CCCXXXVII.—*The Equilibrium in Systems Composed of Water and Alcohols: Methyl Alcohol, Pinacone, Glycerol, and Erythritol.*

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The System Methyl Alcohol-Water.

IN a previous communication (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 100) it was shown that, contrary to statements in the literature, ethyl alcohol does not form a definite hydrate with water. With methyl alcohol also, the existence of a long series of definite compounds with water has been inferred from various properties of the solutions (Varenne and Godefroy, *Comp. rend.*, 1904, **138**, 990; De Forcrand, *Ann. Chim. Phys.*, 1892, [vi], **27**, 546; Jones and Getman, *J. Amer. Chem. Soc.*, 1910, **32**, 308). As will be shown in this communication, the study of the equilibrium in the system methyl alcohol-water does not support the supposition that there exists any definite chemical compound of the two substances.

The freezing points of mixtures of methyl alcohol and water were determined by Pickering (T., 1893, **63**, 1015) up to 50 mols. per cent. of alcohol, and by Baume and Borovsky over the whole range (*J. Chim. physique*, 1914, **12**, 276), but neither of these authors examined the eutectic freezing points, so that no conclusions can be drawn from their work as to the existence of solid compounds.

Many temperatures recorded by Baume and Borovsky are far
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too low, owing to supercooling, some of them lying considerably below the true eutectic temperature.

The investigation of the equilibrium in the system methyl alcohol-water was carried out according to the method employed in the case of the system ethyl alcohol-water (*loc. cit.*). The mixture to be examined was placed in a glass vessel, which was enclosed in two or three glass mantles, and the whole system was cooled with liquid air. The temperature was recorded by a thermo-element and a galvanometer.

If the necessary precautions are not taken, methyl alcohol and many of its mixtures with water, when cooled to the temperature of crystallisation, do not crystallise at all but become transformed into a hard, glassy mass. In order to induce crystallisation it is necessary that at temperatures near the point of crystallisation the rate of cooling be very slow and that the mixture be continually stirred.

The results of the study of the system methyl alcohol-water are given in Table I and Fig. 1, A.

TABLE I.
Methyl alcohol and water.

Concentration of methyl alcohol in mol. %	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.	Concentration of methyl alcohol in mol. %	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.
0	0°		60	-87.5°	-101.5°
10	-13.5°		70		-111
20	-30.2	-102°	72		-101
33.3	-59	-100.5	80		-102
40	-65	-102	85		-107
44	-78.5	-100.5	90		-103.5
50	-83.5	-100.5	95		-100.5
54		-100.5	100	-96°	

Pure methyl alcohol crystallises at -96° . Its cooling curve, which is that characteristic of a pure substance, is shown in Fig. 1, B, 1—1.

Solutions with a content of 10—60 mol. per cent of alcohol gave a definite temperature of first crystallisation (in most cases with great overcooling), and also a definite temperature of eutectic crystallisation. Fig. 1, B, 2—2 and 3—3 show the cooling curves for solutions containing 60 and 40 mol. per cent. of alcohol, respectively.

In solutions with a content of more than 60 mol. per cent. of

alcohol the temperature of first crystallisation could not be determined. For this reason the branch of the diagram connecting the freezing point of pure alcohol and the eutectic point remained undetermined. The eutectic crystallisation at -100.5° was determined over the whole range of composition. Some of the solutions showed a great overcooling of the eutectic point. By repeated determinations, this point was raised from -122° to -103.5° in the case of 90 mol. per cent. of alcohol, and from -110.5° to -107° in the case of 85 mol. per cent. of alcohol. For mixtures of 80 and 72 mol. per cent. of alcohol, not only the cooling curve, but also the heating curve was determined. The melting point for the first mixture was determined as -102° , for the second as -101° . The temperature for the second mixture is very close to that obtained by the method of cooling (-102°). As concerns the position of the eutectic point, the maximum of the duration of crystallisation at the eutectic temperature (-100.5°) was determined for a mixture containing 80 mol. per cent. of alcohol. Near this ordinate is the eutectic point.

It will be seen that the equilibrium diagram of the system methyl alcohol-water is characterised by two branches, which cross at the eutectic point and can be traced through the whole diagram. It follows, therefore, that in the crystalline state methyl alcohol does not form any definite compound with water. Both substances give mechanical mixtures only.

