

was 0.15 mv. lower than the average potential of the static junctions, while with the 0.10 *M* solution it was 0.2 mv. higher. These results indicate that saturated potassium chloride does not eliminate the boundary potential against hydrochloric acid solutions, that the remaining potential is different for different concentrations, and that it cannot be assumed that boundaries of different concentrations will respond in the same manner to disturbing influences.

### Summary

1. An apparatus has been developed for the direct comparison of static, flowing, "stopped flowing," and stirred junctions.

2. For concentration cells of 0.10 *M* and 0.01 *M* hydrochloric acid the potential is practically the same for all these types of junction.

3. For the junctions 0.10 *M* HCl / satd. KCl and 0.01 *M* HCl / satd. KCl the potential in each case depends upon the type of junction and the rate of flow, but these two junctions respond in opposite ways to certain treatments.

4. The effective part of this type of flowing junction is that contained in the first three cm. of the horizontal outlet tube.

5. For the systems involving saturated potassium chloride, the potentials with static junction are less empirical than those with flowing, because the variations of the potentials of the former with time are less than the variations of the latter with rate of flow.

ANN ARBOR, MICHIGAN

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SYRACUSE UNIVERSITY]

## THE FREE ENERGY OF FORMATION OF ETHYL ACETATE. EQUILIBRIUM IN THE GASEOUS STATE<sup>1</sup>

BY HARRY ESSEX AND JOSEPH D. CLARK

RECEIVED AUGUST 3, 1931

PUBLISHED APRIL 6, 1932

### Introduction

In this investigation the standard free energy change of the reaction

$$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$$

has been calculated at several temperatures from values of the equilibrium constant of the reaction in the gaseous state, which, together with data already available in the literature, leads to an evaluation of the standard free energy of formation of ethyl acetate.

Sabatier and Mailhe<sup>2</sup>, working with metal oxides, reported that titanium oxide catalyzed only the esterification reaction in a gaseous mixture

<sup>1</sup> Submitted to the Faculty of Syracuse University by Joseph D. Clark in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, January, 1931.

<sup>2</sup> Sabatier and Mailhe, *Compt. rend.*, **152**, 669, 1044 (1911); **150**, 823 (1910); *Ann. chim. phys.*, **20**, 289, 351 (1910).

of an alcohol and an organic acid even at temperatures as high as 300°. With this catalyst, the authors claim to have reached equilibrium for the reaction in the gaseous state proceeding in either direction.<sup>3</sup> Sabatier reports a 70% esterification at 300°, which corresponds to a value of 5.4 for

$$K_p = \frac{P_{(\text{ester})} \times P_{(\text{H}_2\text{O})}}{P_{(\text{acid})} \times P_{(\text{alcohol})}}$$

at this same temperature.

Mailhe, and Mailhe and DeGodon<sup>4</sup> obtained data showing that zirconium oxide was exclusively an esterification catalyst. This conclusion was supported by the researches of Mailhe.<sup>5</sup> In this same paper it was claimed that equilibrium was reached starting from either side and using thoria as a catalyst. Mailhe did not attempt to purify completely his reagents and made no claim to a high degree of accuracy. For purposes of comparison, values of  $K_p$  have been calculated from the concentrations at equilibrium in the separate experiments of Mailhe at the same temperature and found to differ from each other by several hundred per cent. Edgar and Schuyler<sup>6</sup> determined the composition of the vapors above an equilibrium liquid mixture. They found a value of  $K_p$  for the gaseous equilibrium varying from 344 at 52.2° to approximately 500 at 77.6°. No high degree of accuracy was claimed by these authors. Swietoslawski and Poznanski,<sup>7</sup> using the same method but with some changes in technique, found  $K_p$  to have a value of 59.0 and to be independent of temperature.

The results of Milligan, Chappell and Reid,<sup>8</sup> who first used silica gel as a catalyst, show a marked decrease in  $K_p$  with increasing temperature. While the work to be described in the present paper was in progress, Tidwell and Reid<sup>9</sup> presented data for this same reaction showing a decrease in  $K_p$  with increase in temperature, confirming the conclusions of Milligan, Chappell and Reid. Using the same catalyst they obtained the results given in Table I.

TABLE I  
ESTERIFICATION DATA

	Per cent. of esterification			
	150°	200°	250°	300°
From acid side	84.2	82.6	77.7	74.2
From ester side	85.2	84.0	78.5	75.5

<sup>3</sup> Sabatier and Mailhe, *Compt. rend.*, **152**, 358, 949-97 (1911); Sabatier, "La Catalyse en Chimie Organique," C. Beranger, 1922, p. 297, 2d ed.

<sup>4</sup> Mailhe, *Caoutchouc et gutta-percha*, **18**, 10,679 (1921); *Chem. Abstracts*, **15**, 1023; Mailhe and DeGodon, *Bull. soc. chim.*, **29**, 101 (1921).

<sup>5</sup> Mailhe, *J. usines gaz.*, **48**, 17-21 (1924); *Chem. Abstracts*, **18**, 1419 (1924).

<sup>6</sup> Edgar and Schuyler, *THIS JOURNAL*, **46**, 64 (1924).

<sup>7</sup> Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1929); *Chem. Abstracts*, **23**, 2093 (1929).

<sup>8</sup> Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

<sup>9</sup> Tidwell and Reid, *THIS JOURNAL*, **53**, 4353 (1931).

The figures obtained in approaching the equilibrium from opposite directions differ appreciably.

Assuming that the reactants were in the ratio of one mole of acid to one mole of alcohol,  $K_p$  calculated from the average of the limits of esterification from both directions has the values indicated in Table II.

