definite number of lattice points. If a solution of long paraffin molecules is somewhat idealized as a parallel arrangement, the number of possible interchanges is the same as it would be for spherical molecules of equal size in a point lattice. This leads to the entropy and free energy of an ideal solution. The rather meager experimental evidence supports the ideal character of such solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY, INDIAN INSTITUTE OF SCIENCE]

Vapor Phase Esterification Equilibria

BY S. K. KULKARNI JATKAR AND N. G. GAJENDRAGAD

A study of various papers[1] on the vapor phase esterification of alcohols and acetic acid would seem to indicate a high temperature coefficient on the basis of Sabatiers[1e] value of 70% at 300° and Edgar's[1h] figure of 97% at 53°, but the large possible error admitted by Edgar and the lack of precision in the data of earlier workers, leaves doubt as to the actual position of equilibrium at intermediate temperatures, especially in view of the agreement of the constants found by Frolich, Carpenter and Knox[1l] at 280–300° and Swietoslawski[1,i,j] at 75°. Parks and Huffman[2] have used these values in calculating the free energy of ethyl acetate, and obtained satisfactory concordance with estimates based on the third law, but in disagreement with results of other workers.

Swietoslawski and co-workers apparently did not correct for acetic acid polymerization nor for the activities of the compounds, both of which are appreciable at 75°. As to the high values of Frolich and coworkers, the only probable explanation for them is that some of the catalyst must have been in the cooler portion of their apparatus. On account of the high temperature coefficient of the equilibrium constant, the reaction products must be "frozen," and it seems probable that temperature errors may account for some of the other experimental discrepancies.

Figure 1 shows a plotting of log Kp against $1/T$ of the results of various workers, and harmonizes out all the values from 77 to 300° except those of Frolich, *et al.* The fact that a straight line can be drawn among most of the values shows that ΔC_p for this reaction is practically zero, and it is only coincidence that our values lie between those extrapolated from the results of others. The acetic acid dissociation and the compressibility corrections are too small to affect our results. Perhaps the dotted line drawn through the more accurate values of Essex and Clark represent the true position of affairs.

The object of the present work was to obtain results with silica and potassium alum catalysts and discuss them in the light of the work of other investigators.

Experimental

The previously described method[1b] was used, in which the alcohol–acid mixture is allowed to flow drop by drop into a copper tube vaporizer (not attacked by acetic acid above 180°), superheated, passed through the catalyst tube and the products condensed in a test-tube in a freezing mixture.

The silica catalysts were prepared from iron-free water glass, analyzing for an $Na_2O:SiO_2$ ratio of 1.07:1 and 30.8% of water. The silicate solution was allowed to flow dropwise into 1.5 liters of vigorously stirred dilute hydrochloric acid contained in a 4-liter beaker, until the resulting gel set and stirring was impossible. The gel was then broken up, washed well with hot distilled water and dried in various ways, the most active catalyst being produced in partial vacuum. For this catalyst the optimum temperature was 260°, and the initial and final total acids agreed well except at temperature extremes.

Esterification of Ethyl Alcohol and Acetic Acid with Silica Catalyst at 260°.—For various rates of passage the esterification limit was found to be 75% for the 1:1 mixture and 91% for the 2:1 mixture (Table I).

The equilibrium also was studied from the hydrolysis side, pure ethyl acetate being taken into the buret and ester vapor saturated with water passed through the superheater into the reaction chamber, the proportion of water being