Since the calorific effect is positive when methyl alcohol is mixed with water (De Forcrand, *loc. cit.*), it follows that hydrates of a definite composition, if they exist at all, should be of an exothermic nature. Their stability should increase with decrease of temperature and with the transition from the liquid to the solid state. Therefore it can be stated with great probability, that if definite compounds of methyl alcohol and water do not exist in the

TABLE II.

Pinacone and water.

Concen- tration of pinacone in mol. %.	Temperature		Duration of eutectic crystallisation in minutes	Concen- tration of pinacone in mol. %.	Temperature		Duration of eutectic crystallisation in minutes
	of first crystal- lisation.	of eutectic crystal- lisation.			of first crystal- lisation.	of eutectic crystal- lisation.	
0		0°		31.1	43.3	40.2	
0.5	16.7°	—	0.45°	34.3	41.8	40.3	
0.79	22.4	—	0.45	36.5		40.4	
0.86	22.0			37.8	40.7	40.2	2.0
1.3	28.0			39.6	40.6	40.0	1.9
2.0	33.8			40.0		40.4	
2.2	34.7	—	0.5	42.0		39.5	1.4
2.7	37.4			45.0	41.2		
3.6	40.2	—	0.5	50.0	41.25		
5.1	42.6	—	0.6	53.3	41.2		
5.5	43.2	—	0.4	57.5	41.0	27.2	0.2
6.5	43.7	—	0.6	63.7	39.4	28.2	
8.0	44.4	—	0.7	64.8	39.5	27.9	
9.6	44.9	—	0.7	70.8	36.6	29.2	1.4
11.6	45.2	—	1.0	75.0		29.3	1.6
12.7	45.3	—	1.5	76.4	33.7	29.3	1.7
14.27	45.4	—		80.4		29.4	2.1
14.34	45.4	—		82.8	30.2		
17.0	45.3			86.2	32.4	29.1	
19.5	45.2	37.3	0.2	87.0	33.2	29.35	1.3
21.9	45.1	37.8	0.6	93.4	38.6		
24.4	44.8	40.1	1.0	97	39.7		
29.1	43.7	40.2	1.2	100	41.1°		

crystalline state below -100° , their existence in the liquid state at the ordinary temperature is still less probable.

The System Pinacone-Water.

Fittig (*Annalen*, 1859, **110**, 25; 1860, **114**, 54) showed the existence of a hydrate of pinacone with the definite composition $C_6H_{14}O_2 \cdot 6H_2O$. Linnemann (*Annalen Suppl.*, 1864, **3**, 374; *J. Chem. Soc.*, 1871, **24**, 422) found that pure pinacone melts at $35-38^{\circ}$ and its hydrate at 46.5° . Couturier (*Ann. Chim. Phys.*, 1892, [vi], **26**, 479) states that the melting point of pinacone hydrate is 56° . Systematic investigation of the system pinacone-water has not hitherto been carried out.

The cooling curve of commercial pinacone was of the kind characteristic of an impure substance (the first crystals were deposited at 33° and the eutectic temperature appeared to be 29.4° ; Fig. 2, B, 1—1). It was necessary, therefore, to purify the substance before investigation. After several crystallisations, the freezing point rose from 33° to 41.1° , and the eutectic point at 29.4° disap-

peared completely (Fig. 2, B, 2—2). Further purification did not change the temperature of crystallisation.

Contrary to the behaviour of methyl and ethyl alcohols, pinacone and its aqueous solutions crystallise well. A slight overcooling can easily be avoided by stirring the liquid and by inoculation with crystals. On account of the great volatility of pinacone, superfluous heating of its solution should be avoided in order to prevent perceptible change in concentration.

The results of the investigation are given in Table II and shown graphically in Fig. 2, A.

The equilibrium diagram consists of five branches:

1. From pure pinacone to a mixture containing 80 mol. per cent. of pinacone. To the latter composition corresponds a eutectic point at 29.4° . The duration of the eutectic crystallisation renders improbable the existence of solid solutions of water in pinacone.