TABLE II  
VALUES OF  $K_p$

Temp., °C.	Ester at equilibrium, %	$K_p$
150	84.7	30.64
200	83.3	24.88
250	78.1	12.75
300	74.8	8.81

According to a recent article by Frolich, Carpenter and Knox,<sup>10</sup> the equilibrium position is at 87.5% of a mole of ethyl acetate at 280°, corresponding to a value of 49 for  $K_p$ , and 88.8% at 300°.

## Experimental Part

### A. Preparation of Pure Reagents

**Alcohol.**—Commercial ethyl alcohol was purified by the method of Brunel.<sup>11</sup> Only that fraction distilling over within 0.1° was accepted for use in this investigation. This purified alcohol had a specific gravity at 25° compared to water at 4° of 0.789305, which corresponds to 99.916% of alcohol. The alcohol was transferred to the pycnometer in an atmosphere of dry nitrogen. The 95.74% alcohol used in making up the reaction mixtures was prepared by dilution with water.

**Acetic Acid.**—The acid used was a product from the General Chemical Company labeled 99.55% acid. The only impurity indicated was water. This was purified by a method outlined in Allen's "Commercial Organic Analysis" (Vol. I, p. 643) under "Acetic Acid." The portion distilling within 1.5° was used. The specific gravity corresponded to 99.96% acid.

**Ethyl Acetate.**—This was a "C. P." product from the Eastman Kodak Company. It was fractionally distilled through a fractionating column, approximately 80% distilling over within a range of 1.0°; specific gravity,  $d_4^{20}$  0.9003.

**Base.**—Barium hydroxide was used to follow the progress of the esterification reaction. It was standardized by weight titration against the 99.96% acetic acid.

**Water.**—Only twice distilled water was used.

**Catalyst.**—The silica gel was the commercial product from the Silica Gel Corporation of Baltimore, Md. It was used without further treatment.

### B. Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. The air-bath was a box 61 × 61 × 122 cm. inside measurements, built from 13-cm. 80% magnesia slabs buffered on the inside by 3.8-cm. Kieselguhr slabs and cemented together by asbestos cement. Heat was supplied by a series of 10-cm. nichrome heaters of the type used in electric radiators, placed in the bottom of the box and as far removed from the reaction tube as the inner space would permit. The temperature was controlled by the volume changes

<sup>10</sup> Frolich, Carpenter and Knox, *THIS JOURNAL*, **52**, 1565 (1930).

<sup>11</sup> Brunel, *ibid.*, **45**, 1334 (1923); **43**, 561 (1921).

of a nitrogen reservoir. Only an approximate automatic control was possible because of barometric changes. For at least one-half hour preceding and throughout any one run the temperature was kept constant to within  $\pm 0.1^\circ$ , manually. The air medium of the bath was kept in circulation by means of a 15-cm. motor-driven fan. Thermometers placed in various parts of the bath in the region of the reaction tube showed a maximum difference of  $0.1^\circ$ .

Equilibrium was determined by a dynamic method. The reactants entered the reaction chamber from bulb "A." To ensure a constant flow through the glass stop-cock regulator a positive gas pressure of about one-third of an atmosphere was maintained above the reaction mixture. Nitrogen, which has no effect on the reactants, was used for this purpose. The reaction mixture was vaporized in a bead-filled preheater, which had the neck and side arm thoroughly insulated to prevent condensation.

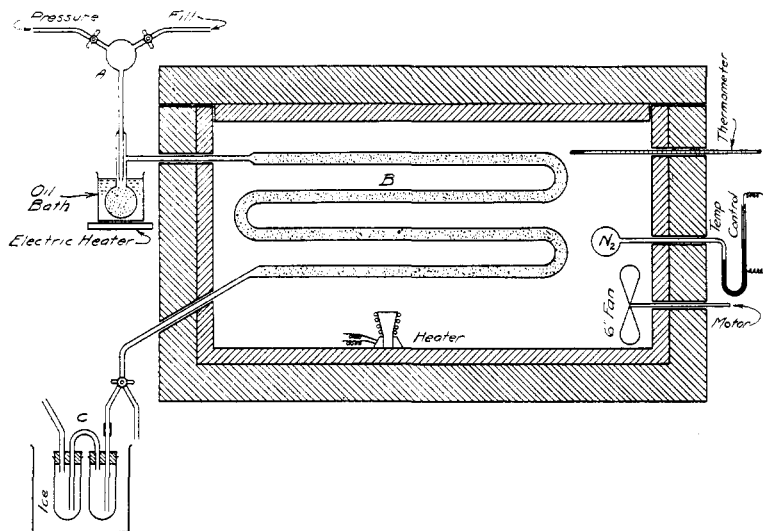


Fig. 1.

The reaction tube "B" was constructed from about 9.5 meters of 18-mm. Pyrex tubing sealed into one continuous coil. The original 1100 g. of silica gel required to fill the tube was used throughout the investigation. The products were collected through a delivery tube in two tared  $3.8 \times 15$  cm. test-tubes in series. The collection tubes were cooled by ice. The collected product, test-tubes and fittings were weighed and the weight of the product determined. The contents were then carefully washed into a beaker and weight-titrated against the standard barium hydroxide solution. The concentration of the other constituents was calculated from the acid concentration of the product and the composition of the reaction mixture. The formation of gaseous products or a positive test for aldehydes was accepted as sufficient evidence of decomposition reactions.

At the beginning of any run or with each change of ratio of the reactants, the gaseous mixture was passed through the reaction tube until the concentration of the acid in the product became constant. In some cases it required two or three days and never less than 400 cc. of the reactants were used for this purpose.

