scopic analysis the fraction consists of: 65% 2,5-dimethyl-hexane, 15% 2,2,4-trimethylpentane, 5% 2,2,3-trimethyl-pentane, 15% unknown octanes. *Fraction 23*, b. p. 114–115° (742 mm.), $n^{20}D$ 1.4021, d^{20}_4 0.7124. The Raman spectroscopic analysis shows that it consists chiefly of 2,3,4-trimethylpentane.

Isobutane–Propene.—The reaction was made at −30° and under conditions similar to those described in detail for the isobutane–*n*-butene alkylation. The amount of aluminum chloride used and the feed rate of the hydrocarbons and the hydrogen chloride were the same. The concentration of propene in isobutane was 23% on molar basis. The contact time of the hydrocarbons with aluminum chloride was of the order of four minutes. In total 3230 cc. of liquefied gaseous hydrocarbons was contacted with the 15 g. of aluminum chloride; even at the end of that period the catalyst was still active. Six hundred and fifty cc. of liquid product was obtained which contained 42% of heptanes and 20% decanes. Ninety per cent. of the total product distilled below 220°. The liquid product was stable toward a nitrating mixture, indicating the absence of olefinic hydrocarbons. The exit gases did not contain any unreacted propene.

The heptanes were redistilled on a 20 theoretical plate column; 89% of product distilled from 84 to 89°. The following fractions were analyzed. *Fraction 4*, b. p. 86°; $n^{20}D$ 1.3883, d^{20}_4 0.6865. Raman spectroscopic analysis: 50% 2,4-dimethylpentane; 50% 2,3-dimethylpentane.

Fraction 11, b. p. 88–89°, $n^{20}D$ 1.3908, d^{20}_4 0.6921. *Analysis.* Found: C, 83.60; H, 16.20. Calcd. for C_7H_{16}: C, 83.90; H, 16.10. Raman spectroscopic analysis: 10% 2,4-dimethylpentane, 90% 2,3-dimethylpentane.

The decanes were redistilled; 92% of the product distilled at 150 to 154°: *Fraction 2*, b. p. 150–151°, $n^{20}D$ 1.4099, d^{20}_4 0.7302. *Fraction 6*, b. p. 153°, $n^{20}D$ 1.4112, d^{20}_4 0.7322. *Analysis.* Found: C, 84.25; H, 15.71. Calcd. for $C_{10}H_{22}$: C, 84.40; H, 15.60.

Summary

The reaction between isobutane and olefins at low temperature was studied. Isobutane reacts with propene in the presence of aluminum chloride–hydrogen chloride catalyst at −30°, yielding 42% of heptanes composed of 2,3- and 2,4-dimethylpentane.

Isobutane and *n*-butene under similar conditions yield 60% of octanes of which the following were identified by Raman spectroscopic analyses: 2,2,4-, 2,2,3-, 2,3,4-trimethylpentane and 2,5-dimethylhexane.

The Vapor Phase Esterification Equilibrium*

BY J. O. HALFORD AND DONALD BRUNDAGE

Studies[1] of the equilibrium in the reaction

$$CH_3COOH(g) + C_2H_5OH(g) = CH_3COOC_2H_5(g) + H_2O(g) \quad (1)$$

conducted with the aid of catalysts at 150 to 300° have yielded widely divergent results which could not be extrapolated to give reasonable values of the equilibrium constant at room temperature. The data of Jatkar and Gajendragad appear to be the most reliable. At lower temperatures, the distillation method of Edgar and Schuyler[2] has been improved by Swietoslawski and Poznanski[3] and further refined by Salcewicz,[4] who obtained uncorrected constants of 41 at 75.9° and 39 at 73.7°, using vapor samples containing acetic acid in apparent mole fractions of 0.0213 and 0.0033,

respectively. When these results are corrected for association, as described below, they yield 68 and 45 for the vapor phase constant, showing that the experimental method is still subject to large errors.