2. From 80 mol. per cent. to 50 mol. per cent. of pinacone. The eutectic crystallisation in this section is very prominent and can be traced up to the maximum of the curve. This maximum corresponds to a definite compound of pinacone and water, the monohydrate, $C_6H_{12}(OH)_2 \cdot H_2O$. It crystallises at 41.25° . The curve is very flat on both sides of this maximum.

3. From 50 mol. per cent. to 38.5 mol. per cent. of pinacone. To the latter composition corresponds a second eutectic point at 40.4° .

4. From 38.5 to 14.3 mol. per cent. of pinacone. The curve rises again and reaches, at 14.3 mol. per cent., a maximum, which corresponds to another compound of pinacone and water, the hexahydrate, $C_6H_{12}(OH)_2 \cdot 6H_2O$, which crystallises at 45.4° . This compound was described for the first time by Fittig. The statement

FIG. 2.
Mol. per cent. of pinacone.

of Couturier that it crystallises at 56° is incorrect. The eutectic crystallisation at 43° can be traced through the whole section from 38.5 to 14.3 mol. per cent. of pinacone.

5. From 14.3 mol. per cent. of pinacone to pure water. The phenomenon of overcooling at the eutectic temperature becomes more marked with increasing content of pinacone (from -0.45° to -1.5°). The eutectic temperature can be traced up to the hexahydrate.

Investigation of the system pinacone–water established the existence of two definite compounds, the monohydrate, $C_6H_{12}(OH)_2 \cdot H_2O$ (m. p. 41.25°), and the hexahydrate, $C_6H_{12}(OH)_2 \cdot 6H_2O$ (m. p. 45.4°); and the existence of two eutectic mixtures, containing respectively 80 mol. per cent. (m. p. 29.4°) and 38.5 mol. per cent. (m. p. 40.4°) of pinacone.

The System Glycerol–Water.

The sample of glycerol crystallised at 13.3° instead of 17° , the value given by Henninger (*Ber.*, 1875, 8, 643). In order to purify it, the specimen was exposed to quicklime for some time and distilled in a vacuum; it then crystallised at 18.0° . It was not found possible to raise the crystallisation point above this value. The purified material crystallised well, formed colourless crystals, and gave the characteristic cooling curve of a pure substance. As is well known, crystallisation of glycerol without inoculation is very difficult. Stirring alone is not sufficient; the cooled liquid does not crystallise, but is transformed into a gelatinous, transparent mass, as in the case of some other alcohols. Crystallisation becomes more difficult as the water content increases. From solutions the concentrations of which are near the eutectic concentration glycerol crystallises with very great difficulty. Solutions containing 70–75 mol. per cent. of glycerol could not be induced to crystallise at all.

The mixture under examination was cooled either at once by solid carbon dioxide or successively by a mixture of snow and salt and by solid carbon dioxide. In order to make the rate of cooling slower, the mixture was enclosed in two glass mantles.

The results of the investigation are given in Table III, and shown graphically in Fig. 3, A. Fig. 3, B shows the cooling curve of pure glycerol.

As has already been shown, pure glycerol crystallises at 18.0° . The addition of water lowers the temperature of crystallisation. By interpolation of the values from Table III, it can be seen that the temperature of first crystallisation at 13.3° corresponds with a concentration of water of 11.3 mol. per cent. or 2.25 per cent. by

TABLE III.
Glycerol-water.

Concentration of water in mol. %.	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.	Concentration of water in mol. %.	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.
0	18.0°		46.0	-4.3	0.3
1.8	17.3°		58.0	-14.7	
2.8	16.9		66.4	-18.5	0.5
5.5	15.7		80.0		0.7
17.0	9.5		85.0	-21.0	0.5
18.8	9.1	0.1	90.0	-7.5	0.4
26.5	4.8		100	0°	
35.1	-1.3	0.2			

weight. This was the quality of the sample of glycerol before purification.

The diagram of the system consists of two branches which cross at the eutectic point. This point corresponds to a temperature of 28.0° and an average concentration of glycerol of 20 mol. per cent. Owing to the reluctance to crystallisation of mixtures near the eutectic composition, it was very difficult to determine precisely the concentration corresponding to the eutectic point. Eutectic crystallisation was observed with all the solutions investigated. The duration of eutectic crystallisation, determined for 1 gram of the mixture, shows that water does not form a solid solution with glycerol. In the crystalline state, both substances form only a mechanical mixture.

