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The following papers were read:

Chemistry. — "*On the composition of the vapour-phase in the system Water-Phenol, with one and with two liquid-phases*".
By Dr. F. A. H. SCHREINEMAKERS (Communicated by Prof. J. M. VAN BEMMELEN).

(Read April 21, 1900.)

1. *The apparatus.*

To determine the composition of the vapour phases the apparatus shown in fig. 1 was used. The flash *A* into which the mixture to

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be investigated was introduced is closed by means of a ground joint in tube *B* containing a little mercury in which the thermometer was placed.

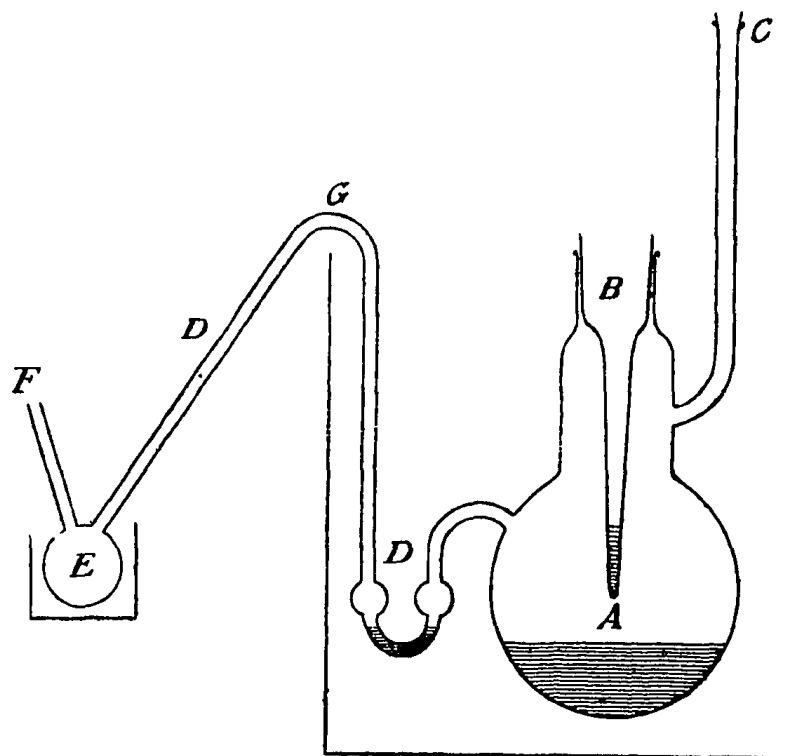


Fig. 1.

The tube *C* is connected by means of a ground joint with the condenser and through this with a space of about 18 litres capacity, in which the pressure can be altered as desired by means of a pump; the pressure in this space was determined by means of an open mercury-manometer.

The flask *A* is further connected by means of the tube *D* with the little flask *F* which is connected by a ground joint with *D*. This flask may further be connected by means of *F* with the outer air, or with the space with which *A* is always connected or with another space in which the pressure may be regulated at will. In order to determine the vapour tension at a certain temperature, the bath was raised a few degrees above the desired temperature and the pressure in the space which is connected with *A*, afterwards altered, until the liquid contained in *A* began to boil. By a further slow change of the pressure, the boiling point of the liquid was brought to the desired temperature and read off on the thermometer placed in *B*.

The vapour evolved in *A* ascends through *C* into the condenser,

where it is condensed and returned to *A*; it cannot pass into the space *E*, because the tube *D* contains a little mercury between the two small bulbs, and the space *E* is connected with the same space as *A*.

To determine the composition of the vapour phase, some vapour from *A* was transferred to the flask *E*, which was placed in a freezing mixture in order to completely condense the vapour. In order to transfer the vapour from *A* to *E* the latter was connected, by means of the tube *F*, with a space in which the pressure was a little less than that in the space connected with *A*. The vapour evolved in *A* now bubbles through the mercury in the tube *D*; the rapidity with which this takes place may be regulated at will by making the difference in pressure between *A* and *F* greater or smaller. By means of this arrangement, it is not only possible to regulate the rate at which the vapour is conveyed from *A* to *E*, but also to stop or to restart the transference at will, the temperature and pressure in *A* remaining unchanged. Because the bath has always a higher temperature than the liquid and vapour in *A*, no condensation can take place in that part of the tube *D* which is immersed in the bath, but condensation may occur in the part of the tube which is outside the bath. To prevent condensation at *G* this part of the tube was maintained at a higher temperature by means of a small flame; the vapour which condensed in the further end of *D*, was transferred to *E* by heating after the distillation was ended.