### C. Preliminary Experiments

Before attempting a study of the equilibrium, the stability of the reactants, except water, was tested relative to heat. Each substance, in the gaseous state, was passed

through the reaction chamber, void of catalyst, at a temperature of about 350°. In no case could any decomposition be detected. The maximum temperature was then determined at which a mixture of the reactants could be passed over the catalyst without decomposition. The products were collected in an ice cooled receiver. At about 225° very small amounts of uncondensed gases were produced. These gases consisted of unsaturated compounds, as shown by complete absorption when tested with bromine water or fuming sulfuric acid. At higher temperatures the presence of aldehydes was indicated by the ammoniacal silver oxide and sodium bisulfite tests. Whenever decomposition occurred it was noted that carbon was deposited upon the catalyst. This deposited carbon seemed further to promote decomposition. It was removed from the catalyst by treatment with oxygen at a temperature of about 300° after all the reaction gases had been expelled by air. The oxygen was then displaced and the catalyst thoroughly saturated with nitrogen. This cleaning method was satisfactory and apparently had no detrimental effect upon the catalytic action of the silica gel.

#### D. The Equilibrium Measurements

The equilibrium was determined at three temperatures, 150, 165 and 200°. At each temperature, after an approximate determination of the equilibrium position by preliminary experiments, carefully controlled runs were made with (a) a reaction mixture richer in alcohol and acid than the equilibrium mixture, (b) a reaction mixture richer in ester and water than the equilibrium mixture and (c) a reaction mixture having exactly the equilibrium concentrations as calculated from the average composition of the products of the runs (a) and (b). Each reaction mixture was made up in proportions which would be reached at some stage in the reaction

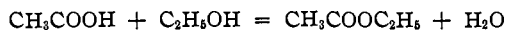


TABLE III

## RESULTS OF EXPERIMENTS

Reaction mixture ratios  $\text{CH}_3\text{COOH}$ , 0.16 mole;  $\text{C}_2\text{H}_5\text{OH}$ , 0.16 mole;  $\text{CH}_3\text{COOC}_2\text{H}_5$ , 0.84 mole;  $\text{H}_2\text{O}$ , 0.84 mole. 150°C. Weight per cent. of acid in the reaction mixture, 9.05.

Duration of run, min.	Wt. of product collected, g.	Wt. of base required to neutralize product, g.	Wt. % of acid in product
60	11.1526	45.9595	8.78
60	8.8483	36.1264	8.70
120	5.0493	20.7048	8.74
240	10.2164	41.4298	8.65
90	3.9230	15.9315	8.66
210	9.0407	36.8308	8.69
240	6.4205	26.0948	8.67
135	4.3924	18.1483	8.81
120	6.1928	25.6064	8.83
120	6.1619	25.3752	8.87
240	10.1200	41.6031	8.76
150	14.4505	59.4433	8.77

Average, 8.74

$$K_a \left( K_a = \frac{a(\text{ester}) a(\text{H}_2\text{O})}{a(\text{acid}) a(\text{alcohol})} \right) \text{ for average} = 33.69$$

if the initial mixture contained alcohol and acid alone in the proportion 1 mole of alcohol to 1 mole of acid. Runs were made over a considerable range of rates of flow with each reaction mixture at each temperature. The results of the run at 150° from the acid rich side are presented in detail in Table III. The results of the runs at this temperature and at 165 and 200° both of which were determined with a precision equal to that at 150, are presented in summary in Table IV.

TABLE IV

Temp., °C.	SUMMARIES OF RESULTS		$K_a$
	Wt. per cent. of acid in reaction mixture	Average wt. of acid in product	
150	8.48	8.75	33.61
	8.77	8.76	33.55
	9.05	8.74	33.69
165	9.05	9.56	26.36
	9.62	9.55	26.39
	10.18	9.55	26.39
200	8.48	11.51	15.98
	11.31	11.47	16.10
	14.14	11.46	16.13

The probable error in the determination of the percentage of acid at each temperature was calculated by the method of least squares.

The results of all the equilibrium determinations have been summarized in Table V. The probable errors in the average percentage of esterification are tabulated in column 3 of Table V.

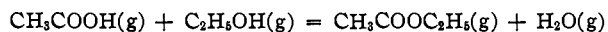
TABLE V

Temp., °C.	PROBABLE ERRORS		Average values of $K_a$
	Average percentage of acid in products	Probable error in data of column 2	
150	8.75	0.0107	33.62
165	9.55	.0056	26.38
200	11.48	.0067	16.07

## Calculations

### A. Molal Composition of the Equilibrium Mixtures

1. **The Number of Moles of Each Constituent.**—At the temperatures at which measurements were made, no products were detected other than those entering into the reaction



The molal composition of the gaseous mixture leaving the reaction tube was calculated from the composition of the entering mixture and the acid in the product.

For example, in one experiment at 150° the mixture entering the reaction

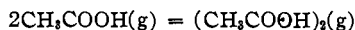
tube contained 9.05% of acetic acid, corresponding to the following number of formula weights of each constituent per 100 g. of the mixture

Acid	0.15080	Ester	0.79165
Alcohol	.15080	Water	.79165

This mixture was passed over the heated catalyst. The final product, after constancy in the acid percentage had been reached, analyzed 8.74% of acetic acid. This shows a shift of the equilibrium in the direction of ester and water formation, and corresponds to a decrease of 0.0052355 formula weights of acid and of alcohol per 100 g. and a like increase in the number of formula weights of ester and water. Therefore, in this final product, there were 0.145565 formula weights of acid and alcohol, and 0.7969 formula weights of ester and water. For alcohol, ester and water, the formula weights are the number of moles and these are listed in Table IX, in the columns headed  $n_3$ ,  $n_4$  and  $n_5$ , respectively.

