

223. The Ternary System, Methanol–Methyl Acetate–Water.

By A. G. CRAWFORD, G. EDWARDS, and D. S. LINDSAY.

The presence of a binary azeotrope of methanol and methyl acetate is confirmed. Its composition has been established as 33.2 mols. % of methanol, 66.8 mols. % of methyl acetate (previously reported as 35 mols. % of methanol). Vapour–liquid equilibrium diagram for the systems methanol–methyl acetate and methanol–methyl acetate–water are given.

A SOLVENT for organic materials, miscible in nearly all proportions with water, has lately been introduced. This consists of a mixture of methanol and methyl acetate. As the recovery of the solvent would customarily be carried out by distillation, a knowledge of the volatility relationships in the ternary mixture methanol–methyl acetate–water is desirable.

As a necessary preliminary to the elucidation of the equilibrium conditions a rapid method of estimation based on physical constants was evolved. It is customary to utilise the refractive index and specific gravity when suitable (York and Holms, *Ind. Eng. Chem.*, 1942, **34**, 345) because of the convenience of measurement, and these constants were chosen in this case. Determinations were conducted at 25°, and the results are shown in Table I. Fig. 1 is a ternary diagram of the lines of constant refractive index and specific gravity constructed from the results in Table I. The experimental results represent a point of estimation of refractive index

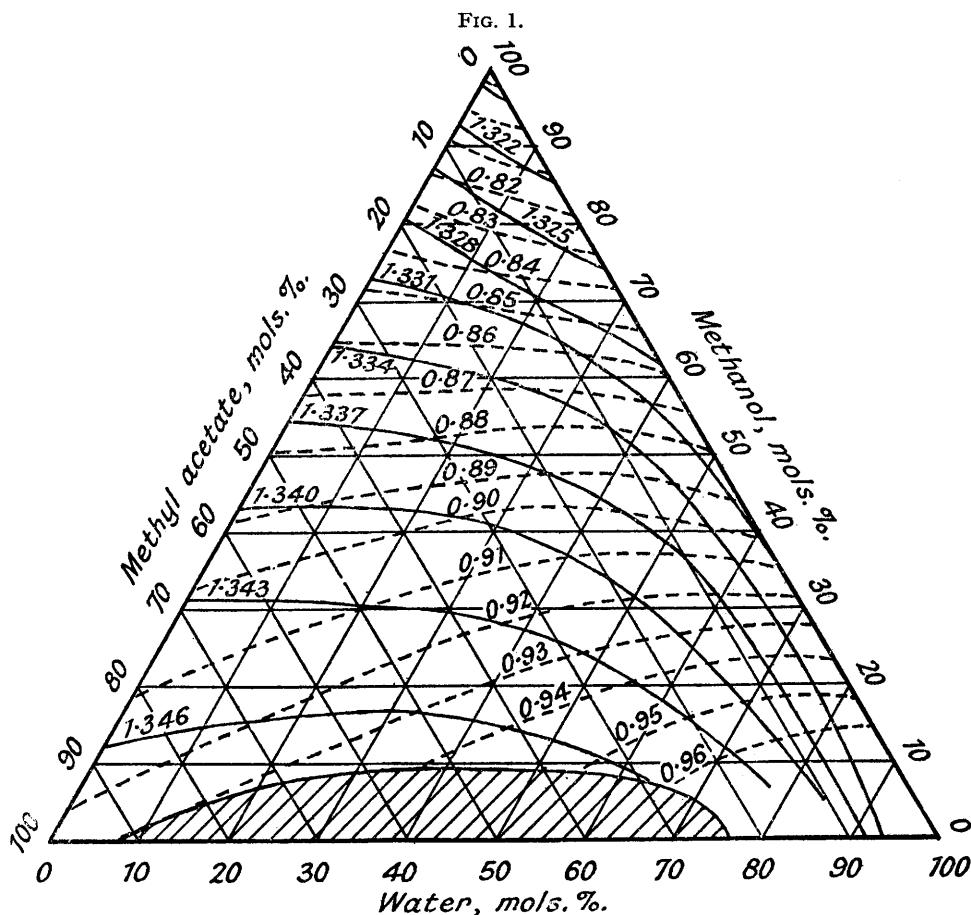
TABLE I.

