CXLVI.—*Freezing-point Curve for Mixtures of Camphor and Phenol.*

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PHARMACOLOGISTS are well acquainted with the fact that when a small amount of camphor is added to phenol, the mixture assumes the liquid state, and remains in that condition even when cooled to temperatures considerably below the freezing point of phenol. This liquefaction might simply be due to the camphor dissolving in the phenol, thereby lowering the freezing point of the latter; a second reason for the liquefaction might be the formation of a compound of the two substances, the freezing point of the compound being lower than that of phenol. Léger (*Compt. rend.*,

1890, 111, 109) has stated that phenol and camphor unite to form two compounds, a monocamphoride melting at -23° , and a hemi-camphoride which remained in the liquid state even when cooled to -50° . Should these statements be correct, the liquefaction which succeeds the addition of camphor to phenol is easily explained. A reference to Léger's paper will show, however, that these conclusions were drawn from what, according to modern physico-chemical ideas, would be regarded as very slight and insufficient experimental evidence. This fact, coupled with the natural interest of the subject, and the additional fact that statements of Léger's relating to mixtures of camphor with the naphthols and other phenolic substances have recently been disproved by Caille (*Compt. rend.*, 1909, 148, 1458), led the authors to re-investigate the subject.

In any such investigation, trustworthy results can only be obtained by examining the behaviour of a large number of mixtures containing the two components in varying proportions. By constructing, therefore, the complete freezing-point curve for all mixtures ranging from pure phenol on the one hand to pure camphor on the other, it will be possible to say, from the form of the curve, whether compounds of phenol and camphor are produced or not when the two substances are mixed.

The phenol used for the experiments was obtained from Kahlbaum, and was freed by distillation from any small amount of water which it might contain. The camphor was the best Japan variety. The results obtained from determinations of the melting points showed both substances to be quite pure.

Suitable amounts of the two substances were weighed into a large test-tube, and were completely mixed by melting them together. The tube was then surrounded by a wider one, thus forming an air jacket, and the whole placed in a vessel filled with a suitable cooling medium. For the mixtures which contained only small amounts of camphor, water formed a suitable cooling agent, whilst in the case of mixtures in which only small quantities of phenol were present, the outer vessel was filled with hot mineral oil. For the cooling of the other mixtures, mixtures of ice and salt or of alcohol and solid carbon dioxide were employed. Uniformity of temperature in the mixture undergoing examination was secured in most cases by means of a mechanical stirring arrangement; with some of the mixtures stirring was difficult, because of the great viscosity of the mixture. Various thermometers were used to indicate the freezing point of the mixtures, a pentane thermometer being used to record the lowest temperatures. The different thermometers were compared with one another, and a table of

corrections compiled, by means of which the readings given by different instruments could be made comparable. The commencement of freezing was quite apparent in the case of the mixtures containing small amounts of camphor, but with all other kinds of mixtures the most satisfactory way to detect the freezing point was found to be to measure the rate of cooling of the mixture, and note the point at which that rate changed. The change in the rate of cooling was in some cases of small dimensions, thus making it a matter of some difficulty to accurately determine the freezing point. It may also be mentioned that with those mixtures which contained large amounts of camphor, it was difficult to see when the camphor began to separate, owing to the refractive indices of the liquid and the solid being very nearly equal. On account of these difficulties, coupled with the difficulty of stirring already mentioned, many of the temperatures given in the table of results may be subject to an error which may amount to 1° . Several determinations of the freezing point were, as a rule, made with each mixture, the results of the different experiments being, for the most part, in close agreement when due allowance is made for the above-mentioned experimental difficulties.

In order to prevent the mixture from being too greatly under-cooled, the consequence of which would, in all probability, be the

TABLE OF RESULTS.