The present work was undertaken to provide further data by a new experimental method at a temperature as near to 25° as might prove feasible. The acid and ester were treated as solutes in a large excess of a solvent containing alcohol and water in a fixed ratio. The liquid phase equilibrium constant at 40° has been obtained from measurements at 40, 60, 79 and 99°, and has been transferred to the vapor phase with the aid of vapor compositions measured separately for the solvent and for dilute solutions of the acid and ester. The result is $K_{313} = 122 \pm 3$.

Table I and Fig. 1 show the logarithm of the equilibrium constant as a function of the reciprocal of the absolute temperature. No relation of the expected linear or slightly curved form is

(1) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); Tidwell and Reid, *ibid.*, **53**, 4353 (1931); Essex and Clark, *ibid.*, **54**, 1290 (1932); Jatkar and Gajendragad, *ibid.*, **59**, 798 (1937).

(2) Edgar and Schuyler, *ibid.*, **46**, 64 (1924).

(3) Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1928).

(4) Salcewicz, *ibid.*, **14**, 702 (1934).

TABLE I

EQUILIBRIUM: $CH_3COOH(g) + C_2H_5OH(g) = CH_3\text{-}COOC_2H_5(g) + H_2O(g)$

Author	1000/T	Log K(g)
Frolich, Carpenter and Knox	1.808	1.690
	1.745	1.799
Tidwell and Reid	2.364	1.486
	2.114	1.396
	1.912	1.106
	1.745	0.945
Essex and Clark	2.364	1.527
	2.283	1.421
	2.114	1.206
Jatkar and Gajendragad	1.988	1.029
	1.876	0.954
aSwietoslawski and Poznanski	2.873	1.959
aSalcewicz	2.884	1.650
	2.865	1.833
Halford and Brundage	3.194	2.076 to 2.097

a After correcting for association.

uniquely determined, and only a provisional solution of the problem of temperature dependence is suggested for the present. This is based upon the new data presented here and the results of Jatkar and Gajendragad, and should not be far from correct. A straight line passing between their points at 230 and 260° and through a point within the limits assigned to the new result at 40° has a slope corresponding to $\Delta H^0 = -3970 \pm 80$ cal. There is no evident basis for estimating a more significant probable error. Other thermodynamic quantities with variations prescribed by the same limits are: $\Delta F^0_{313} = -2990 \pm 15$ cal. and $\Delta S^0 = -3.1 \pm 0.2$ e. u. For the free energy as a function of the absolute temperature

$$\Delta F^0 = -3970 + 3.1 T \qquad (2)$$

Reagent quality acetic acid was used, *anal.* 99.55% by titration and 99.54 ± 0.05% by the freezing point, assuming that the only impurity was water. Ethyl acetate was dried with phosphoric anhydride and refractionated: *anal.* 99.9 to 100.0%; free acid, at first below the limit of detection, was less than 0.02% after one year. Commercial ethyl alcohol and distilled water boiled to expel carbon dioxide were used for the fixed ratio solvent.

The composition of the solvent, based upon the initial weight proportions and the density of the alcohol, was checked by direct density measurements after mixing, with agreement to within 0.02%. A 14-cc. U-shaped double-chambered pycnometer was used, and conversion to weight per cent. was made with the aid of tabulated data.[5]

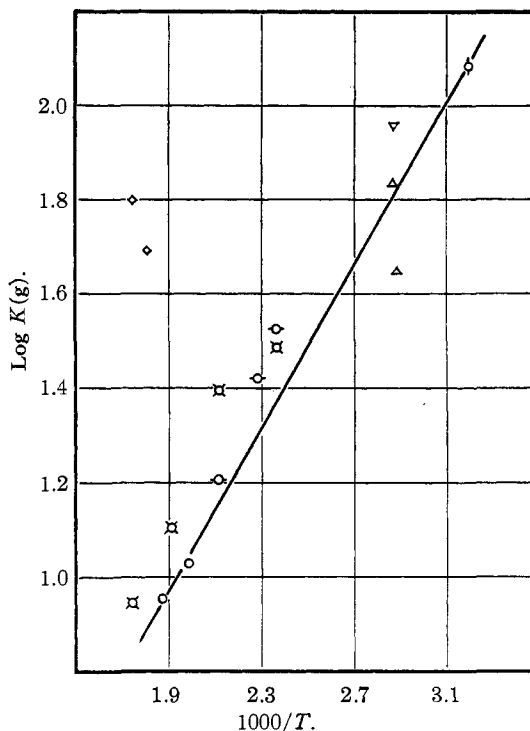(5) "I. C. T.," Vol. III, p. 116; Smithsonian Physical Tables, 8th ed., 1st reprint (1934), p. 172.