Soln. Molar % (by wt.).				Soln. Molar % (by wt.).							
no.	MeOH.	Ester.	H ₂ O.	no.	MeOH.	Ester.	H ₂ O.				
1	10	80	10	1.34681	0.9243	32	20	20	60	1.34242	0.9428
2	20	70	10	1.34498	0.9143	33	30	10	60	1.33767	0.9259
3	30	60	10	1.34308	0.9061	34	10	20	70	1.34365	0.9636
4	40	50	10	1.34072	0.8953	35	20	10	70	1.33824	0.9460
5	50	40	10	1.33807	0.8823	36	10	10	80	1.33903	0.9726
6	60	30	10	1.33466	0.8674	37	90	10	0	1.32367	0.8132
7	70	20	10	1.33137	0.8500	38	80	20	0	1.32812	0.8343
8	80	10	10	1.32599	0.8275	39	70	30	0	1.33205	0.8524
9	10	70	20	1.34714	0.9287	40	60	40	0	1.33546	0.8667
10	20	60	20	1.34539	0.9202	41	50	50	0	1.33839	0.8811
11	30	50	20	1.34308	0.9098	42	40	60	0	1.34062	0.8929
12	40	40	20	1.34054	0.8977	43	30	70	0	1.34308	0.9033
13	50	30	20	1.33736	0.8832	44	20	80	0	1.34489	0.9129
14	60	20	20	1.33382	0.8686	45	10	90	0	1.34639	0.9196
15	70	10	20	1.32789	0.8496	46	90	0	10	1.32076	0.8044
16	10	60	30	1.34759	0.9394	47	80	0	20	1.32374	0.8225
17	20	50	30	1.34531	0.9214	48	70	0	30	1.32606	0.8425
18	30	40	30	1.34292	0.9133	49	60	0	40	1.32834	0.8612
19	40	30	30	1.34030	0.9028	50	50	0	50	1.33008	0.8817
20	50	20	30	1.33570	0.8842	51	40	0	60	1.33083	0.8950
21	60	10	30	1.33267	0.8656	52	30	0	70	1.33106	0.9253
22	10	50	40	1.34747	0.9413	53	20	0	80	1.32964	0.9459
23	20	40	40	1.34497	0.9307	54	10	0	90	1.32664	0.9674
24	30	30	40	1.34218	0.9185	55	0	90	10	immiscible	
25	40	20	40	1.33807	0.9034	56	0	80	20	„	
26	50	10	40	1.33477	0.8863	57	0	70	30	„	
27	10	40	50	1.34681	0.9469	58	0	60	40	„	
28	20	30	50	1.34407	0.9367	59	0	50	50	„	
29	30	20	50	1.34063	0.9223	60	0	40	60	„	
30	40	10	50	1.33617	0.9058	61	0	30	70	„	
31	10	30	60	1.34572	0.9564					„	

and specific gravity for all intersections of the composition lines on the ternary diagram (Fig. 1) except those along the base. No advantage would be gained, and considerable complexity

would be introduced, by plotting these as points on the diagram, and they have accordingly been omitted.

Because the refractive indices of methanol and methyl acetate differ by only 0.03011, it was essential to evaluate these to the fifth decimal place, and the Pulfrich refractometer was the only suitable instrument. Sufficient accuracy in the determination of specific gravity was obtained with Oswaldt–Sprengel picnometers (Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw Hill, 1934, p. 318) of 5 ml. capacity. For both refractive index and specific gravity estimations the temperature was controlled to $\pm 0.1^\circ$. This shaded area in Fig. 1 represents a region in which the solutions were not homogeneous. It will be appreciated that use of the experimental mixtures of Table I does not permit of accurate prediction of the



boundary of this area. Values for mutual solubility of water and methyl acetate at 25° are given (International Critical Tables, Vol. 3, p. 387; Hill and Morrow, private communication; Raymann, Diss., Budapest, 1906) as 0–24.1% of methyl acetate in water and 0–8.7% of water in methyl acetate. Owing to this immiscibility it was not possible to plot the physical constants in the region. The refractive index line 1.32299 to 1.33100 on the left of the apex of Fig. 1 should reappear in the lower right-hand corner of the graph and to the right of the tangential line 1.33100. Since these re-entrant curves all refer to solutions containing less than 4% of methyl acetate, and as determinations were only conducted for solutions differing in concentration by 10%, no attempt was made to indicate their position.