The composition of the liquid remaining in *A* was, of course, altered by the removal of vapour; as, however a quantity of 100—200 grams was introduced into *A* and only 5—10 grams of liquid condensed in *E*, the change in *A* was as a rule comparatively small, unless the vapour- and liquid-phases differed very much in composition. In such cases I give the composition of the liquid-phase both at the beginning and the end.

During the transfer of vapour from *A* to *E*, vapour was continually rising into the condenser where it was condensed. This condensed liquid, the composition of which was, of course, in general different from that of the liquid in *A*, gave off a different vapour when flowing down the sides and so caused an error. As a rule, however, this error will doubtless be small. Some determinations have been repeated without admitting any vapour into the condenser during the transfer from *A* to *E*. For this purpose a little apparatus was used by means of which the tube *C* could be closed and reopened below the level of the bath. The use of this apparatus, however, gave rise to many difficulties and it was therefore only used a few times.

As experience showed, the determinations of the vapour tension

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are not quite correct but may be wrong to the extent of a few m.m.; this was found by repeating several times the determination of the vapour-tension of pure water or of a three-phase system in the same apparatus at the same temperature and with the same thermometer, when the determinations sometimes differed among themselves to the extent of 2 or 3 m.m. The liquid collected in the flask *E* was at the end of the operation weighed and analysed. In the system Water-Phenol, the phenol was estimated by the method of KOPPESCHAAR, i. e. by titration with a solution of K Br and K Br O₃.

II. *The three-phase system.*

In the system: Water-Phenol, three phases can be in equilibrium with each other between the transition-temperature (about 1°5) and the critical temperature (about 68°), namely two liquid-phases and the vapour. The composition of the two liquid-phases, which may be in equilibrium with each other at the different temperatures, has already been investigated several times, among others, by ALEXEJEFF ¹⁾ and V. ROTHMUND ²⁾; I have now determined the composition of the vapour-phase in the way described.

In table I *T* stands for temperature; *P* for the pressure of the three-phase system in m.m.; *L*₁ *L*₂ and *L*_v for the composition of the three phases, *L*₁ and *L*₂ for those of the two liquids and *L*_v for that of the vapour. The composition is expressed in percentage by weight of phenol in the mixture of phenol and water.

TABLE I.

<i>T</i>	<i>P</i>	<i>L</i> ₁	<i>L</i> ₂	<i>L</i> _v
29.°8	29	8	70	5.96
38.°2	48	9.5	67	6.98
42.°4	62	10	66	6.91
50.°3	94	12	63	7.28
56.°5	126	14.5	60	7.83
60.°1	150	17	57	8.06
64.°4	182	22.5	48	8.66

The composition of the three phases is shown graphically in figure 2; the temperature is measured along the horizontal axis, the pressure along the vertical axis. The lines *L*₁ and *L*₂ represent

¹⁾ Wied. Ann. 28. 305.

²⁾ Zeitschr. f. Ph. Ch. 26. 433.

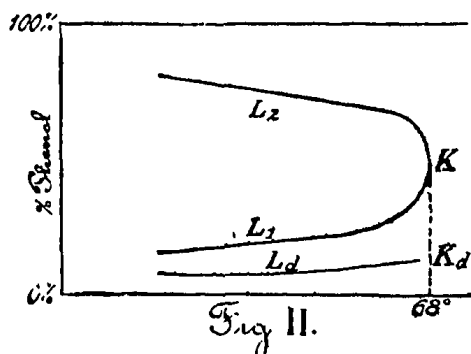
the two liquid-phases, the line L_v the vapour-phase. It will be seen from the figure, that the two liquid-phases L_1 and L_2 gradually approach the same composition as the temperature rises, and that at 68° they become identical at a point k which indicates about 34 pCt. of phenol. The line L_v , which shows the vapour phases, which may be in equilibrium with both the liquid-phases, lies entirely below the line L_1 . The vapour-phase, therefore contains less phenol than occurs in either of the other liquid-phases.