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(1) (a) Jatkar and Watson, *J. Indian Inst. Sci.*, **9A**, 71 (1926); (b) Gajendragad, Jatkar and Watson, *ibid.*, **15A**, 59 (1932); (c) Gajendragad and Jatkar, *J. Indian Chem. Soc.*, **12**, 486 (1935); (d) H. T. Briscoe and F. E. Dolian, *Proc. Indiana Acad. Sci.*, **42**, 101 (1933); *C. A.*, **27**, 5719 (1933); (e) Sabatier and Mailhe, *Compt. rend.*, **152**, 358, 494 (1911); (f) Mailhe and Godon, *Bull. Soc. Chim.*, [4] **29**, 101 (1921); (g) Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924); (h) Edgar and Schuyler, THIS JOURNAL, **46, 64** (1924); (i) Swietoslawski and Poznanski, *Compt. rend.*, **184**, 92 (1927); (j) Swietoslawski and Salcewicz, *ibid.*, **199**, 130 (1934); (k) Gajendragad, *Proc. 15th Indian Sci. Cong.*, 148 (1928); (l) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); (m) Jatkar and Gajendragad, "Proc. Indian Sci. Cong., Nagpur," 1931; (n) Tidwell and Reid, THIS JOURNAL, **53**, 4353 (1931); (o) Essex and Clark, *ibid.*, **54**, 1290 (1932).

(2) Parks and Huffman, "Free Energy of Organic Compounds," Reinhold Publishing Corporation, New York, N. Y., 1935, p. 174.

TABLE I

SILICA CATALYST, 48 G. AT 260°

EtOH: AcOH = 1:1

Expt.	142	143	132	133	140	141
Rate	18	18	10	10	5	5
Esterification, %	45.0	45.5	61.9	63.0	74.7	75.3

EtOH: AcOH = 2:1

Expt.	154	155	159	160	157	158
Rate	8.0	8.0	5.9	5.6	4.0	3.8
Esterification, %	79.1	79.6	83.8	88.7	88.0	91.0

controlled by the humidifier temperature. The reaction should produce equivalent quantities of acid and alcohol, so the free acid and total acid per gram of product were determined, the alcohol assumed to be equal to the free acid and the water found by difference (Table II).

TABLE II

REVERSE REACTION: 48 G. OF SILICA CATALYST AT 260°

	Init. compn. mixt.			Compn. prod., mole %				
Expt.	Ester	Water	Rate	Ester	Water	Alc. = Acid	Kp	Conv., %
146	67	33	8	57.0	23.4	9.8	14	79.9
147	66	34	5	55.5	22.6	10.9	10	76.2
148	66	34	5	55.5	22.6	10.9	10	76.2
149	68	32	5	57.5	21.3	10.6	10	76.2
175	81	19	6.2	69.2	6.6	12.0	3.2	
176	74	26	6.2	63.0	15.1	10.9	7.9	73.6
177	72	28	6.0	61.5	17.3	10.6	9.5	75.6
178	74	26	6.0	62.4	15.2	11.2	7.6	73.2
179	73	27	4.5	62.2	16.0	10.9	8.4	74.4
180	73	27	3.4	62.2	16.0	10.9	8.4	74.4
197	57	43	20	45.5	31.0	11.7	10	76.2
198	54	46	20	42.1	34.9	11.5	10	76.1

The calculated equilibrium constants expressed in terms of percentage esterification of an equimolecular alcohol-acid mixture are given in the last column. Our results and those of others show the necessity of slow passage for equilibrium. Plotting the percentage conversion in the last column against rate of passage for direct, reverse and "equilibrium" runs, and extrapolating from different rates of passage, gives values for Kp at zero rate, complicated by difficulty in maintaining the activity of the catalyst constant during a series. The curve for expts. 146–149, carried out with fresh catalyst and initial mixtures of 2:1 ester and water, gives 75% as the limit for the reverse reaction. Experiments 175–180, with another catalyst and a 3:1 mole mixture of ester and water gave 74.4% conversion for an equimolecular mixture. Experiments 197–198 were made with 60 g. of fresh catalyst and a 1:1 mixture of ester and water, the result showing that even with the passage of 20 g. per hour equilibrium is attained within 1%. Some experiments to find the limit of the reverse reaction have been carried out by passing over the catalyst at various rates synthetic mixtures corresponding to the constants 4, 6, 8, 10 and 14 (Table III).