A number of stills have been suggested for the determination of vapour–liquid equilibria (York and Holms, *loc. cit.*; Baker, *Ind. Eng. Chem.*, 1943, 35, 614; Jones, Schoenborn, and Colburn, *ibid.*, p. 666; Langdon and Keyes, *ibid.*, 1942, 34, 938). The chief defect of these is the use of stopcocks, the lubrication of which is troublesome in presence of organic solvents. A

FIG. 2.

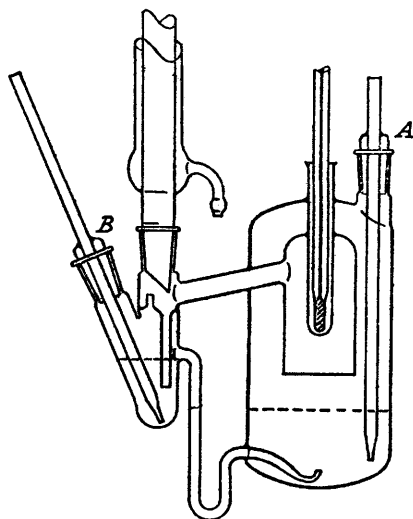


FIG. 3.

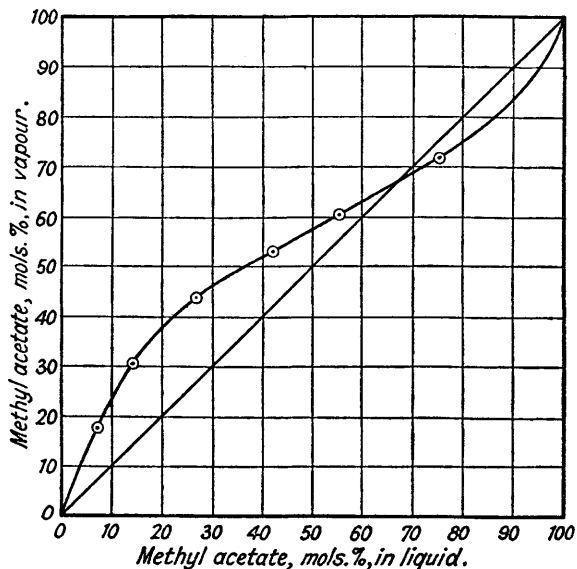
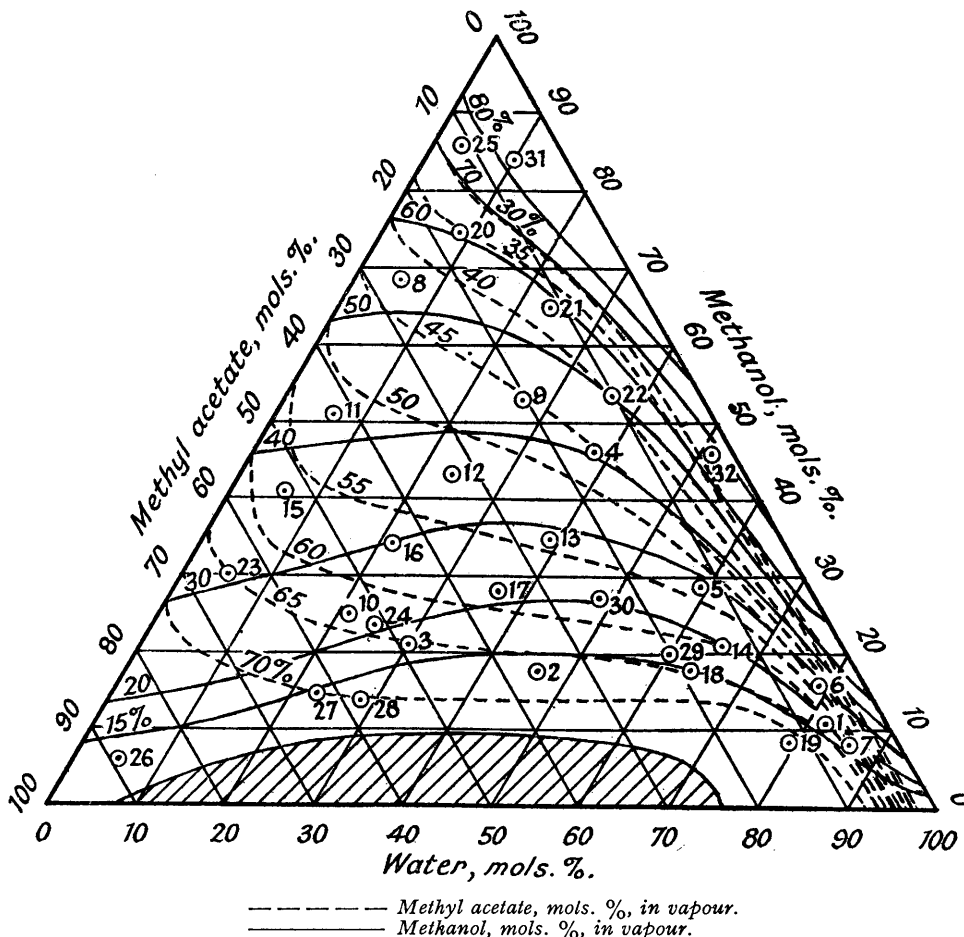