If we call L_1 , which contains the most water, the aqueous, and L_2 , which contains the most phenol, the phenol-layer, then the vapour contains still less phenol than the aqueous layer.

If a mixture of two liquid-phases of water and phenol is distilled at a constant temperature, say $56^\circ.5$, then according to the preceding table the vapour pressure is 126 m.m.; the aqueous layer then contains 14.5 pCt. of phenol, the phenol-layer on the other hand 60 pCt., whilst the vapour only contains 7.83 pCt. of phenol. The aqueous layer has, therefore, a composition between that of the vapour and the phenol-layer; on distillation the aqueous layer will be resolved into the phenol-layer and the vapour, its volume decreasing continually until finally only the phenol-layer remains in the retort. If now the distillation is pushed further at constant T , the pressure cannot longer remain constant, but it must fall as there are now only two phases remaining instead of three. I will revert to this matter presently.

The vapour-curve L_v has in this system, a position *outside* the two liquid-curves L_1 and L_2 . In other systems it may, however, be situated between them; this is for instance the case with the system Water-Aniline which I will mention later on.

It is plain that the different position of branch L_v may give rise to other phenomena during the distillation of two liquid phases. This will be discussed subsequently.



In Figure 2, the pressure has not been included; this might be done by introducing a third axis perpendicular on the plane of the drawing and marking on this the pressure. The lines L_1 L_2 and L_v then no longer lies in the plane of the drawing, but in space, in such a way that their three

projections on the plane P—T form a curved line.

This line on the plane P—T shows the relation between the temperature and the pressure of the three-phase system. It is, according to table 1, a line which rises with the temperature.

III. *The two-phase system.*

The different two-phase systems which may appear in a binary system, leaving solid phases out of account, are:

1st The system of two liquid-phases.

2nd The system of a liquid with vapour.

The first system has been investigated by VAN DER LEE¹⁾; he determined the influence of the increase in pressure on the lines L_1 and L_2 , and found it to be very small.

I have now examined the second system, mainly in order to discover the connection between the composition of the liquid and the vapour. This may be done in two widely different ways; first the boiling-points and the compositions of the vapours of liquids of different composition may be determined at a constant pressure; secondly the vapour-pressure and composition may be determined at a constant temperature. I have chosen the last method at the temperatures 56°3, 75° and 90°. The first temperature is situated below the critical point; two liquid phases therefore make their appearance; at the two other temperatures this is not the case.

The following table contains the determinations at 56°3.

TABLE 2.

N ^o .	L	D	P
1	0 pCt.	0 pCt.	125 mm.
2	2.0	2.55	125
3	5.58	5.49	127
4	7.42	6.57	126.5
5	10.88	7.42	127
6	14.5—60	7.83	126
7 ^b	69.2	} 9.88	124
7 ^e	76.7		122
8 ^b	80.34	} 11.98	118
8 ^e	83.06		102

The percentage of phenol in the liquid is given under L ; the composition of the vapour under D , and the vapour pressure under P .

Determination N^o. 6 relates to the *two* liquid-phases which may

¹⁾ Dissertation. Amsterdam.

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be in equilibrium with each other at 56°.3, one of which contains 14.5 pCt., the other 60 pCt. of phenol.

Determination N^o. 7 is entered under 7^b and 7^e ; 7^b gives the initial, 7^e the final concentration of the liquid. As will be seen, these differ by 7.5 pCt., whilst the vapour differs immensely in composition from the liquid.

The same applies to determination 8.

As will be seen from the table, a liquid containing about 5.5 pCt. of phenol yields a same composition. Liquids containing less than 5.5 pCt. of phenol yield a vapour containing more phenol than the liquid; liquids containing more phenol, however, yield a vapour containing less phenol.

Table 3 gives the determination at 75°.

TABLE 3.

No.	L	D	P
1	0	0	289
2	2.43	3.44	293
3	4.15	5.21	293
4	7.51	7.41	294
5	16.82	9.11	294
6 ^b	22.53	} 9.36	294
6 ^e	24.18		294
7 ^b	44.44	} 9.85	294
7 ^e	49.2		294
8 ^b	60.47	} 10.43	292-293
8 ^e	65.75		± 289
9 ^b	76.7	} 12.63	280
9 ^e	82.4		259
10 ^b	88.06	} 21.37	218
10 ^e	91.7		177

In determination N^o 4, the vapour and liquid have again about the same composition; with a percentage of 7.2 of phenol they are identical.