TABLE III

QUADRUPLE MIXTURES WITH 48 G. OF SILICA CATALYST AT 260°

		Composition of product, mole %					
Expt.	Rate	Ester	Water	Alc.	Acid	Kp	Conversion, %
		33.7	31.6	17.0	17.6	4	
191	23	37.1	35.8	13.4	13.7	7	72.4
189	16	37.9	35.8	12.8	13.5	8	73.7
188	15	37.0	37.8	12.7	12.4	9	75.0
184	10	39.3	37.1	11.5	12.1	10	76.2
185	10	36.7	36.3	13.4	13.6	7	72.8
186	9.5	39.3	35.8	12.2	12.6	9	75.0
187	9	38.6	37.4	11.8	12.2	10	76.2
183	9	39.8	36.6	11.3	12.2	10	76.2
190	5	37.8	37.7	12.9	13.5	8	73.7
		37.8	36.0	12.8	13.4	8	
93	20	39.3	37.0	11.5	12.2	10	76.2
195	18	38.6	37.1	12.0	12.4	10	76.2
196	12	38.9	37.2	11.7	12.2	10	76.2
194	10	37.4	37.5	12.6	12.5	9	75.0
		37.0	42.5	10.3	10.3	14	
201	20	35.5	41.6	11.4	11.5	11	77.1
202	5	36.7	39.8	11.8	11.8	10	76.2
		36.1	40.1	11.9	11.9	10	
210	12	39.7	44.2	13.4	13.4	9	75.0
211	6	34.3	41.6	12.0	12.0	9	75.0
		65.0	12.5	11.0	11.5	6	
212	20	65.3	12.0	11.1	11.7	6	71.0
213	10	64.4	13.7	10.9	11.0	7	72.5
		68.2	12.0	9.7	10.1	8	
214	20	67.3	13.1	9.3	10.3	9	75.0
215	10	68.2	12.0	9.7	10.1	8	74.1

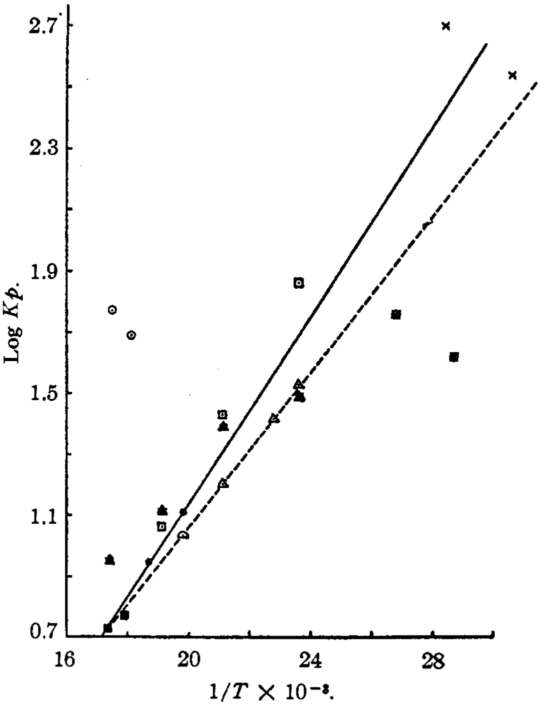

Fig. 1.—Esterification equilibria in the vapor phase: ■, Sabatier and Mailhe, 1911; ⊠, Mailhe and Godon, 1921; □, Milligan, Chappell and Reid, 1924; ▲, Tidwell and Reid, 1931; △, Essex and Clark, 1932; ○, Frolich and co-workers, 1930; ⊗, Swietoslawski and co-workers, 1929, 1934; ×, Edgar, 1924; ●, SiO_2, ⌓, alum, authors, 1931, 1936.

The results in Table III on graphical extrapolation show that the limit is reached when the product composition is such that $C_{\text{ester}}C_{\text{H}_2\text{O}}/C_{\text{alc.}}C_{\text{acid}} = 9$ approximately. The equilibrium point does not change with variation of water content in the initial mixture, the value of Kp remaining sensibly the same in expts. 212–216 with an ester/water ratio of 5, and in expts. 182–191 where the ratio was 1.