Fig. 1.—Vapor phase esterification equilibrium: ◇, Frolich, Carpenter and Knox; ◻, Tidwell and Reid; -O-, Essex and Clark; O, Jatkar and Gajendragad; ▽, Swietoslawski and Poznanski; △, Salcewicz; ◌, Halford and Brundage.

The solvent contained 67.62 wt. per cent. alcohol, 44.97 mole per cent. or 1.2237 moles of water per mole of alcohol. The equilibrium vapor at 40°, analyzed by the air saturation method, contained 82.97 wt. per cent. alcohol as compared with 83.17 derived by graphical interpolation from tabulated partial pressures. The mean value, 82.07 ± 0.10, 65.8 mole per cent., corresponding to 0.520 ± 0.003 mole of water per mole of alcohol has been used in calculations.

Liquid Phase Equilibrium.—In order to determine the equilibrium constant at 40°, where reaction is slow enough to permit vapor composition studies of solutions not at equilibrium, measurements were made, to permit extrapolation, at 99, 79 and 60°, using vapor baths of water, carbon tetrachloride and chloroform. In addition, some solutions reached equilibrium after standing for several months at 40°.

Solutions made up to compositions not far from equilibrium were left in the constant temperature baths for periods of twelve to 414 days. Reaction vessels were sealed Pyrex tubes. Concentrations at equilibrium were calculated from the initial composition and the final acid content.

In a number of cases, the final ester content was checked by titration.

Table II shows examples of the liquid phase equilibrium measurements. Each example is representative of from three to twelve runs made at the same temperature and in the same region of concentrations, and yields an equilibrium constant close to the arithmetical mean for the set. With one exception, all the runs give constants within the range 2.53 ± 0.06. At either the upper or the lower level of solute concentrations the average value decreases with decreasing temperature, but the change is greatest between 80 and 100° and has disappeared between 40 and 60°. Runs at both temperatures, with identical solutions equilibrated for more than one year, gave almost exactly the same constants. For this reason, and because relatively few data were collected at 40°, the correct value at this temperature is taken to be equal to the average of all results obtained at 40 and 60°. The constants so obtained are 2.52 at the upper concentration level, and 2.50 at the lower one, with a probable error of 0.02. Linear extrapolation leads to 2.49^5 at infinite dilution, a value with no real significance in view of the ultimate ionization of the acid, but one which may be combined with similarly extrapolated vapor composition data to yield a limiting vapor phase constant.

TABLE II

LIQUID PHASE EQUILIBRIUM IN THE REACTION

$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$

| Time, days | Concentrations in moles/1000 g. of solution | | | | Final acid | $K(1)$ | Temp., °C. |
	Initial Acid	Ester	Alcohol	Water			
12.130	0.3799	0.7230	13.408	16.406	0.3564	2.572	99
68	.0779	.1451	14.422	17.645	.0721	2.562	99
67	.3877	.7217	13.403	16.399	.3622	2.533	79
86	.0810	.1585	14.402	17.621	.0783	2.519	79
216	.3987	.7801	13.318	16.295	.3862	2.516	60
181	.0770	.1555	14.409	17.630	.0764	2.501	60
183	.3835	.7780	13.334	16.314	.3785	2.532	40
394	.0770	.1555	14.409	17.630	.0768	2.480	40