If therefore a liquid containing less than 7.2 pCt. of phenol is distilled at 75°, the vapour contains more phenol than the liquid; the reverse is the case if the liquid contains more than 7.2 pCt. of phenol.

The determinations at 90° are given in table 4.

TABLE 4.

N ^o .	L	D	P
1	0	0	525 mM.
2	2.36	3.64	528
3	7.00	7.69	531
4	8.29	8.30	531
5	9.74	8.96	530
6 ^b	17.4	10.40	530
6 ^e	20.4		530
7 ^b	33.6	10.78	530
7 ^e	35.0		530
8 ^b	42.2	10.87	530
8 ^e	44.2		530
9 ^b	56.3	11.24	530
9 ^e	58.0		530

As shown in this table, the liquid which at this temperature is in equilibrium with a vapour of the same composition contains about 8.29 pCt. of phenol.

The results shown in the first three tables may be represented graphically in different ways.

I will here, however, make use of only one of these, namely that showing the composition of the vapour-phase as a function of the liquid. The vapour-pressure is thus not considered.

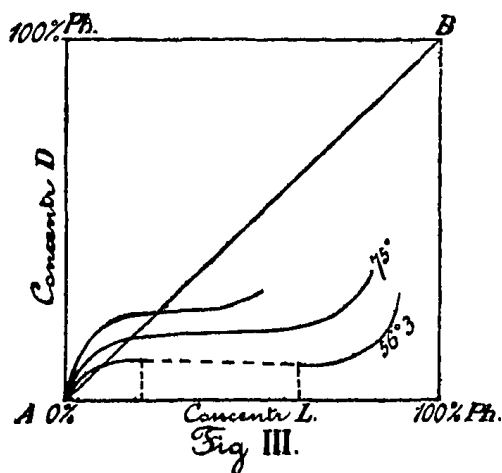


Figure 3 is a graphical representation of this kind; the concentration of the liquid is measured along the horizontal axis, that of the vapour (in percentage of phenol) along the vertical axis.

If we draw the line AB through the square, the points on it represent liquids whose vapour has the same composition. If a point is situated to the left of AB , the vapour contains more phenol than the liquid; if to the right it contains less phenol.

From the drawing it is seen that at each of the three temperatures, a liquid containing a small quantity of phenol yields a vapour containing more, and one containing much phenol yields a vapour containing less phenol than itself.

The point of intersection of a curve with AB represents a liquid which is in equilibrium with a vapour of its own composition. The proportion of phenol in this liquid increases with the temperature. This liquid must have a maximum or a minimum vapour pressure; in our case a maximum one.

In our case, according to table 2, the maximum must be at N^o. 3 namely 127 m.m.; in No. 4 the vapour-pressure is certainly not quite accurate, as N^o. 5 again indicates 127 m.m. The deviation is, however, far within the experimental error which may amount to several mm. That, in figure 3, the line of 56.3° ends, at least experimentally, in the points L_1 and L_2 is clear, because L_1 and L_2 indicate the composition of the two liquid-phases which are in equilibrium with the vapour. If, therefore, water and phenol are brought together in such a proportion, that the mixture is represented by a point situated between L_1 and L_2 , this will break up at 56°3 into the two liquid-phases L_1 and L_2 and vapour, the concentration of which is indicated by the ordinate of one of these points.

In the two other curves the straight line $L_2 L_1$ does not occur; they belong to temperatures above the critical point. They, however, present the peculiarity, that they are almost horizontal for a considerable distance; or in other words — as may also be seen from the tables 3 and 4 — when the liquid has reached a certain percentage of phenol the composition of the vapour is but little affected even by considerable variations in the amount of phenol in the liquid. According to table 3, the vapour at 75°0 only changes from 9.11 to 10.43 pCt. of phenol, when the liquid changes from 16.82 to 65.75 pCt. With a still larger percentage of phenol in the liquid the amount of phenol in the vapour increases more rapidly, finally increasing very fast indeed, since all the lines in figure 3 must terminate at B .

Not only the amount of phenol contained in the vapour, but also the vapour-pressure alters but little, when the composition of the liquid varies between very wide limits.