Esterification with Silica Gel at 230°.—Various silica catalysts were tested at 230°, but they were found to be relatively inactive, giving no limit of esterification. The maximum conversion was 73%, and in hydrolysis experiments with initial mixtures of 2 moles of ester to 1 mole of water the lowest value was 80% and that extrapolated from different flow rates was 78%. A mixture of ester, water, alcohol and acid in the mole ratio of 30.2:38.7:10.1:15.6 corresponding to $Kp = 4$, was passed at 10 cc. per hour over the catalyst and the mole ratio of the product was 34.9:42.8:11.6:10.8, corresponding to an equilibrium constant of 11.7.

It is evident that silica gel is not sufficiently active at 230°, and as the equilibrium is less favorable for ester at higher temperatures, various other catalysts have been studied, potassium hydrogen sulfate being the best (results to be published elsewhere).

Esterification with Potassium Alum Catalyst at 230°.—The optimum esterification temperature for this catalyst, prepared as described by Jatkar and Watson,[1a] is 230°, just as for ether dehydration of methyl and ethyl alcohols.[1a,b] Some experiments (Table IV) were made passing equimolecular mixtures of ethyl alcohol and acetic acid at 10 cc. per hour over 100 g. of potassium alum catalyst in the space which previously contained 50 g. of silica. Esterification begins at 160–170°, the same temperature at which alcohol begins to dehydrate if passed alone.

TABLE IV

Expt.	48	49	50	51	52	53	54
Temp., °C.	185	200	210	220	230	240	250
Esterification, %	14.0	33.5	41.2	53.2	62.7	60.6	61.9

Experiments also were run to ascertain the maximum esterification at various rates, using a mixture of alcohol 47.6 moles, acetic acid 47.4 moles and water 4.94 moles. In all the experiments (Table V) the initial and final total acid agreed, and the results show that a limit is reached easily, in contrast with silica catalysts.

The hydrolysis of ethyl acetate has been studied with the same catalyst in the same apparatus. For rates of 20–10 g. per hour the value of Kp was about 10 (Table VI), while with slower rates hydrolysis went further and gave $Kp = 5$. This was due to ether formation in a side reaction. No ether could be detected in either direct or reverse reactions at rates of 10–20 cc. per hour.

TABLE V

POTASSIUM ALUM CATALYST, 105 G. AT 230°

Expt.	9	10	19	13	14	15	20	21
Rate	25.0	25.0	20.0	10.0	10.0	5.0	3.8	2.4
Esterif., %	63.7	61.8	64.7	65.5	65.0	65.5	61.5	63.5
Expt.		57	58	55	56	59	60	
Rate		20	20	10	10	5	5	
Esterif., %		64.0	63.7	65.3	64.6	66.1	64.8	

Table VI

Experiment		25	24	23	28
Rate, g.		20	14.6	13	13
Mole % compn. prod.	Ester	32.2	34.1	26.9	22.5
	Water	43.7	42.4	48.4	55.1
	Alc. = acid	12.0	11.7	12.3	11.5
Kp		9.9	10.7	8	9.9

Taking the equilibrium value $Kp_{\text{ether}} = C_{\text{Et}_2\text{O}}C_{\text{H}_2\text{O}}/C^2_{\text{EtOH}} = 7$ at 230° found by Jatkar and Watson for the ether reaction and the limiting esterification value of a 1:1 alcohol-acetic acid mixture as 67% (the lower observed value 65% being due to initial water) the equilibrium constant for ester formation at 230° calculates to be 10.7, in good agreement with the figure found by extrapolation of the results of Essex and Clark.

Acknowledgment.—Our thanks are due to Dr. H. E. Watson for his keen interest during the progress of this work.

Summary

Measurements have been made on the vapor phase esterification equilibria of ethyl alcohol and acetic acid at 230 and 260°, using silica gel and potassium alum as catalysts, and the results found to correspond to 77 and 75% conversion of the equimolecular mixtures.

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.

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