Vapor composition of dilute solutions of ethyl acetate and acetic acid in the fixed ratio solvent was measured by the air saturation method at 40.0 ± 0.1°. Apparatus included an air thermostat heated by shielded lamps and a saturation train containing, in order, a soda-lime tube, a preheater of coiled copper tubing, a half liter flask, six 75-cc. saturators of the type designed by Bichowsky and Storch,[6] an electrically heated outlet tube and two condensers, in the form of weighing vessels, immersed in dry-ice baths. No conden-

(6) Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

sate was ever found in the second condenser. The apparatus was checked against possible spray error by means of a run at a high bubbling rate with 5.4% aqueous sulfuric acid which showed less than 0.001% acid in the condensate. After collecting a sample over a twenty-four hour period, the condenser was allowed to come to room temperature with the stopper lightly in place to effect equalization of pressure.

The data for the ester solutions are summarized in Table III, which shows in order the liquid mole fraction N_2^*, the vapor mole fraction X_2^* and the ratio N_2^*/X_2^*. In calculating the vapor mole fraction the ratio of the solvent components in the vapor is assumed to remain constant at the value determined for the pure fixed ratio solvent.

The asterisk distinguishes the three-component mole fractions in the vapor composition studies from those in the four component systems at equilibrium with respect to Eq. 1.

TABLE III

VAPOR-LIQUID MOLE FRACTION RELATION FOR ETHYL ACETATE IN 45 MOLE PER CENT. ALCOHOL AT 40°

$10^3N_2^*$	$10^3X_2^*$	N_2^*/X_2^*
151.0	463.3	0.3829
103.0	401.9	.2564
63.3	312.4	.2028
36.2	216.9	.1671
24.5	158.3	.1549
13.2	94.9	.1394
5.23	41.25	.1267
5.18	41.03	.1262
3.42	27.44	.1247
2.60	21.21	.1224
1.69	13.99	.1211
0.962	8.04	.1196

Plotting X_2^* against N_2^* yields a smooth curve directed toward the origin and almost linear in the range of dilute solutions. The ninth and twelfth listed points appear, however, to be slightly out of line. Their deviation is confirmed by examining the more sensitive plot of N_2^*/X_2^* against N_2^* which according to Henry's law should produce a straight line in dilute solution. This conclusion is reached by substituting $p_2 = hN_2^*$ and $p_1 = p_1^0 (1 - N_2^*)$ into the expression $X_2^* = p_2/(p_1 + p_2)$ and rearranging to give the equation

$$N_2^*/X_2^* = N_2^*(1 - p_1^0/h) + p_1^0/h \qquad (3)$$

in which h is the Henry's law constant and p^0 is the vapor pressure of the pure solvent. A particularly useful feature of Eq. 3 is the numerical relation between slope and intercept. The limiting value of N_2^*/X_2^* consistent with this relation is

0.119 ± 0.001. When the extrapolation is made without regard for the slope–intercept relation, the intercept is 0.1185 ± 0.0005, showing that the data permit little latitude of interpretation.

Considerable difficulty was encountered in the sampling and analysis of the vapor over solutions of acetic acid. It was found that as much as 1.0% of the acid would esterify during a twenty-four hour run, whereas there had been no measurable hydrolysis of the ester in a similar period. Consequently the run could not be lengthened appreciably to compensate for the low volatility of the acid, and it became necessary to weigh and titrate the entire condensate in the condensing vessel. A second condenser was used as a counterbalance, and the titration was performed with 0.01 N alkali. Preliminary experiments in which the saturated vapors were passed through a glass wool spray filter showed that a large proportion of the acid was lost by adsorption and indicated that a small but measurable loss could occur even in the tube leading to the condenser. A tube of minimum length and diameter was therefore used. After introducing the Bichowsky–Storch saturators and proving that they were free from spray error, the results remained erratic until special precautions were adopted in rinsing the lower part of the condenser outlet tube during the titration. A preliminary end-point was first obtained, then the side arm was washed with the neutralized solution by the use of a rubber suction bulb. Thereafter a second end-point was obtained and the alternation of washing and titration was continued until the end-point was permanent.

