

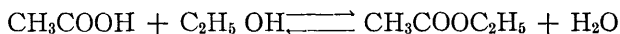
# VAPOR PHASE ESTERIFICATION OVER SODIUM ACID SULFATE<sup>1</sup>

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## INTRODUCTION

The esterification reaction of acetic acid with ethyl alcohol, as shown by the equation,



has long excited the curiosity of chemists and has been studied extensively by both organic and physical chemists. The reaction has been one of the most useful in preparative organic chemistry, a classical example of the law of mass action, and one of the baffling problems in homogeneous catalysis.

Berthelot and St. Gilles (1) obtained experimental results in 1862 from which a value for the liquid equilibrium constant was later determined. The value of 4.0 calculated from their data, is still quoted to students studying the problem of reaction equilibrium, although it is known that this K value will vary depending upon the starting proportions of the reaction mixture.

The vapor phase equilibrium value, unlike the liquid phase "constant," should be very nearly a constant for a given temperature throughout an entire range of possible starting compositions. However, the works of the various investigators have yields results from which a true constant for a given temperature cannot yet be deduced. The principal results on vapor phase esterification are now described.

Edgar and Schuyler (2), in 1924, made the first definite attempt to determine an equilibrium constant for the vapor phase reaction. They analyzed the vapor above a liquid equilibrium mixture of alcohol, acid, ester, and water. Their values varied from 347 to 559 for a vapor phase temperature range of 72.6° to 77.6° C.

In 1928, Swietoslawski and Poznanski (3) repeated this work, but with somewhat greater accuracy. Their average numerical value for K at 75° C. was reported as  $59 \pm 10$ .

Tidwell and Reid (4) published results of esterification experiments, which showed the value of the equilibrium constant increased as the temperature of the reaction mixture decreased. Their runs were made at fifty degree intervals from 150° to 300° C. The experimental data were obtained from equilibrium runs made over silica gel as the catalyst.

In 1932 Essex and Clark (5) determined the equilibrium constant over silica gel at 150°, 165° and 200° C. Their final values for K were arrived at after allowing for association of acetic acid in the vapor state.

The results for the equilibrium constants obtained by Essex and Clark and by Tidwell and Reid are shown in Table I.

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<sup>2</sup>Presented as a thesis in partial fulfillment of the requirements for the Master of Science degree.

TABLE I

T° C.	Essex Clark	Tidwell Reid
150	33.0	30.9
165	26.4	....
200	16.1	24.9
250	....	12.7
300	....	8.9

The values obtained by both sets of investigators check rather well at low temperatures but tend to diverge at high temperatures.

Jatkar and Gajendragad (6), 1937 carried out esterification experiments at 230° C. and 260° C. At 260° C. their K value averaged 10, and at 230° C. the values round ran from 9.9 to 12. These values, when checked with Table I appear to coincide rather favorably.

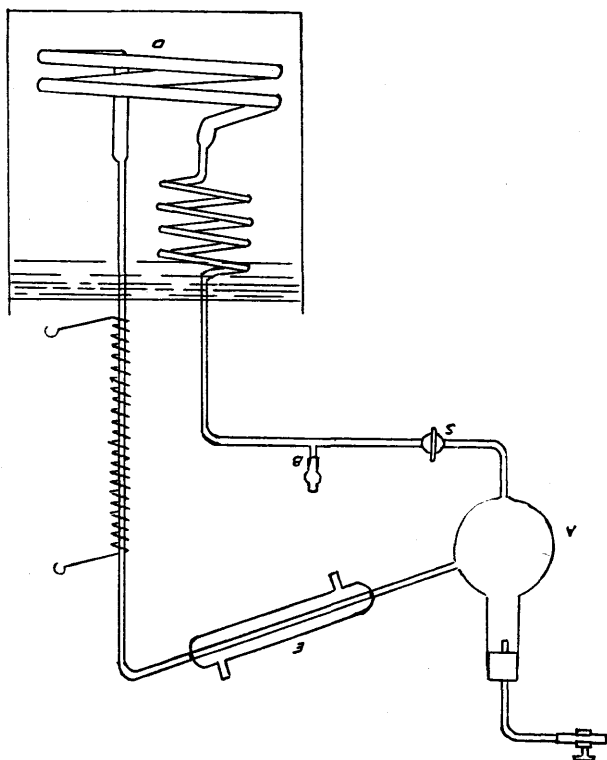


FIG. 1. Equilibrium apparatus.