A sample of pure glycerol being available, it seemed of interest to determine the hitherto unknown cryoscopic constant. Although the difficulty of crystallising glycerol did not allow of great precision,

FIG. 3.

yet the values obtained agreed moderately well with one another. The results are recorded in the following table.

TABLE IV.

The determination of the cryoscopic constant of glycerol.

Weight of glycerol in grams.	Weight of water in grams.	$\Delta t.$	K for 1000 grams of solvent.
11.4474	0.0435	0.690°	3.27
10.7008	0.0610	1.116	3.52
11.4474	0.1297	2.326	3.69

The lowering of the freezing point of pure glycerol was determined with the aid of a Beckmann thermometer. Crystallisation was attained by inoculation with a small crystal of glycerol. Without the latter precaution, overcooling of the mixture could not be prevented. As shown in Table IV, the cryoscopic constant for 1000 grams of substance lies within the limits 3.27 and 3.69. As the most accurate value for the constant corresponds to the most dilute solution, we can, by extrapolating to 0, assume that the cryoscopic constant of glycerol, determined for 1000 grams of the solvent, is nearly 3.1.

From Table IV it will be seen that a mixture containing 11.4474 grams of glycerol and 0.0435 gram of water, that is, with a content of 0.38 mol. per cent. of water, has a freezing point 0.69° lower than that of pure glycerol. A depression of the freezing point of 1.82° therefore corresponds to a content of 1 per cent. by weight of water, and a depression of 0.1° corresponds to a content of 0.055 per cent. by weight of water. As depressions smaller than 0.1° can be easily detected with the Beckmann thermometer, it is obvious that the determination of the freezing point of glycerol affords a sensitive and precise method for the quantitative estimation of even small quantities of water in glycerol.

The System Erythritol-Water.

A sample of erythritol showed a crystallisation point of 116.6° instead of 120°, the temperature given by Ruff (*Ber.*, 1899, **32**, 3677). As only a small quantity of the erythritol was available, the crystallisation point of the pure substance could not be determined. However, the cooling curve of the sample (Fig. 4, B) was not unlike that of a pure substance.

All our investigations were made with this sample. Both pure erythritol and its aqueous solutions crystallise moderately well, yet to avoid overcooling it was necessary to inoculate with a crystal

TABLE V.
Erythritol-water.

Concentration of erythritol in mol. %.	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.	Concentration of erythritol in mol. %.	Temperature of first crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.
100	116.6°		17.5	54.6	3.9
92.4	114.0°		14.4	40.4	
91	113.2	1.3	13.4	36.5	—4.4
80	110.2	— 7.2	11.1	27.4	—4.4
75.2	106.5		9	22.8	—4.1
65.7	102.5		7.0	14.0	—4.4
56.4	97.5	2.4	4.8	— 1.0	—4.4
42.4	87.8	2.7	3.0		—4.1
38.9	82.0		2.5	— 3.1	—4.5
33.3	76.2	3.1	2	— 2.4	
29	70.5	3.3	0.9	— 1.1	
26.1	65.0	— 4.7	0	0°	

of erythritol. The results are recorded in Table V and shown graphically in Fig. 4, A.

It will be seen that the diagram of the system erythritol-water consists of two branches, which cross at the eutectic point. The concentration of erythritol at this point is 3 mol. per cent. and the temperature -4.4° . The eutectic crystallisation can be followed through the whole diagram. Erythritol forms with water neither compounds nor solid solutions, and in the crystalline state, erythritol and ice yield mechanical mixtures only.

The determination of the cryoscopic constant of water, with erythritol as solute, gave the value 1.94 for 1000 grams of the solvent as the mean of three determinations, which is near the theoretical value 1.86. This fact

FIG. 4.

TABLE VI.

Grams of water.	Grams of erythritol.	$\Delta t.$	The cryoscopic constant calcu- lated for 100 grams of the solvent.
12.3414	0.5598	0.724°	19.5
12.3414	0.8648	1.097	19.1
12.1644	1.5504	2.06	19.6
			Mean 19.4

confirms our conclusion that erythritol does not form solid solutions with water.

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