments with silica catalysts.

The optimum temperature for the esterification over potassium alum catalyst prepared as described by Jatkar and Watson (*loc. cit.*)

is the same, *viz.*, 230° as has been found for the dehydration of methyl and ethyl alcohols to ethers.

Experiments were made to find out the maximum esterification at various rates and the results are given in the following table. In all the following experiments the initial and the final total acid agreed within experimental error.

Catalyst: Potassium Alum.  
230°.

Expt. No.	Rate	Acid	Ester	% Esterified	Expt. No.	Rate	Acid	Ester	% Esterified
1	12	6.5	14.5	68.1	6	3	10.9	28.2	72.1
2	12	13.8	27.8	66.8	7	3	9.1	27.5	75.1
3	9	13.2	28.3	68.2	8	3	11.1	30.4	73.1
4	6	10.6	27.2	72.0	10	6	10.4	30.6	74.7
5	6	17.1	49.1	74.2	11	6	10.7	30.4	73.8

The above results show that a limit is reached even at high rates unlike the silica catalysts.

In order to duplicate the above values, a fresh sample of the potassium alum catalyst was prepared and put in the apparatus. A mixture of methyl alcohol (35%), acetic acid (63.8%) and water (1.21%) was passed over the fresh catalyst. The results are given in the following table:—

Expt. No.	Rate	Composition of the distillate				K <sub>p</sub>	% Conversion
		Mols Ester	Mols H <sub>2</sub> O	Mols MeOH	Mols Acid		
12	20	35.4	35.8	14.1	14.7	6.1	71.8
13	16	36.6	38.0	12.3	13.3	8.5	74.8
14	10	38.2	37.2	12.2	12.4	9.4	75.8
15	10	37.4	37.7	12.1	12.7	9.1	75.7
16	5	36.8	37.5	12.5	13.2	8.3	74.5
17	5	37.3	37.8	12.1	12.8	9.1	75.4

These results also indicate that the reaction reaches the limit within a few per cent. even at the rates up to 20 c.c. per hour, the maximum conversion being 75.8%.

*Reverse Reaction.*—The study of the hydrolysis of methyl acetate has been made on the same catalyst with the arrangement described in the case of silica catalyst. The lowest value for  $K_p$  was about 7–8.

Expt. No.	Ester : H <sub>2</sub> O	Rate	Mols Ester	Mols H <sub>2</sub> O	Mols MeOH = Acid	$K_p$	% Conversion
24	41 : 59	12	31.2	51.4	8.7	21	88.2
25	46 : 56	8	36.9	44.6	9.2	10	76.0
26	60 : 40	8	49.4	30.3	10.1	14	79.0
27	57 : 43	8	46.7	32.4	10.5	13.7	78.8
30	60 : 40	6	49.9	29.5	10.3	14	79.0
31	61 : 39	6	51.5	29.1	9.7	16	80.0
28	71 : 29	5	58.7	17.3	12.0	7.1	72.6
29	69 : 31	5	56.9	19.7	11.7	8.2	74.0

The following experiments were made by passing over the catalyst a quadruple mixture of ester, water, acid and alcohol corresponding to  $K_p = 8$  at various rates.

Expt. No.	Rate	Passing an equilibrium mixture				$K_p$	% Conversion
		Mols Ester	Mols H <sub>2</sub> O	Mols MeOH	Mols Acid		
		36.7	37.5	12.7	13.1	8	74.0
22	20	38.8	39.5	10.4	11.3	13	78.4
18	12	38.5	39.4	10.9	11.1	12	76.8
19	12	32.6	47.8	10.5	9.2	13	78.4
20	5	36.6	39.9	11.2	12.2	10	76.0
21	5	38.6	37.1	11.2	13.1	9.7	75.9

With potassium alum as catalyst, the maximum conversion of the equimolecular mixtures of methyl alcohol by acetic acid is 75.8% in the direct reaction. This was confirmed by passing equilibrium mixtures over the catalyst.

The results obtained in the present investigation point out an elegant way of preparing methyl acetate on a laboratory scale. The same plant which is used for the production of ethyl ether and ethyl acetate, can be used for the preparation of methyl acetate.

### SUMMARY.

Silica gel has been shown to be a very inefficient catalyst for the vapour phase esterification of acetic acid by methyl alcohol. Activated potassium alum has been found to be far more efficient for this reaction, and has been shown to be quite satisfactory for the study of the equilibrium constant at  $230^{\circ}$ , which corresponds to 75.8% conversion of the equimolecular mixtures, in agreement with the value obtained at  $260^{\circ}$  with silica gel.

In the case of vapour phase esterification of acetic acid by ethyl alcohol, it was shown that there was simultaneous establishment of ether equilibrium at low space velocities. The corresponding side reaction did not occur in the case of mixtures of acetic acid and methyl alcohol, showing the preference of esterification over dehydration of the alcohol.

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