Table IV contains the results of the last eight runs conducted with the acid. The first column gives the numerical mean of the mole fractions in the liquid at the beginning and end of the run, and the last column contains the ratio $X_3{}^*/N_3{}^*$ rather than its reciprocal as shown in Table III for the ester. Here the direct ratio is nearer to a linear function of $N_3{}^*$ than the reciprocal and has been used in making the extrapolation to infinite dilution. Equation 3 has not been applied because there is no reason why an associated solute should obey Henry's law. The six points of Table IV which most nearly define a smooth curve of $X_3{}^*$ against $N_3{}^*$ directed toward the origin were determined consecutively. No reason is apparent for the low values of $X_3{}^*$ obtained in the remaining two measurements. Consequently, the possibility that results obtained in

TABLE IV
VAPOR–LIQUID MOLE FRACTION RELATION FOR ACETIC ACID IN 45 MOLE PER CENT. ALCOHOL AT 40°

$10^2 N_3{}^*$	$10^3 X_3{}^*$	$X_3{}^*/N_3{}^*$
44.50	3.837	0.0862
34.00	2.870	.0844
25.42	2.082	.0819
14.28	1.121	.0786
13.17	0.953	.0724
10.80	.793	.0734
9.578	.706	.0737
6.144	.456	.0742

the more dilute solutions tend to be low must be considered in the interpretation. An extrapolation based upon the first four points together with the eighth point gives 0.073 ± 0.001 for the limiting value of $X_3{}^*/N_3{}^*$ in dilute solution. This extrapolation is taken to have significance parallel to the one performed with the liquid phase equilibrium constant.

Acetic Acid Association.—It is well known that even at low pressures acetic acid vapor exhibits appreciable deviations from the ideal gas laws. The deviations have been explained, as a good first approximation, by describing the vapor as an equilibrium mixture of a monomer and a dimer in accordance with Eq. 4.

$$(CH_3COOH)_2 = 2CH_3COOH; \quad k = p_3^2/p_4 = X_3^2P/X_4 \tag{4}$$
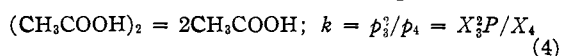
P is the total pressure and X_3 and X_4 are the mole fractions of monomer and dimer, respectively. An adequate correction of the vapor phase esterification data for the presence of the dimer can be made without introducing activity functions such as those developed by Essex and Clark.

For x_2 moles of ester, x_3 moles of monomer, x_4 moles of dimer, x_{aq} moles of water and x_{alc} moles of alcohol at equilibrium

$$K(g) = \frac{x_{aq}x_2}{x_{alc}x_3} \quad \text{and} \quad K'(g) = \frac{x_{aq}x_2}{x_{alc}(x_3 + 2x_4)} \tag{5}$$

where $K(g)$ is the true equilibrium constant of reaction 1 and $K'(g)$ is the constant calculated on the assumption that all the acid is monomeric. From Eqs. 4 and 5

$$K(g)/K'(g) = 1 + 2x_4/x_3 = 1 + 2X_4/X_3 = 1 + 2X_3P/k \tag{6}$$

The apparent mole fraction X'_3 calculated for the acid from experimental data when association is neglected may be expressed in terms of the true mole fractions by the equation

$$X'_3 = (X_3 + 2X_4)/(1 + X_4) \tag{7}$$

X_4 is eliminated from Eq. 7 by substitution from

Eq. 4 to give a quadratic equation which is solved for X_3 and combined with Eq. 6 to give the result

$$\frac{K(g)}{K'(g)} = 1 + \frac{\sqrt{1 + 4X_3'(2 - X_3')P/k} - 1}{2 - X_3'} \quad (8)$$

