NONEXISTENCE OF THE TWO MODIFICATIONS IN LIQUID NITROBENZENE AND CARBON BISULPHIDE.

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It has often been reported that some of the polar liquids undergo a sudden change in their dielectric constant in the neighbourhood of freezing point. Recently, M. Wolfke and J. Mazur, considering that it might be due to some polymorphic transformation of the liquid state and that consequently any change of other physical properties would exist, studied heating curves, dielectric constants and densities of ethyl ether, nitrobenzene and carbon bisulphide.(1) They concluded that a "modification change of liquid" exists at the following temperature.

Ethyl ether, -105°C.
Nitrobenzene, 9.5°C.
Carbon bisulphide, -90°C.

This year, Massy, Warren and Wolfenden(2) have measured the density and viscosity of nitrobenzene and concluded, contrary to the opinion of Wolfke and Mazur, that there is not two modifications in liquid nitrobenzene.

Nitrobenzene.

Material. One kilogram of pure nitrobenzene from Kahlbaum ("aus kryst. Benzol") was dehydrated over calcium chloride and distilled. The part distilled at 206°C. was collected and then subjected to fractional crystallisation. The portion (100 c.c.) of highest melting point was redistilled twice under reduced pressure. The melting point of the

(1) Mazur, *Nature*, **126** (1930), 649 & 993; **127** (1931), 270 & 893; **128** (1931), 673 & 761. Wolfke and Mazur, ibid., **126** (1930), 684; **127** (1931), 236, 741 & 926; **128** (1931), 584.
(2) Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 91.

sample thus obtained was 5.67°C. The melting point of nitrobenzene obtained by various authors are as follows.

5.7°	Hansen, *Z. physik. Chem.*, **48** (1904), 595.
5.82	Meyer, *Chemisches Zentralblatt*, **1909**, II, 1842.
5.70	Timmermans, ibid., **1911**, I, 1669(1),
5.67	Swarts, *Rec. trav. chim. Pays-Bas*, **33** (1914), 284.
5.75	Turner and Polland, *J. Chem. Soc.*, **105** (1914), 1 62.
8.70 (?)	Landolt-Börnstein, "Tabellen", 1923.
5.668	Roberts and Bury, *J. Chem. Soc.*, **123** (1923), 2037.
5.689	Sidgwick and Ewbank, *J. Chem. Soc.*, **125** (1924), 2269.
5.5	Mazur, *Nature*, **127** (1931), 741.
5.77	Massy, Warren and Wolfenden, *J. Chem. Soc.*, **1932**, 92.

It is certain that the sample used by Mazur was not quite pure. Wolfke and Mazur synthesised the nitrobenzene from benzene crystals(2) and found its melting point to be 5.5°C. They said that the substance was thoroughly liquid at 5.7°C.(3) Masson(4) synthesised nitrobenzene from pure benzene and acids and obtained a sample freezing at 5.83°C. and found that the freezing point descends about 0.1° when exposed to air. He pointed out that the value reported by Mazur was decidedly low.

Heating Curve. Wolfke and Mazur(5) found an arrest at 9.5°C. in the rate of temperature rise of nitrobenzene under constant heat supply. The same experiment was repeated by the present author to confirm their results. Some 20 c.c. of nitrobenzene was taken into a glass tube, provided with a thermometer and a stirrer, cooled to 7°C. and placed in a Dewar vessel. Dry air was incessantly passed to prevent the contamination by the moisture. The temperature of the liquid rised slowly. The thermometer was read every one minute. The temperature time curves thus obtained are shown in Fig. 1. Two curves in this figure have different inclinations showing the different heating rate. These curves, contrary to their results, are quite smooth and no arrest can be seen on any part of the curves.

Density. Mazur(6) found a remarkable decrease in density of nitrobenzene between 9.5° and 5.6°C., and a sharp "Knick" in the density temperature curve at 9.5°C. For the sake of convenience, the author studied the volume change with temperature of nitrobenzene by means of a dilatometer. The capacity of the dilatometer was about 7 c.c. and

(1) See Beilsteins Handbuch der organischen Chemie, 4 Aufl. Bd. 5, Erstes Ergänzungswerk, S. 124.
(2) Wolfke and Mazur, *Nature*, **126** (1930), 993.
(3) Mazur, ibid., **127** (1931), 893.
(4) Masson, ibid., **128** (1931), 726.
(5) Wolfke and Mazur, ibid., **127** (1931), 741.
(6) Mazur, ibid., **127** (1931), 893.

the diameter of its capillary was 0.6 mm. The position of menisci of the liquid at various temperatures were read. The results are plotted in Fig. 2. As seen from Fig. 2 there is no sudden change in volume, being against to the result of Mazur.