Percentage of camphor in mixture.	Molecular percentage of camphor.	Freezing point.	Percentage of camphor in mixture.	Molecular percentage of camphor.	Freezing point.
0.00	0.00	40.3	61.51	49.71	-20.1
2.32	1.44	39.0	62.21	50.46	-18.7
4.53	2.85	37.5	64.12	51.22	-19.0
6.87	4.36	36.1	66.64	55.28	-19.3
9.42	6.04	34.2	67.53	56.27	-16.7
14.86	9.75	29.7	67.74	56.48	-20.1
20.31	13.61	25.0	69.32	58.29	-15.9
21.64	14.59	22.0			-26.4
24.10	16.42	19.0	70.12	59.21	-32.0
25.40	17.40	16.1			-13.8
28.52	19.79	10.5	71.48	60.78	-13.5
28.92	20.10	7.9	72.24	61.67	-0.1
30.31	21.19	5.0	73.37	63.02	29.5
32.64	23.05	2.4	76.58	66.91	50.7
34.50	24.57	-3.0	79.73	70.87	67.5
38.57	27.97	-15.7	81.07	72.59	77.0
39.52	28.78	-22.5	82.19	74.06	80.0
40.35	29.50	-28.0	82.88	74.96	88.0
		-30.5	84.72	77.43	112.0
42.43	31.31	-25.7	88.86	83.14	128.0
44.90	33.51	-23.6	90.65	85.69	140.0
49.99	38.19	-20.4	92.55	88.47	151.0
52.52	39.88	-22.6	94.06	90.72	168.0
55.80	43.84	-20.0	95.98	93.65	174.5
58.73	46.80	-19.0	100.00	100.00	

obtaining of too low values for the freezing points, the mixture was inoculated at a temperature near to that at which freezing was expected to take place with small amounts of phenol or camphor, according to which substance was separating out during freezing. The identity of the substance separating from any given

mixture was established by filtering off a portion of the solid and, after thoroughly draining on porous tile, determining its melting point.

The curve showing the relation between the composition of the mixture and the freezing point is shown in the accompanying figure. It will be observed that the curve is made up of three

distinct portions, namely, AB , BC , and CD ; this fact indicates that the phenol and camphor actually combine to form a compound. The composition of this compound and its limits of stability are most readily seen by plotting, as has been done in the figure, the ratio between the number of molecules of each component in a given mixture instead of the relative weights of the two substances. On referring to the figure, it will be seen that the portion BC , which corresponds with the compound, reaches its greatest altitude at a point which corresponds with a molecular percentage of camphor of 50. Now the highest point of such a curve indicates the composition and freezing point of the pure compound; at this point the solid which separates and the liquid with which it is in contact have the same composition. It is obvious, therefore, that in the case of the compound of phenol and camphor, the two simple substances are united in equimolecular proportions, and that the freezing point of the compound is about -18.6° . The results of the authors' experiments confirm, therefore, the statement of Léger as to the existence of a monacamphoride of phenol, while the freezing point of the compound, as found by the authors, is in fairly close agreement with the melting point given by Léger.

When the two components are not present in equimolecular proportions, the freezing point of the mixture is lower than that of the pure compound, and falls towards B or C respectively, according as to whether it is phenol or camphor which is in excess. The points B and C are eutectic points, and represent the limits of stability of the compound. When the ratio between the molecular proportions of phenol and camphor exceeds that of 70.5 : 29.5, or falls below that of about 40 : 60, the compound can no longer exist in equilibrium with the liquid; in the former case, phenol will separate out when the mixture freezes, and in the latter case camphor. The lower freezing point given in the table of results for the mixtures containing molecular percentages of camphor of 29.5 and 59.21 represent the freezing points of the eutectic mixtures.

No indication was obtained by the authors as to the existence of a compound formed by the union of two molecules of phenol with one of camphor, as was stated to be the case by Léger; his statement as to the possibility of cooling the mixture to -50° without freezing taking place is in agreement with some of the authors' observations, they having noticed that mixtures in the neighbourhood of the eutectic point B can often be greatly supercooled without freezing ensuing.

It will be observed from the curve that two or three of the points in the neighbourhood of the eutectic point C do not fall on the

curve. It might be considered that these points lie on another curve, shown by the dotted line in the figure; if such were the case it would show the existence of a second compound, the composition of which would be shown by the summit *G* of the curve, that is, a compound of two molecules of camphor with one of phenol. The authors do not take the latter view because of the quite definite eutectic point obtained with the 59.21 per cent. mixture, and because with mixtures having almost the same composition as those which gave the discordant results, figures were obtained which fall naturally on the portion *BC* of the curve. The points in question must therefore be considered as due to errors in the determination of the freezing point, probably arising from one or other of the causes mentioned in the earlier part of the paper.

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