This equation has been applied to the data of Swietoslawski and Poznanski and the data of Salcewicz to obtain the values shown in Table I and Fig. 1. The constant k was taken as 28 mm. at 75° after consideration of the association data of Drucker and Ullmann,[7] of Fenton and Garner[8] and of MacDougall.[9]

The vapor phase equilibrium constant is calculated for the infinitely dilute solution of the acid and ester by combining the measured water–alcohol ratios in the liquid and vapor with the extrapolated values of $K(1)$, N_2^*/X_2^* and X_3^*/N_3^*. Because of an element of doubt introduced by the failure of acetic acid to follow Henry's law, this result has been accepted as final only after comparison with approximations to $K(g)$ calculated for systems containing finite concentrations of the acid and ester. Any deviation of the vapor ratio of water to alcohol from the value measured for the pure solvent is neglected. It is also assumed that the addition of the second solute produces a negligible effect upon the vapor ratio already established between one solute and the solvent components.

Consistent values of N_3 and $K(1)$ are selected and N_2 is calculated from them. Each mole fraction is converted to its value in the three component system which would be obtained by removing the other solute. The equations for this conversion are

$$N_2^* = N_2/(1 - N_3) \text{ and } N_3^* = N_3/(1 - N_2) \quad (9)$$

For the opposite conversion from the three to the four component mole fractions in the vapor phase, these equations take the form

$$X_2 = X_2^*(1 - X_3^*)/(1 - X_2^*X_3^*) \text{ and } X_3' =$$
$$X_3^*(1 - X_2^*)/(1 - X_2^*X_3^*) \quad (10)$$

Three component vapor phase mole fractions are obtained with the aid of the ratios N_2^*/X_2^* and X_3^*/N_3^* from Tables III and IV. The result for

(7) Drucker and Ullmann, Z. physik. Chem., **74**, 567 (1910).
(8) Fenton and Garner, J. Chem. Soc., 694 (1930).
(9) MacDougall, THIS JOURNAL, **58**, 2585 (1936).

the vapor phase constant prior to correction for association is

$$K'(g) = r\frac{X_2^*(1 - X_3^*)}{X_3^*(1 - X_2^*)} \quad (11)$$

where r is the water/alcohol molal ratio.

For calculating $K(g)$ by means of Eq. 8, k is taken as 1.8 mm. from MacDougall's data and P is assumed to differ only negligibly from 122 mm., the vapor pressure of the solvent. Table V shows the several approximations to the vapor phase equilibrium constant together with some of the quantities required for their calculation.

TABLE V

VAPOR PHASE EQUILIBRIUM CONSTANT AT 40°

10^3N_3	0.00	2.500	7.000	12.50
$K(1)$	2.49$_5$	2.50	2.51	2.52
N_2^*/X_2^*	0.119$_0$	0.125$_5$	0.141$_2$	0.156$_5$
X_3^*/N_3^*	0.073$_0$	0.074$_0$	0.075$_6$	0.077$_8$
$10^3X_3'$	0.00	0.178$_4$	0.472$_0$	0.832$_7$
$K'(g)$	122.1	118.9	112.8	104.0
$K(g)$	122.1	121.7	119.6	114.7

It is evident from the last two tabulated values of $K(g)$ that the effect of the acid and ester upon the water–alcohol ratio decreases rapidly with decreasing concentration of the solutes, and has become negligible at the lowest finite concentration. Consequently the agreement obtained at concentrations below $N_3 = 0.0025$ shows that no large error of extrapolation has been made. The value $K(g) = 122 \pm 3$ has been selected as representative.

Summary

The equilibrium constant for the esterification of acetic acid by ethyl alcohol has been measured from 40 to 100° for dilute solutions of the acid and ester in a solvent containing 1.2237 moles of water per mole of alcohol. The result at 40° has been converted to the vapor phase constant with the aid of vapor composition studies made by the air saturation method.

For the vapor phase esterification, $K(g)_{313} = 122 \pm 3$, $\Delta F_{313}^0 = -2990$ cal., and, by combination with other equilibrium data, $\Delta F^0 = -3970 + 3.1 T$.