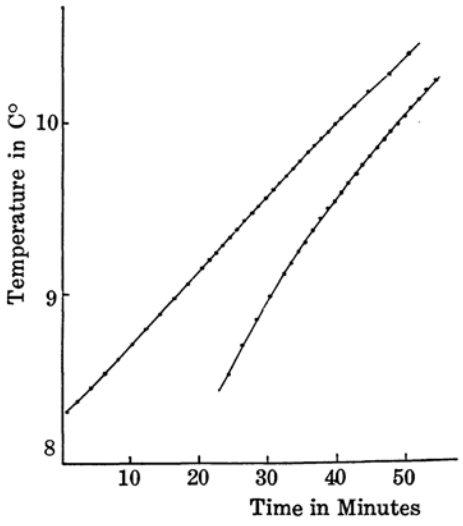

Fig. 1.

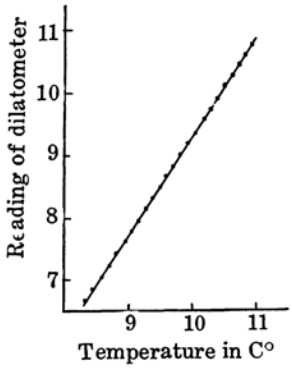

Fig. 2.

The density of nitrobenzene at 20°C. was measured by a pycnometer, and obtained the value, $d_4^{20°} = 1.2030$. The value of $d_4^{20°}$ obtained by other authors are as follows.

1.2039 Brühl, *Z. physik. Chem.*, **16** (1895), 216.
1.20328 Kahlbaum, ibid., **26** (1898), 646.
1.2028 Falk, *J. Am. Chem. Soc.*, **31** (1909), 815.
1.20323 Tyrer, *J. Chem. Soc.*, **105** (1914), 2538.

Refractive Index. Wolfke and Mazur[1] have reported, without any numerical data, that the value of the refractive index also undergoes a very distinct change at 9.6°C.

The refractive index was measured at the temperature between 7° and 20°C., especially carefully in the neighbourhood of 9.6°C., with a Pulfrich refractometer for H_α line. Owing to the construction of the refractometer it was inevitable that the sample was exposed to air, and the refractive index of nitrobenzene was found to decrease by absorbing moisture. To prevent the absorption of moisture, the liquid was protected by covering completely with rubber tubing at the upper part of the cell, as shown in Fig. 3. The vapour tension of nitrobenzene at

(1) Wolfke and Mazur, *Nature*, **128** (1931), 584.

the observation temperatures are comparatively small, so the rubber was hardly corroded, and the measurement was carried out quite satisfactorily.

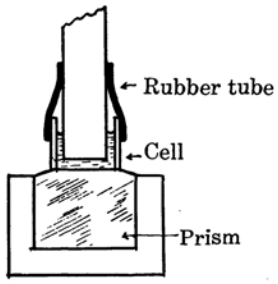

Fig. 3.

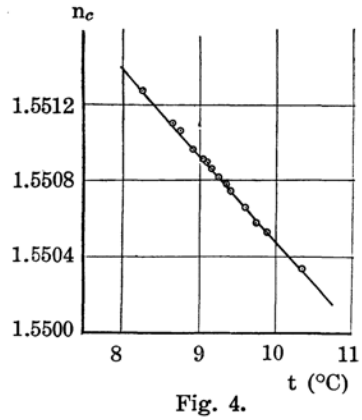

Fig. 4.

The results are given in Table 1, where n_c denotes the refractive index of nitrobenzene for H_α line. Three series of measurements have been done which indicate in Table 1 under No. 1, No. 2 and No. 3. The values of the first series are depicted in Fig. 4.

Table 1.