TABLE II.

Soln. no.	B. p.	Liquid compn., mols. %.			Vapour compn., mols. %.		
		H ₂ O.	MeOH.	Ester.	H ₂ O.	MeOH.	Ester.
1	63.7°	82	11	7	21	19	60
2	60.5	46	18	36	18	17	65
3	57.5	30	22	48	17	18	65
4	58.3	38	46	16	14	41	45
5	59.7	58	29	13	17	29	54
6	62.7	78	16	6	23	28	49
7	64.8	86	8	6	24	19	57
8	65.8	5	69	26	5	53	42
9	57.1	26	54	20	12	46	42
10	56.0	21	25	54	15	22	63
11	56.5	7	52	41	5	44	51
12	56.7	23	43	34	13	34	53
13	58.2	39	35	26	18	29	53
14	60.5	65	22	13	19	21	60
15	57.0	6	41	53	7	36	57
16	57.9	21	34	45	13	30	57
17	58.5	37	28	35	18	23	59
18	59.4	63	18	19	19	16	65
19	62.0	79	9	12	13	10	77
20	57.9	8	75	17	5	60	35
21	59.2	24	65	11	8	57	35
22	63.0	36	54	10	13	51	36
23	55.2	5	30	65	4	31	65
24	57.8	25	23	52	15	20	65
25	61.0	3	86	11	2	74	24
26	56.1	5	6	89	6	13	81
27	57.5	23	15	62	15	15	70
28	58.0	29	13	58	16	14	70
29	60.1	60	20	20	20	16	64
30	60.7	49	27	24	19	22	59
31	63.2	10	84	6	3	83	14
32	62.6	51	46	3	18	67	15
33	56.0	0	24	76	0	28	72
34	55.3	0	45	55	0	39	61
35	54.8	0	58	42	0	47	53
36	55.9	0	73	27	0	56	44
37	58.3	0	86	14	0	69	31
38	60.7	0	93	7	0	82	18

modification of the Othmer still in which stopcocks have been eliminated (Fig. 2) was used to evaluate the vapour–liquid relationships. To ascertain that equilibrium was in fact established in the modified equilibrium still, determinations were made with mixtures of methanol and water, the equilibrium relationships of which have been widely recognised (Doroszewsky and Polansky, *Z. physikal. Chem.*, 1910, **73**, 192; Uchida and Kato, *J. Soc. Chem. Ind. Japan*, 1934, **37**, 525; Cornell and Montonna, *Ind. Eng. Chem.*, 1933, **25**, 1331). Determinations of vapour composition over liquid methanol–water mixtures containing 6, 18, 42, 66, and 90 mols. % of methanol showed agreement with those of the above workers to within 1 mol. % in all cases.

FIG. 4.



The numbers beside plotted points refer to Table II, which shows composition of the vapour at these points in the diagram.

Examination of the system methanol–methyl acetate confirmed the presence of a low-boiling binary azeotrope described by Ryland (*Amer. Chem. J.*, 1899, **22**, 384) and Holley (*J. Amer. Chem. Soc.*, 1902, **24**, 449). These workers reported an azeotrope containing 35 mols. % of methanol of b. p. 54.0°. The composition of the azeotrope now obtained was found in repeated physical and chemical tests to be 33.2 mols. % of methanol and 66.8 mols. % of methyl acetate. Its b. p. was 53.9°/760 mm. The complete equilibrium conditions are shown in Fig. 3.