An examination of the volume-pressure data of Ramsay and Young<sup>12</sup> indicates that even at a temperature of 184.1° and 0.12 atmosphere, acetic acid exists partly as double molecules. At lower temperatures, even higher complexity is indicated.

The association constant of the reaction



is given by the relation

$$K_x = \frac{P_{(\text{CH}_3\text{COOH})_2}}{P_{(\text{CH}_3\text{COOH})}^2} \quad (1)$$

where  $P_{(\text{CH}_3\text{COOH})_2}$  is the partial pressure of the double molecules of acetic acid, and  $P_{(\text{CH}_3\text{COOH})}$  is the partial pressure of the single molecules, and may be calculated from the data of Ramsay and Young.<sup>12</sup>

The number of moles of  $\text{CH}_3\text{COOH}$  ( $n_1$ ) and  $(\text{CH}_3\text{COOH})_2$  ( $n_2$ ) per 100 g. of our reaction product may be calculated from this  $K_x$  and the number of moles of alcohol ( $n_3$ ), ethyl acetate ( $n_4$ ), water ( $n_5$ ), and the number of formula weights of acetic acid ( $w$ ). The partial pressures of  $(\text{CH}_3\text{COOH})_2$  and  $\text{CH}_3\text{COOH}$  in our products are given, respectively, by the equations

$$P_{(\text{CH}_3\text{COOH})_2} = \frac{n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (2)$$

and

$$P_{(\text{CH}_3\text{COOH})} = \frac{n_1}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (3)$$

1 being the total pressure in atmospheres of these experiments. That is, each partial pressure is the product of the mole fraction and the total pressure. Substituting these values into equation 1

$$K_x = \frac{n_2(n_1 + n_2 + n_3 + n_4 + n_5)}{n_1^2} \quad (4)$$

<sup>12</sup> Ramsay and Young, *J. Chem. Soc.*, **49**, 790 (1886); "International Critical Tables," Vol. III, p. 437.

If  $G$  is the weight of acetic acid in the equilibrium products, then  $G = 60.03n_1 + 120.06n_2$  and

$$w = \frac{G}{60.03} = n_1 + 2n_2$$

or

$$n_2 = \frac{w - n_1}{2} \quad (5)$$

Upon substituting the value of  $n_2$  (equation 5) into equation 4

$$K_x = \frac{\frac{w - n_1}{2} \left( n_1 + \frac{w - n_1}{2} + n_3 + n_4 + n_5 \right)}{n_1^2}$$

from which

$$n_1 = \pm \sqrt{\frac{2w}{4K_x + 1} \left( \frac{w}{2} + n_3 + n_4 + n_5 \right) + \left( \frac{n_3 + n_4 + n_5}{4K_x + 1} \right)^2} - \frac{n_3 + n_4 + n_5}{4K_x + 1} \quad (6)$$

In order that  $n_1$  be positive, the sign preceding the square root must be positive. This expression (equation 6) may be used to find the number of single moles of acetic acid ( $n_1$ ) in the equilibrium mixture from its percentage composition. The number of double moles of acetic acid ( $n_2$ ) may be obtained by substituting the numerical value of  $n_1$  into equation 5.

**2. Evaluation of  $K_x$  at the Temperatures of the Experiments.**—The pressure-volume data for acetic acid of Table VI were taken from "International Critical Tables."<sup>12</sup> In Table VI,  $P$  is expressed in atmospheres,  $V$  in liters per gram, and  $T$  in degrees absolute.

TABLE VI

$T$ .....	457.2	391.1	351.5
$PV$ .....	0.605	0.436	0.302

Let  $M$  equal the average molecular weight. Then

$$M = \frac{RT}{P\bar{V}} \quad (7)$$

and for the data at  $T = 457.2$ ,  $M = 62.05$ , the molecular weight of the acetic acid.

If  $\alpha$  represents the degree of dissociation of gaseous acetic acid double molecules, and  $M_0$  the molecular weight of the double molecules, then

$$\alpha = \frac{M_0 - M}{M} \quad (8)$$

or, by substitution

$$\alpha = \frac{120.06 - 62.05}{62.05} = 0.9355$$

That is, at 457.2°K. and 0.12 atmosphere  $(\text{CH}_3\text{COOH})_2$  is 93.55% dissociated.

The equilibrium constant for the reaction





is related to the degree of dissociation by the expression

$$K_x = \frac{1 - \alpha^2}{4\alpha^2 P} \quad (9)$$

from which

$$K_x = 0.303 \text{ at } T = 457.2^\circ\text{K.}$$

In a similar manner  $K_x$ , at two additional temperatures, was calculated. The values of these are presented in Table VII.

TABLE VII

$T$ .....	457.2	391.1	351.5
$PV$ .....	0.605	0.436	0.302
$M$ .....	62.05	73.64	95.57
$\alpha$ .....	0.9347	0.6301	0.2562
$K_x$ .....	.303	3.164	29.66

From these values,  $K_x$  is given as a function of temperature by the relation (throughout this paper,  $\ln = \log_e$ , while  $\log = \log_{10}$ )

$$\log K_x = \frac{8082}{T} + 29.12 \log T - 95.653 \quad (10)$$

Substituting for  $T$  the desired temperature and solving for  $K_x$  the results of Table VIII were computed.

