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Physics. — *"On plaitpoint temperatures of the system water-phenol".* By A. KEESING. (Communicated by Prof. J. D. VAN DER WAALS).

According to observations by LEHFELDT, V. D. LEE, and SCHREINEMAKERS the system water-phenol possesses maximum pressure at low temperatures. So theoretically a minimum critical temperature was to be expected, but as water shows abnormal deviations in other respects, an elaborate investigation was desirable. In view of the high critical temperatures of the components (water 365°,0 according to CAILLETET and COLARDEAU, or 364°,3 according to BATTELLI; phenol 419°,2 according to RADICE) and the impossibility of using glass test-tubes (glass dissolves in water at such a high temperature) a conclusive investigation had not yet taken place as far as is known. Experimenting in a way similar to that indicated by SCHAMHARDT [1]) I have succeeded in arriving at a preliminary result.

As for the determination of the plaitpoint temperature there was no need for me to regulate either the pressure or the volume I did not want a CAILLETET tube, but used small closed test-tubes of *quartz.* This made it possible for me to use a vapour-jacket whose bottom was also glass, and which rested on asbestic iron gauze. In consequence of this one of the two nickelin wires, viz. the one used by SCHAMHARDT to heat his boiling-liquid, could be dispensed with, and replaced by a BUNSEN burner. The second wire, which enabled him to prevent satisfactorily the radiation at temperatures between 200° and 300°, proved insufficient for temperatures between 350° and 400°. A second layer of asbestos round the wire gave some improvement, but the radiation appeared to be completely prevented only when I placed a glass cylindre silvered on the inside, in which two slits were left free for reading, round the vapour-jacket, which had been thus wrapped up. This cylindre of a diameter 5 centimeters larger than that of the jacket, was shut off by means of asbestos wool on the upper and the lower side.

It was not without difficulty that we found a boiling-liquid, for in the Phys. Chem. tables of LANDOLT-BÖRNSTEIN no boiling-liquids are given above 360°. I used *benzidine,* an inactive substance, which boils at 1 atm. pressure at $\pm 400°$ with colourless vapour. We have, however, to bear in mind:

1. that chemically pure benzidine be used, because impure benzidine boils irregularly, and covers the vapour-jacket, the quartz tube, and the thermometer with a tough, tarry layer, which prevents

1) H. C. SCHAMHARDT. Isotherms of mixtures of benzene and aether. Thesis for the doctorate p. 12—16.

the observation and which I could only remove partially by boiling long with water and benzene,

2. that the substance be boiled under nitrogen, as pure benzidine is soon contaminated by the oxygen from the air,

3. that superheating, which causes the liquid benzidine at times to rise $1^1/_2$ decimeter in the jacket, be prevented by a good quantity of glass-wool.

When benzidine was used, a cooler was not wanted, the vapour condensing in the narrowed part of the vapour-jacket.

The benzidine being heated under nitrogen, I required a nitrogen reservoir. For this purpose a 100 L. flask was used, which was filled with nitrogen obtained from a saturate solution of equal units of weight of potassium nitrite and ammonium chloride. When the reservoir had once been filled, the nitrogen could be expelled from the flask by the admission of water, and be conducted through a drying apparatus to the vapour-jacket. The pressure in the reservoir was measured by a manometer.

The experiments proper began with the filling of the nitrogen reservoir. The phenol and water were weighed in the required ratio, and heated with a spirit lamp. The temperatures at which water and phenol do not mix appeared then to be exceeded, and a homogeneous liquid was formed. A thick-walled quartz tube closed on one side, and drawn out capillarly on the other side in the voltaic arc was now heated in the free flame, and the air expelled under the phenol water solution; the liquid now rose in the tube which was filled for more than $^1/_3$, and then fused together in the voltaic arc. The quartz appeared then to be a very suitable material. It is as clear and transparent as glass, but, when hot, may be cooled in cold water without bursting; it may be heated in a free flame, and is proof to high pressures, as the critical pressure of water, viz. 200 atm. Protective measures proved to have been most likely superfluous.

Thermometer and quartz tube were fastened by means of copper wires in a hole of the glass tube which pierces the airtight rubber stopper of the vapour-jacket. The apparatus were filled with nitrogen, the pressure in the boiling vessel was reduced to about 30 cm., the gas-burner lighted, and every five minutes a lamp was inserted of the resistance, by the aid of which the current required to check radiation was regulated. After an hour the thermometer indicated about 350°. As soon as this temperature had become constant, which also appeared from the fact that the boiling phenomena stopped in the quartz tube, nitrogen was gradually admitted. The meniscus began then to become gradually fainter. The incandescent lamps placed behind the slit made the inner wall of the quartz tube look like a streak of light, in which the meniscus made a notch. By moving the eye to and fro in front of this notch I could ascertain the presence of the liquid mirror as long as possible. The temperature at which the meniscus disappeared, was noted down; also the temperature at which the liquid mirror returned on decrease of pressure in the vapour-jacket.