Reports of vapor phase esterification experiments carried out at 40° C. by Halford and Brundage (7) appeared in 1942. Their final K value of  $122 \pm 3$  was the first to have been calculated from data collected at such a low temperature.

In 1943 Knox and Burbridge (8) reported an equilibrium constant for 125° C. This work was the first to be done on catalytic esterification below 150° C., and the K value so obtained was  $45.7 \pm 1.4$ . The catalyst used was zirconium oxide.

A review of existing literature, then, shows that measurements of a number of the earlier workers produced results which in many cases coincide rather well and appear to have considerable merit for the temperature range in which their investigations were carried out. If these same results are extrapolated to 100° C., the approximate values for the equilibrium expression vary from as low as 45 to as high as 90. This wide range of values indicates the desirability of considerably more work to be done on the problem.

It was the purpose of this work, therefore, to obtain data at 100° C. from which the value of the equilibrium constant could be calculated. The catalytic agent used for the vapor phase runs was sodium acid sulfate.

TABLE II

Esterification sample: ethanol 63.17%, water 31.014%, ethyl acetate 4.154%, acetic acid 1.666%.  
Hydrolysis sample: ethanol 62.67%, water 30.768%, ethyl acetate 6.623%, acetic acid 0.000%.

Equilibrium Data at 100° C.					
Run	Time (hrs.)	Reaction	Wt. % Original Acid	Wt. % Final Acid	K. Value
1	20	E	1.666	.0763	75.26
2	22	E	1.666	.0796	72.08
3	16	E	1.666	.0803	71.47
4	10	H	0.000	.0801	71.84
5	8	H	0.000	.0832	69.24
At 125° C.					
1	9	E	1.666	.1163	48.90
2	8	E	1.666	.1203	47.29
3	5	H	0.000	.1218	48.65
4	6	H	0.000	.1180	48.33

## EXPERIMENTAL WORK

The materials used were commercial 95% ethyl alcohol, glacial acetic acid, anhydrous ethyl acetate, and distilled water. The catalytic agent was suspended on glass beads. The beads were coated with sodium acid sulfate by immersing them in the molten salt.

The apparatus used in this work was patterned after one designed by Knox and Burbridge (9). A diagram of the equipment is shown in Figure 1.

The constant temperature bath consisted of a 15 liter pyrex glass container. The liquid used in the bath was dibutyl phthalate.

The bath was provided with an electric stirrer, and the temperature was thermostatically controlled to within one degree.

The flask "A," the reaction mixture container, was capped with a one-holed rubber stopper from which extended a small piece of glass tubing. The tubing was tipped by a piece of rubber tubing which could be closed by a screw clamp.

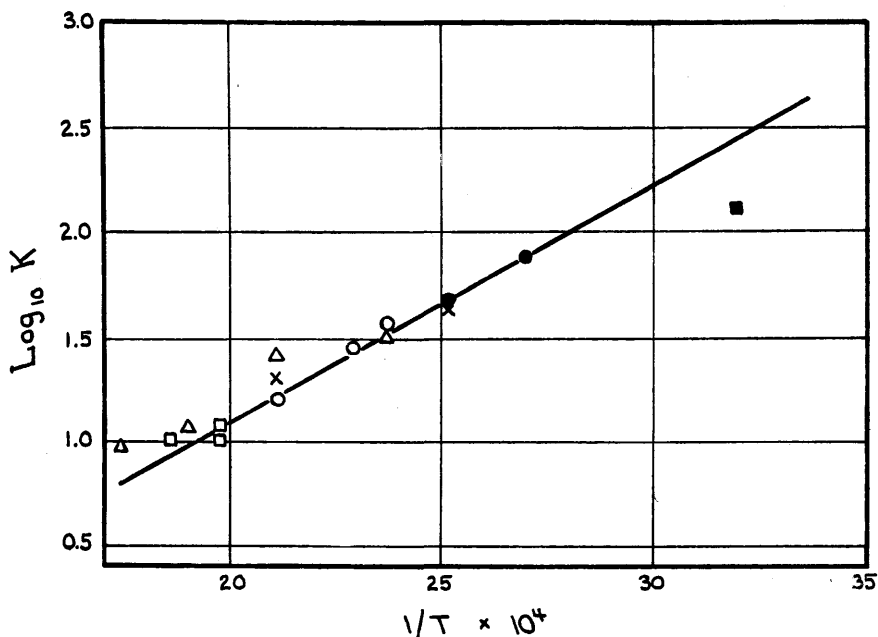
The reaction mixture was allowed to flow slowly through the stopcock "S" into the preheater "C." The sample was here vaporized and allowed to pass into the reaction coil.