TABLE VIII

$T$ .....	423.1	438.1	473.1
$K_x$ .....	0.8512	0.5224	0.2104

The values of  $K_x$  and  $n_1$  calculated from equation 6,  $n_2$  calculated from equation 5, and  $n_3$ ,  $n_4$  and  $n_5$  are listed in Table IX.

TABLE IX

$T$	$K_x$	$w$	$n_1$	$n_2$	$n_3$	$n_4$	$n_5$
423.1	0.8512	0.145898	0.1300	0.0080	0.1459	0.7966	0.7966
		.145731	.1303	.0077	.1457	.7968	.7968
		.145565	.1302	.0077	.1456	.7968	.7968
438.1	.5224	.15906	.1470	.0060	.1591	.7834	.7834
		.15922	.1472	.0060	.1592	.7833	.7833
		.15906	.1470	.0060	.1591	.7834	.7834
473.1	.2104	.19170	.1814	.0038	.1917	.7508	.7508
		.19103	.1833	.0039	.1901	.7515	.7515
		.19087	.1834	.0037	.1909	.7516	.7516

**B. Activities of the Constituents of the Mixture at Equilibrium.**—For the esterification reaction under consideration the activity equilibrium constant  $K_{(a)}$  is

$$K_{(a)} = \frac{a_4 \times a_5}{a_1 \times a_3} \quad (11)$$

in which  $a_1$ ,  $a_3$ , etc., are the activities of the acid, alcohol, ester and water, respectively, in the equilibrium mixture.

At the low total pressure of these experiments, namely, one atmosphere, and the low partial pressure of the several constituents of the resulting mixture at equilibrium, it is justifiable to substitute for the activities of the alcohol, ester and water in the gaseous mixture their mole fractions, and equation 11 becomes

$$K_{(a)} = \frac{N_4 \times N_5}{a_1 \times N_3} \quad (12)$$

The results of Gibson and Sosnick<sup>13</sup> support this assumption. For mixtures of ethylene and argon, the experimental data used by these writers indicate practical identity of fugacity and mole fraction at one atmosphere of pressure. The assumption is further justified by the experimental results obtained by Lurie and Gillespie<sup>14</sup> for mixtures of ammonia and nitrogen.

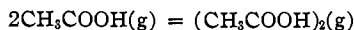
These mole fractions are

$$N_3 = \frac{n_3}{n_1 + n_2 + n_3 + n_4 + n_5}$$

$$N_4 = \frac{n_4}{n_1 + n_2 + n_3 + n_4 + n_5} \text{ etc.}$$

The activity or fugacity of the acetic acid in the equilibrium mixture may be calculated in the following manner.

For the reaction



from equation 9

$$\alpha = \left( \frac{1}{4K_x P + 1} \right)^{1/2} \quad (13)$$

in which  $P$  is the total pressure of the acetic acid. For brevity during this derivation,  $K_x$  will be designated simply as  $K$ .

For a formula weight of acetic acid vapor

$$PV = \frac{1 + \alpha}{2} RT$$

Combining this with equation 13

$$V = \frac{RT}{2P} + \frac{1}{2} \left( \frac{1}{4KP + 1} \right)^{1/2} \frac{RT}{P} \quad (14)$$

Substituting the value of  $V$  from equation 14 into the relation

$$\int RT \, d \ln f = \int V \, dP$$

then

$$\int RT \, d \ln f = \int \frac{RT}{2P} \, dP + \frac{RT}{2} \int \left( \frac{1}{4KP + 1} \right)^{1/2} \frac{dP}{P} \quad (15)$$

which on integration between the very low pressure  $P^*$  and  $P$  gives

$$RT \ln f - RT \ln f^* = \frac{RT}{2} \ln P - \frac{RT}{2} \ln P^* + \frac{RT}{2} \ln \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]} - \frac{RT}{2} \ln \frac{[(4KP^* + 1)^{1/2} - 1]}{[(4KP^* + 1)^{1/2} + 1]} \quad (16)$$

<sup>13</sup> Gibson and Sosnick, THIS JOURNAL, 49, 2172 (1927).

<sup>14</sup> Lurie and Gillespie, *ibid.*, 49, 1146 (1927).

At the very low pressure  $P^*$ ,  $4KP^*$  is always less than unity, and  $(1 + 4KP^*)^{1/2}$  may be expanded by the binomial theorem, becoming  $(1 + 2KP^*)$  and

$$\ln f = \frac{1}{2} \ln \frac{P}{K} \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]} \quad (17)$$

In equation 17 (Note.—Although equation 17 was derived for the association of gaseous acetic acid, it is a perfectly general equation, applicable to any simple association of the type, double molecules in equilibrium with single molecules, and may be used to calculate the fugacity of such a gas at any pressure from the association constant),  $K$  is the quantity previously indicated by  $K_x$ . The fugacity of the acetic acid gas in the equilibrium mixtures of these experiments may be calculated from equation 17 by substituting for  $K$  the association constant of acetic acid at the temperature of the experiment and for  $P$  the partial pressure of the acetic acid gas, which is equal to the sum of the partial pressures of the single and double molecules, and given by the expression

$$P_{(\text{acid})} = \frac{n_1 + n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (18)$$

The values of  $P_{(\text{acid})}$  and  $K_x$  of Table X, when substituted into equation 17, give the values for the fugacity of acetic acid,  $f_{(\text{acid})}$ , listed in this same table.