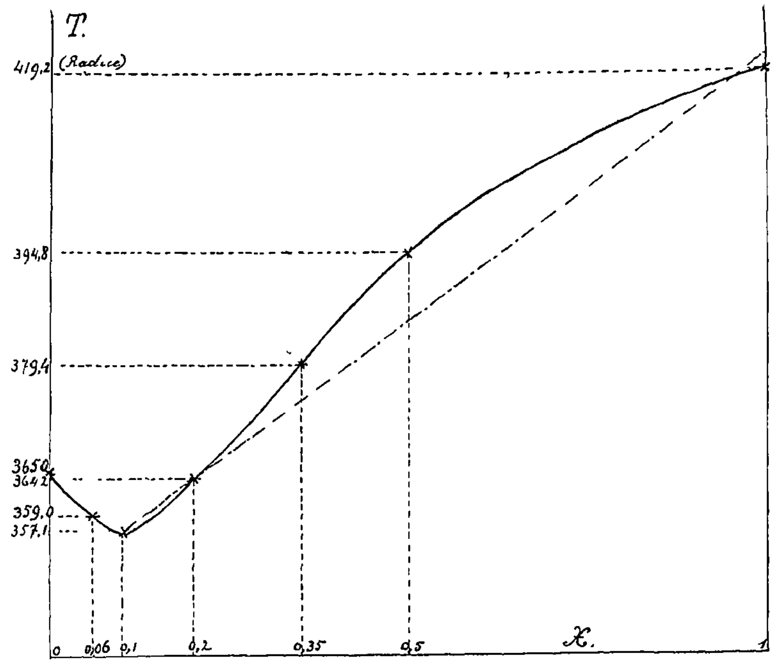
First the T_k of the mixture $x = 0,1$ was determined; compared with CAILLETET and COLARDEAU's observations this gave a *decrease* of 8° in the critical temperature. So there was no doubt but a minimum of temperature was present in the plaitpoint-line.

To see whether the decrease would continue, $x = 0,2$ was determined; we found $\pm$ 364°; the T_k, though rising, was still below the value given by CAILLETET and COLARDEAU for $x = 0$. In order to determine the place of the minimum more accurately, the first component ($x = 0$) and the mixture $x = 0,06$ were then examined; finally also $x = 0,5$ and $x = 0,35$ with a view to the course of the plaitpoint line beyond the minimum.

The observations have been put together in the subjoined table; they have been reduced on a thermometer tested at the Reichsanstalt, which does not show any deviation at 300°, but points one degree too low at 400°.

X	The meniscus disappeared at	The meniscus returned at	The meniscus disappeared for the second time at	The meniscus returned again at
0	365.0	363.9	365.0	364.2
0.06	359.0	358.5	359.0	358.4
0.1	357.0	356.0	357.1	356.0
0.2	364.2	363.0	364.1	363.3
0.35	379.4	378.0	379.3	378.0
0.5	394.8	393.8	394.8	393.9
1	419.2 according to Radice			

Graphically represented we obtain the following Tx-projection of the plaitpoint line:



From this graphical representation follows:

1. that the system water-phenol really possesses a *minimum* plaitpoint temperature,

2. that it lies in the neighbourhood of $x = 0{,}1$. Now SCHREINEMAKERS has found that the mixture $x = 0{,}011$ has maximum pressure at 56°, the mixture $x = 0{,}015$ at 75°, and $x = 0{,}017$ at 90°. These observations deviate from the theory, for the maximum pressure point does not move to the right with higher temperature, but to the left. If, however, we choose one of SCHREINEMAKERS' observations, no matter which, then the fact that the minimum plaitpoint temperature lies at an x *larger* than that of the mixtures for which maximum pressure is still possible, is in accordance with the theory.

3. As the extremities of the ordinates belonging to the abscissae $x = 0.1$, $x = 0.2$, and $x = 1$ lie about on a straight line, and as those belonging to $x = 0.35$ and $x = 0{,}5$ are obviously above it, we must conclude to the presence of a *point of inflection* in the Tx projection of the plaitpoint curve. It is doubtful whether we must attach physical significance to this.

In conclusion I have still to mention that in these observations no electro-magnetic stirring-apparatus has been used, which, however, may be applied as soon as a quartz stirrer of sufficiently small diameter is ready.

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