In table 3 the maximum of vapour-pressure must lie between the two determinations 3 and 4 and very close to N^o. 4. In determinations 4, 5, 6 and 7, the vapour pressure is constant at 294 m.m.; theoretically this is, of course, impossible, but experimentally the differences may fall quite within the limits of experimental errors.

VAN DER LEE has also measured the vapour pressure at 75°; he also finds a vapour-pressure of 294 mm. when working with a liquid of widely varying concentration. His other determinations agree fairly well with my own; only liquids containing a very large amount

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of phenol show differences. As I have now determined the composition of liquid and vapour, it is possible to test the observations by means of the approximately accurate formula of VAN DER WAALS:

$$\frac{dP}{dx_d} = \frac{P(x_d - x_l)}{x_d(1 - x_d)}.$$

The best way would be to take the values of x_d and P from the determinations as also the values of $\frac{dP}{dx_d}$, and then to calculate x_l by means of the formula and compare this value with the experimental result. In our case, however, $\frac{dP}{dx_d}$ cannot accurately be deduced from the experiments, as P does not change or very little between very wide limits.

I have therefore, followed a different plan and calculated $\frac{dP}{dx_d}$ by means of the experimental values of P , x_d and x_l from the formula. For this purpose let us take the determinations at 75° (table 3) and recalculate everything in molecules; let us then take the mean of the initial and final compositions and pressures in experiments 7, 8, 9 and 10. We then obtain:

TABLE 5.

No	x_l	x_d	$x_d - x_l$	P	$\frac{dP}{dx_d}$
1	0	0	0	289	
2	0.0047	0.0067	+0.0020	293	+ 88
3	0.0082	0.0104	+0.0022	293	+ 62
4	0.0153	0.0151	-0.0002	294	- 3
5	0.0372	0.0188	-0.0184	294	- 294
6	0.0551	0.0193	-0.0358	294	- 556
7	0.1446	0.0204	-0.1242	294	-1825
8	0.2477	0.0218	-0.2259	291	-3083
9	0.4296	0.0269	-0.4027	270	-4154
10	0.6322	0.0493	-0.5829	197	-2449

From the values of $\frac{dP}{dx_d}$ in the preceding table I have calculated the values of ΔP for each pair of successive observations.

Considering for example observations 2 and 3, the value of $\frac{dP}{dx_d}$ may be regarded as the mean of the values found in the two exper-

iments, i. e. $\frac{88 + 62}{2} = 75$; the value of ΔP between observations 2 and 3 is therefore,

$$\Delta P = \Delta x_d \frac{dP}{dx_d} = (0.0104 - 0.0067) \times 75 = 0.35.$$

The values of $\frac{dP}{dx_d}$ and ΔP thus obtained are given in table 6; also, for comparison, the values of ΔP obtained by direct experiment.

TABLE 6.

Between observations	$\frac{dP}{dx_d}$	ΔP calculated	ΔP found
No. 2 and No. 3	75	0.3 m.M.	0 m.M.
3 > 4	30	0.1	1
4 > 5	— 149	— 0.5	0
5 > 6	— 425	— 0.2	0
6 > 7	— 1190	— 1.3	0
7 > 8	— 2454	— 3.4	— 3
8 > 9	— 3618	— 18.5	— 21
9 > 10	— 3302	— 73.9	— 73

As may be seen from the table, ΔP calculated and ΔP found agree satisfactorily; the difference are smaller than the experimental errors which may amount to several m.ms.

Chemistry. — "*Echinopsine, a new crystalline vegetable base*".

By Dr. M. GRESHOFF (Communicated by Prof. A. P. N. FRANCHIMONT).

(Read April 21, 1900).

Of late years alkaloids have been discovered in plantfamilies which, previously, had been made but little the subject of phyto-chemical studies, and in which, at any rate, no vegetable bases had been found or even suspected. So, for instance, in the large family of the *Compositae*, which comprises about one-tenth part of all the phanerogamia, with more than 800 genera.

The writer has been engaged for many years in the systematic study of alkaloidal distribution in plants, also in this family,¹⁾ and

¹⁾ Compare: *On the distribution of alkaloids in the family of the Compositae*. Ned. Tijdschr. v. Pharm., Mei 1900, blz. 137. In this article 50 alkaloid-containing genera are summarised, mostly the result of my own investigations.