TABLE X

$T$	$K_x$	$P_{(\text{acid})}$	$f_{(\text{acid})}$	$N_3$	$N_4$	$N_5$	$K_a$	Average $K_a$	$\Delta F^\circ$ from $K_a$
423.1	0.8512	0.0735	0.0691	0.07765	0.4242	0.4242	33.55		
		.0735	.0691	.07760	.4245	.4245	33.61	33.62	-2957.4
		.0734	.0690	.07755	.4245	.4245	33.69		
438.1	.5224	.0814	.0778	.08462	.4168	.4168	26.39		
		.0815	.0779	.08468	.4169	.4169	26.36	26.38	-2851.3
		.0814	.0778	.08462	.4168	.4168	26.39		
473.1	.2104	.0999	.0979	.1019	.3992	.3992	15.98		
		.0996	.0976	.1016	.3996	.3996	16.10	16.07	-2612.4
		.0995	.0975	.1015	.3995	.3995	16.13		

### C. Equilibrium Constant and Standard Free Energy Change of the Gaseous Reaction

**Heat of Gaseous Reaction.**—At any temperature, the standard free energy change,  $\Delta F^\circ$ , of a reaction is related to the activity equilibrium constant by the equation

$$\Delta F^\circ = -RT \ln K_a \quad (19)$$

By substituting the numerical values of  $K_a$  and the corresponding temperatures, the values of  $\Delta F^\circ$  listed in Table X were calculated.

The maximum variation in the  $\Delta F^\circ$  values for any one temperature is 13 calories.

Expressing  $\Delta F^\circ$  as a function of temperature by means of

$$\Delta F^\circ = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT \tag{20}$$

and solving three simultaneous equations involving the values of  $\Delta F^\circ$  from the experimentally determined equilibrium constants, the following equation was obtained

$$\Delta F^\circ = -8385 - 5.06 T \ln T + 46.70T \tag{21}$$

From equation 21,  $\Delta F^\circ_{(298.1)}$  equals  $-3975.1$  calories, or  $K_a$  equals 817.3.

The heat of the reaction,  $\Delta H$ , may be calculated by plotting  $R \ln K_a$  against  $1/T$ . This has been done in a curve of Fig. 2. The individual

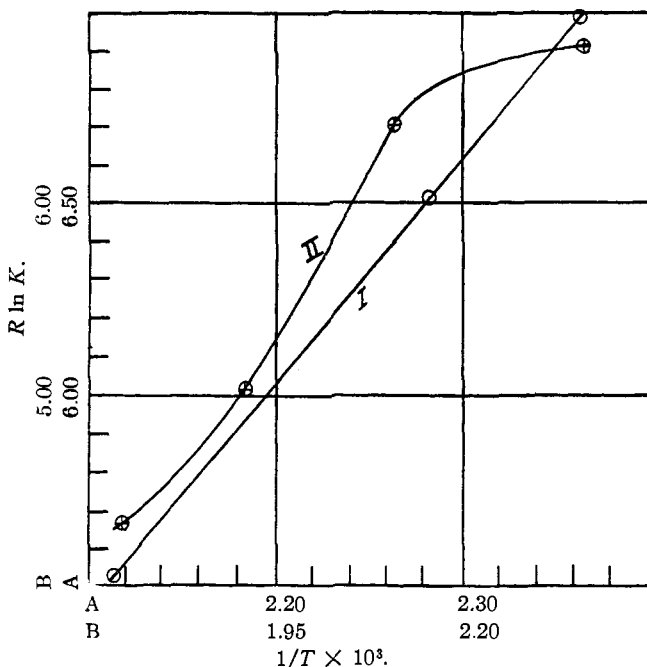


Fig. 2.—Curve I, A axes. Curve II, B axes.

points fall upon a curve (Curve I) which is very nearly a straight line, showing that the heat of the reaction is practically independent of the temperature. The negative values of the slope of the curve,  $\Delta H$ , at different temperatures are listed.

Temperature, °C.....	157.5	182.5
$\Delta H$ in calories.....	-5935.3	-5825.0

A similar curve constructed from the results of Tidwell and Reid (Curve II), exhibits double flexure. On substituting the previously determined values  $\Delta H_0$  and  $\Delta \Gamma_0$  into the integrated form of Kirchhoff's equation

$$\Delta H_{(298.1^\circ)} = -6716.4 \text{ calories}$$

### D. Standard Free Energy Change on Vaporization of the Liquid Constituents

**Heats of Vaporization.**—The vapor pressure data of Table XI are taken from the Critical Tables.<sup>15</sup>

<i>T</i>	Vapor pressure for alcohol, mm.	Vapor pressure for ethyl acetate, mm.
293.1	43.9	72.8
303.1	78.8	118.7
313.1	135.3	186.3

From each vapor pressure the standard free energy change on vaporization was calculated from the relation

$$\Delta F^\circ = -RT \ln P$$

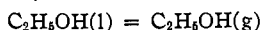
From the three values of  $\Delta F^\circ$  obtained in this manner for the vaporization of each liquid, the constants  $\Delta H_0$ ,  $\Delta \Gamma_0$ , and  $I$  were found by solving the three equations of the form

$$\Delta F^\circ = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT \quad (22)$$

for the unknowns. The standard free energy change on vaporization at 298.1°K. was then calculated from equation 22 and the heat of vaporization at the same temperature from the constants  $\Delta H_0$  and  $\Delta \Gamma_0$  and the equation

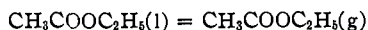
$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T$$

For alcohol, the values of the constants are:  $\Delta H_0 = 14502.8$ ;  $\Delta \Gamma_0 = -13.95$ ; and  $I = -123.067$ ; and for the reaction



$$\Delta F_{(298.1)}^\circ = 1513.5 \text{ cal. and } \Delta H_{(298.1)} = 10,344.3 \text{ cal.}$$