No examination of the system methyl acetate–water was made because of the difficulties introduced by the low mutual solubility range.

The vapour–liquid equilibrium conditions for the ternary mixture were determined from a study of 32 mixtures. The results are shown in Table II. In Fig. 4, lines of constant concen-

tration of methyl acetate (broken lines) and of methanol (continuous lines) in the vapour over the liquid ternary mixtures have been plotted from the results of Table II. (The numbers beside plotted points refer to the vapour compositions given in the table.) It was found impossible to draw lines which would accurately represent the molecular concentration of water in the vapour phase. The lines representing concentrations of water in the vapour between 16 and 20 mols. % are exceptionally widely distributed over the graph so that an error of only 0.5% in its estimation results in a considerable displacement of the line. For this reason no attempt has been made to draw the water concentration lines. The mols. % of water in the vapour phase can be obtained by addition of corresponding percentages of methyl acetate and methanol obtained from Fig. 4 and subtraction from 100%. The accuracy of all ternary mixture estimations is $\pm 0.5\%$.

EXPERIMENTAL.

Preparation of Solutions.—For a ternary mixture, the molar fractions of water, methyl acetate, and methanol, X , Y , and Z , are respectively A/SM_a , B/SM_b , and C/SM_c , where M_a , M_b , and M_c are the respective molecular weights, A , B , and C , the weights, and $S = A/M_a + B/M_b + C/M_c$.

Then $A/B = XM_a/YM_b$, $B/C = YM_b/ZM_c$, and $A/C = XM_a/ZM_c$, and for 10 g. of solution* ($A + B + C = 10$), the weights of water, ester, and methanol required are given by

$$\begin{aligned} A &= 10/(4.108Y/X + 1.777Z/X + 1) & B &= 10/(0.2434X/Y + 0.4325Z/Y + 1) \\ C &= 10/(0.5627X/Z + 2.312Y/Z + 1) \end{aligned}$$

These weights were converted into volumes at 15° by using the densities given in the International Critical Tables (Vol. 3, pp. 25, 27, 28), and the mixtures were then made up by running the requisite volumes of the liquids from microburettes of the reservoir type. The reservoirs of the burettes were kept at $15^\circ \pm 0.1^\circ$ by immersion in a thermostat. The burettes were graduated to 0.01 ml., and 0.002 ml. could be estimated by use of a lens. All numerical calculations were carried out to the fifth decimal place and rounded to the fourth.

Refractive-index and Specific-gravity Determinations.—Picnometers were cleaned with acetone and dried with filtered compressed air. After being filled, they were supported in a thermostatically controlled water-bath till no further expansion of the liquid occurred (2 hours). Excess of liquid was removed with a filter-paper, and the picnometers were carefully dried with a soft cloth and weighed. An electrically driven pump circulated water from the same thermostat through the temperature-compensating system of the Pulfrich refractometer to keep its temperature at $25^\circ \pm 0.1^\circ$. All refractive-index measurements were made by using a sodium lamp as light source. The methanol and methyl acetate were carefully fractionated before use, and conductivity water was used in all estimations.

The accuracy of the graph was tested by trial estimation of 8 standard mixtures. It was found to be accurate to ± 0.5 mol. % in all cases.

Vapour-Liquid Equilibrium Estimations.—The "cowl" surrounding the thermometer pocket in conventional equilibrium stills was retained in the modified still used in the tests described here. The purpose of the cowl is to prevent fractional condensation of the vapour before it reaches the product condenser, and further to reduce the possibility of condensation the still was jacketed with asbestos fibre. The method of operation was as follows. Approximately 100 ml. of liquid were placed in the boiler, which was heated on a sand-bath. The still was heated for 3 hours (determined by trial and error to be the time necessary for the establishment of equilibrium). At the end of this period samples of the product and residue were removed by gently applied air pressure to the still with the sample pipettes in the sample points A and B . Samples of approximately 7 ml. were necessary for the determination of refractive index and specific gravity. Temperatures were noted with an N.P.L. standardised thermometer calibrated to 0.1° .