This coil was constructed from four feet of twenty millimeter pyrex glass tubing and wound into a continuous coil. This tube contained the catalyst.

From the reaction coil the vapors passed into the condenser "E" and finally back into the flask "A." To prevent excessive condensation of the vapors between the bath and the condenser, the tubing from "D" to "E" was wrapped and heated with No. 20 chromel wire.

Thus the system prepared was a closed one and did afford an opportunity for continuous circulation without the loss of any reactants.

The hydrolysis and esterification samples were prepared by weight and the percentages of acid and ester were checked volumetrically using standard NaOH and standard HCl. The reaction mixtures were stored in an electric refrigerator, and the acid content was checked at intervals to note any change in the sample.



$\Delta$ , Tidwell and Reid;  $\circ$ , Essex and Clark;  $\times$ , Knox and Burbridge;  $\square$ , Jatkar and Gajendragad;  $\blacksquare$ , Halford and Brundage;  $\bullet$ , this work

FIG. 2. Vapor Phase Esterification Equilibrium.

The compositions of the esterification and hydrolysis samples are given in Table II. At the beginning of a run, the sample was introduced into flask "A," and the screw clamp was left slightly open. The stopcock "S" was opened, and the sample was vaporized, catalyzed and condensed. As soon as the first vapors reached the condenser the screw clamp was closed and the reaction mixture allowed to circulate for several hours.

After some time, approximately a one gram sample was pipetted from the reaction mixture, weighed and titrated against N/100 NaOH.

Circulation of the main sample was begun again and continued for at least another four hours. When the acid content became a constant equilibrium was assumed to have been reached.

At 100° C. equilibrium was reached in about twenty hours and the acid content was very near 0.08%; while at 125° C. reaction time was nearer twelve hours and the acid content, 0.12%.

From the data of Table II, and after allowing for the association of acetic acid to the dimer, using experimental results of Ritter and Simon (10), the average K values for the vapor phase esterification equilibrium reaction were found to be  $74.5 \pm 3.3$  at 100° C. and  $48.2 \pm 1.3$  at 125° C.

The results of this investigation are shown on Figure 2 in the form of a plot of the  $\log_{10}K$  against the reciprocal of the absolute temperature. The data here obtained are extrapolated to both higher and lower temperatures and compared with the previous investigations.

From the extrapolation to higher temperatures, it can be seen that all the results of Essex and Clark are closely approximated. At 150° C. our theoretical value checks almost exactly the actual value obtained by Tidwell and Reid. At 250° C., however, our result more nearly checks those of Jatkar and Gajendragad.

When the results of this investigation are extrapolated to a lower temperature; namely, 40° C., our theoretical value diverges sharply from previous data. However, it should be pointed out that we have plotted only average values.

It appears that it would be desirable to obtain more values especially at lower temperatures.

Nevertheless, the close approximation of extrapolated values of this work to experimental values of higher temperature work, makes one feel that the value obtained for the equilibrium constant at 100° C. is a creditable one.

It might also be pointed out that the results of this investigation at 125° C. coincide well with the K value obtained by Knox and Burbridge at the same temperature.

#### SUMMARY

1. The vapor phase esterification reaction for dilute solutions of ethyl acetate and acetic acid in a predominantly alcohol-water solution over sodium acid sulfate has been studied by a static method at 125° C. and 100° C.

2. At 125° C. the K value of  $48.3 \pm 1.2$  was obtained and is in fair agreement with Knox and Burbridge as well as the extrapolated values of earlier workers.

3. At 100° C. the value of  $74.5 \pm 3.3$  was obtained.

4. Sodium acid sulfate was found to be a suitable catalyst at the temperatures at which this work was carried out. Its catalytic action appeared to be much more pronounced at low temperatures than the action of silica gel or zirconium oxide used by some previous investigators.

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