For ethyl acetate, the values of the constants are:  $\Delta H_0 = 13692.2$ ;  $\Delta \Gamma_0 = -16.833$ ; and  $I = -137.68$ . And for the reaction



$$\Delta F_{(298.1)}^\circ = 1244.2 \text{ cal. and } \Delta H_{(298.1)} = 8674.3 \text{ cal.}$$

For the reaction



the standard free energy change and heat of vaporization were taken directly from the Critical Tables, and are:  $\Delta F_{(298.1)}^\circ = 2053 \text{ cal.}$ ;  $H_{(298.1)} = 10,450 \text{ cal.}$

Saturated acetic acid vapor is highly associated at 298.1°K. Its vapor pressure therefore cannot be substituted for its activity. Neither can its fugacity or activity be calculated by equations 8, 9 and 17, nor by the extrapolation equation 10, because these methods are justified if the acetic acid vapor contains only double and single molecules. The vapor density of saturated acetic acid vapor at 298.1°K. is sufficiently high that molecules

<sup>15</sup> "International Critical Tables," Vol. III, pp. 217, 219.

of higher complexity than that of double molecules may be present in considerable concentration.

The fugacity of the saturated acetic acid vapor at 298.1°K. was finally determined by an indirect method. The fugacity was first calculated at the three temperatures, 351.5, 378.2 and 406.0°K., in the following manner: using  $P$ - $V$ - $T$  data of Ramsay and Young,<sup>12</sup> the fugacity of acetic acid vapor at each of these temperatures was calculated at the respective pressures of 0.1200 atmosphere, 0.1238 atmosphere, and 0.1338 atmosphere by equation 17 and the fugacity of saturation from the relation

$$\log f_{p_2} = \frac{A}{2.303 RT} + \log f_{p_1}$$

in which  $f_{p_2}$  is the fugacity at the saturation pressure at the temperature  $T$ ,  $f_{p_1}$  the fugacity at the lower pressure at which it was determined by equation 17.  $A$  is the area under the  $P$ - $V$  curve from  $P_1$  to  $P_2$ .

This method should give the correct fugacity of the saturated vapor even though molecules of high complexity are present in the saturated vapor, provided that single and double molecules only are present at the lower pressure  $P_1$ . In each case the density of the gas at  $P_1$  was sufficiently low to indicate that this was probably true. The lowest pressures given in the data of Ramsay and Young were not picked for  $P_1$  because of the apparently large experimental errors involved in the density measurements at these very low pressures. The data and results of these calculations are presented in Table XII.

TABLE XII

$T$ , °K.	$P_1$ , atm.	$P_2$ , atm.	$K_x$	$A$ , liter-atm.	$f_{p_1}$	$f_{p_2}$
351.5	0.1200	0.2500	29.66	12.54	0.048945	0.0756
378.2	.1238	.6775	6.23	36.55	.081956	.2659
406.0	.1338	1.540	1.567	56.97	.11359	.6273

From the values of the fugacity of the saturated vapors at the three temperatures, the standard free energy change on vaporization was calculated from

$$\Delta F^\circ = -RT \ln f$$

The values obtained are:  $\Delta F_{(406.0)}^\circ = 376.5$ ;  $\Delta F_{(378.2)}^\circ = 996.2$   $\Delta F_{(351.5)}^\circ = 1804.9$ .

$$\Delta F_{(406.0)}^\circ = 376.5; \Delta F_{(378.2)}^\circ = 996.2 \Delta F_{(351.5)}^\circ = 1804.9$$

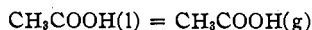
which, upon substitution in the relation

$$\Delta F^\circ = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT$$

gives the values of the constants indicated by

$$\Delta F^\circ = 55,071 + 116.671T \ln T - 835.6$$

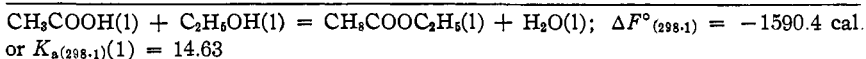
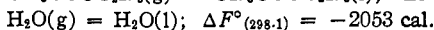
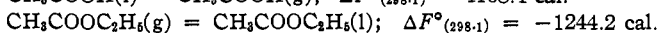
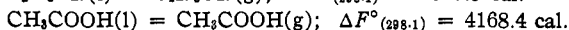
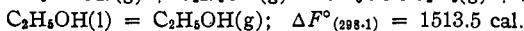
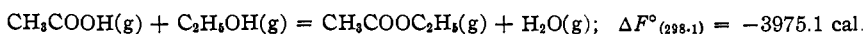
from which, for the reaction



$$\Delta F_{(298.1)}^\circ = 4168.4 \text{ cal. and } \Delta H_{(298.1)}^\circ = 20291.4 \text{ cal.}$$

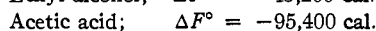
### E. Standard Free Energy Change of the Liquid Reaction. The Free Energy of Formation of Ethyl Acetate

(1) **Standard Free Energy Change of the Liquid Reaction.**—By combining algebraically the vaporization equation of each pure constituent and the esterification reaction in the gaseous state, the standard free energy change for the esterification reaction in the liquid state may be calculated.

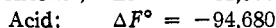
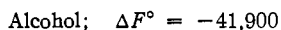


$K_a$ , the true activity ratio, may be quite different from the concentration ratio,  $K_c$ . That they are not identical for this reaction is shown by the experimental results of Poznanski<sup>16</sup> and Schwab.<sup>17</sup> Poznanski, by varying the concentration of his reactants, found that for this reaction  $K_c$  varied from 2.45 to 4.73. Schwab found  $K_c$  to vary between 1.0 and 6.8.