No. 1.		No. 2.		No 3.	
Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)	Temp. (t)	Refractive index (n_c)
8.25°C.	1.55127	8.40C°	1.55118	7.45°C.	1.55167
8.60	1.55114	8.55	1.55112	8.40	1.55123
8.75	1.55106	8.65	1.55105	8.65	1.55109
8.92	1.55096	8.75	1.55102	8.90	1.55099
9.05	1.55091	9.23	1.55079	9.57	1.55079
9.10	1.55089	9.45	1.55068	9.58	1.55069
9.15	1.55086	9.55	1.55063	10.00	1.55052
9.25	1.55081	9.87	1.55050	10.30	1.55038
9.35	1.55078	9.90	1.55049	10.63	1.55025
9.42	1.55075	10.30	1.55030	11.30	1.54990
9.60	1.55066	10.45	1.55025	11.85	1.54964
9.75	1.55058	10.85	1.55006	13.30	1.54899
9.90	1.55053	10.95	1.55001	14.62	1.54837
10.35	1.55034	19.88	1.54590	16.68	1.54751
				19.30	1.54625
$n_c = 1.554992 - 0.000450t$		$n_c = 1.555037 - 0.000459t$		$n_c = 1.555060 - 0.000455t$	

The relation between refractive indices and temperatures are quite linear and no sudden change is found in any part of the line. The experimental equations calculated by the method of least squares are shown in the above table. From these three equations we obtain the following one.

$$n_c = 1.555030—0.000455\ t.$$

Falk[1] obtained by measurement between 20° and 70°C. the relation:

$$n_c = 1.55453—0.000458\ t.$$

The temperature coefficient in the Falk's equation is practically identical to that of the author.

The values of refractive index for H_α line at 20°C. obtained by various authors are as follows:

1.54593 Brühl, *Z. physik. Chem.*, **16** (1895), 216.
1.54537 Falk, loc. cit. Interpolated value.
1.54582 Brand and Kranz, *J. prakt. Chem.*, **115** (1927), 153.
1.54593 Murakami.

Carbon Bisulphide.

Wolfke and Mazur[2] have reported that carbon bisulphide also exhibits the analogous phenomena as nitrobenzene in the heating curve at –90.03°C., and that the two modifications are discernible as they separate into two layers. The following experiment was carried out to ascertain this report.

Carbon bisulphide from Kahlbaum was purified with mercury and by distillation. The freezing point of the material was –111.0°C. The method of measurement of the heating curve was the same to that of nitrobenzene, excepting, in this case, the Dewer vessel containing a mixture of alcohol and ether was cooled with liquid air. When the carbon bisulphide was cooled down to —100°C., further cooling was stopped, and the rate of temperature rise was measured by means of a pentane thermometer. The result is shown in Fig. 5. As seen from this figure, the time temperature curve is nearly straight in the neighbourhood of —90°C.

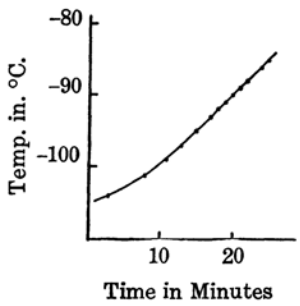

Fig. 5.

(1) Falk, loc. cit.
(2) Wolfke and Mazur, *Nature*, **127** (1931), 926.

and shows no arrest of temperature. In this case, however, as the rate of elevation of temperature is comparatively large, and the accuracy of the thermometer is not so good, the observed result may not be so accurate as the case of nitrobe zene. Moreover, two layers could not be observed anywhere between the room temperature and the freezing point.

In conclusion the author wishes to express his hearty thanks to Professor J. Sameshima for his kind guidance throughout this experiments.

Summary.

The heating rate and the volume dilatation of nitrobenzene have been measured between 8° and 11°C. and the refractive index between 7° and 20°C. The density of nitrobenzene is $d_{20}^{4} = 1.2030$, and the refractive index for H_α line is given by the equation.

$$n_c = 1.555030 - 0.000455\, t.$$

The heating curve of carbon bisulphide has been measured between −100° and −85°C.

No arrest in the heating curves, no distinct change of the slope in the dilatation curve and no distinct change in the value of the refractive index have been observed within the range of the observed temperatures. Two layers in liquid carbon bisulphide at −90°C. could not be observed.

None of these results proves the existence of the two modifications of the liquid nitrobenzene and carbon bisulphide such as suggested by Wolfke and Mazur.

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