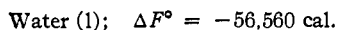
(2) **The Free Energy of Formation of Ethyl Acetate.**—From heat capacity measurements at low temperatures, Parks, Kelley and Huffman<sup>18</sup> have computed, with the aid of the third law of thermodynamics, the standard free energy of formation of the following substances at 298.1°K. to be



Allowing for the new value of the entropy of hydrogen, 31.23, as computed by Giauque,<sup>19</sup> these standard free energies of formation become:



The standard free energy of formation of water at 298.1°K. has been calculated by Lewis and Randall<sup>20</sup> and found to be



Using these values the standard free energy of formation of the ester was calculated to be  $-81,610.4$  calories at 298.1°K.

### F. Heat of the Liquid Reaction

The heat of the reaction in the liquid state was obtained at 25° from the heats of vaporization of the various constituents as previously cal-

<sup>16</sup> Poznanski, *Chem. Abstracts*, **23**, 1559 (1922).

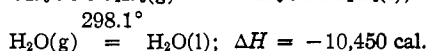
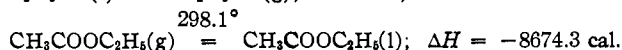
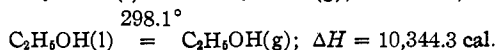
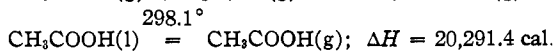
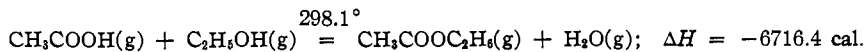
<sup>17</sup> Schwab, *Rec. trav. chim.*, **2**, 46 (1883).

<sup>18</sup> Parks, Kelley and Huffman, *THIS JOURNAL*, **51**, 1969 (1929).

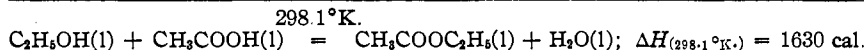
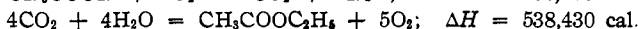
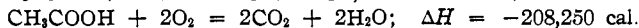
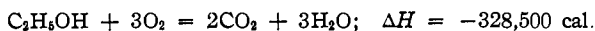
<sup>19</sup> Giauque, *ibid.*, **52**, 4816 (1930).

<sup>20</sup> Lewis and Randall, "Thermodynamics," p. 485.

culated, and the  $\Delta H$  for the reaction taking place in the gaseous state. Combining these algebraically



Kharasch<sup>21</sup> made a general and critical review of the data to be found in the literature for heats of combustion. By using the data of his choice, the heat of the esterification reaction in the liquid state was calculated, as follows



Kharasch estimated that the figures to be found in the literature for the heats of combustion may be in error by from 1.0 to 1.5%. It is to be noted that the value of the heat of the esterification reaction calculated from the heats of combustion of the several constituents of the reaction agrees with the heat of the reaction calculated from the equilibrium constants determined in this work, within the 1.0% error involved in the heat of combustion data.

### G. The Entropy of Ethyl Acetate

Because of the one per cent. error that may exist in the determined value of the heat of combustion of ethyl acetate, the entropy of ethyl acetate calculated by means of the equation

$$\Delta F^\circ = \Delta H - T\Delta S$$

can be considered as no more than an approximation. Accepting 112,500 calories as the heat of formation of ethyl acetate

$$\Delta S_{(298.1^\circ)} = -96.85 \text{ calories}$$

and

$$S_{(298.1^\circ)} = 81.27$$

### Summary

1. Equilibrium has been reached in the gaseous phase for the system: acetic acid, ethyl alcohol, ethyl acetate and water, approaching it by a

<sup>21</sup> Kharasch, *Bur. Standards J. Research*, **2**, 359 (1929).



dynamic method from both sides at the three temperatures, 423°K., 438°K. and 473°K.

2. The activity ratio  $K_a$  has been calculated for the gaseous state equilibrium to be

Absolute temp., °K.....	298.1	298.1	423.1	438.1	473.1
State.....	Liquid	Gas	Gas	Gas	Gas
$K_a$ .....	14.63	817.3	33.62	26.38	16.07

3. The standard free energy change for the esterification reaction calculated from the determined activity ratios is

Absolute temp., °K.....	298.1	298.1	423.1	438.1	473.1
State.....	Liquid	Gas	Gas	Gas	Gas
$\Delta F^\circ$ in cal.....	-1590.4	-3975.1	-2957.4	-2851.3	-2612.4

The standard free energy of formation of ethyl acetate in the liquid state at 298.1°K. is found to be -81,610.4 calories.

4. From the curve for the change of  $K_a$  with temperature, the heat of the esterification reaction has been calculated for the gaseous state at two high temperatures. For the temperature of 298.1°K. it was calculated from Kirchhoff's equation for the gaseous state and from the vapor pressures and heat of the gaseous reaction for the liquid state. The results are

Absolute temp., °K.....	298.1	298.1	430.5	455.5
State.....	Liquid	Gas	Gas	Gas
Heat of the reaction, cal.	4795.0	-6716.4	-5935.3	-5825.0

5. The equation

$$\ln f = \frac{1}{2} \ln \frac{P}{K} \frac{[(4KP + 1)^{1/2} - 1]}{[(4KP + 1)^{1/2} + 1]}$$

has been developed for the calculation of the fugacity of a gas which is partially associated as double molecules.

SYRACUSE, NEW YORK