114. *The Vapour-pressure Curve of Formaldehyde, and Some Related Data.*

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A NUMBER of measurements of the vapour pressure of formaldehyde have already been reported by Mali and Ghosh (*J. Indian Chem. Soc.*, 1924, **1**, 37). Their specimen polymerised rapidly above $-30°$ but was sufficiently stable at lower temperatures to allow five determinations to be made between $-91°$ and $-34.5°$. However, these points are insufficient for the accurate determination of the curve. Accordingly, a new series of measurements has been carried out with relatively stable specimens (cf. Spence and Wild, this vol., p. 338).

Liquid formaldehyde, prepared from paraformaldehyde (*idem, ibid.*), was distilled, the head and tail fractions being discarded. The condensate was redistilled, and about 2 ml. of the middle fraction collected in the vapour-pressure vessel, which was then sealed off. All condensing surfaces had previously been heated in the presence of formaldehyde vapour. The cylindrical vapour-pressure vessel was surrounded by a brass tube carrying the copper wire of a resistance thermometer, and the whole immersed in a 3-litre Dewar flask filled with ligroin (b. p. 40—60°) at the desired temperature. A U-tube containing pure redistilled α-bromonaphthalene separated the formaldehyde vessel from the manometric system, but the former could be pumped out by opening a stop-cock placed across the limbs of the U. All exposed tubing except the portion containing bromonaphthalene was maintained at 100°.

Measurement of Temperature.—The resistance of the thermometer was measured on a Pye dial resistance box. With the galvanometer used, measurements were accurate to 0·01 ohm. For purposes of calibration, the copper thermometer was immersed in ligroin (b. p. 40—60°) in a large Pyrex test-tube. Four fixed points were determined, *viz.*, the transition point of sodium sulphate decahydrate (32·38°; Landolt–Börnstein, " Tabellen "), the m. p. of ice, the transition

point of carbon tetrachloride (— 47·66°; Johnston and Long, *J. Amer. Chem. Soc.*, 1934, **56**, 31), and the sublimation point of solid carbon dioxide (— 78·5°; Landolt–Börnstein, " Tabellen ") : all these materials had been carefully purified before use. The variation of resistance with temperature could be represented by the empirical equation $R_{t°} = 72·01 + 0·30506t - 73 \times 10^{-6}t^2$. Resistances calculated from this equation are here compared with the experimental values :

$t°$	32·38°	0·00°	−47·66°	−78·50°
$R_{obs.}$, ohms	81·89	72·01	57·35	47·59
$R_{calc.}$, ohms	81·81	72·01	57·31	47·61

During the vapour-pressure measurements, the ligroin bath was stirred by a stream of dry air. With a properly regulated rate of flow, the bath temperature remained constant to within 0·05° for the period of a determination.

Measurement of Pressure.—The apparatus was first thoroughly evacuated by a mercury-diffusion pump, the stop-cock connecting the two limbs of the U-tube closed, and the formaldehyde bulb, together with the thermometer, immersed in the ligroin bath at the desired temperature. Pressures less than 10 mm. of mercury were measured directly by using the bromonaphthalene U-tube as a differential manometer. At higher pressures, the differential manometer was approximately balanced by admission of dry air to the evacuated limb. Balancing pressures up to 86·00 mm. of mercury were measured on a bromonaphthalene manometer, whilst mercury was used for the higher values. The reading on the differential manometer was added to or subtracted from the balancing pressure according to whether the vapour pressure was greater or less than the latter. Data given in the table below (*p* in mm. of Hg) represent the average of three or four settings.

Attainment of the maximum vapour-pressure was rapid, but in a few cases a slow drift occurred owing to increasing bath temperature. On the other hand, solution and polymerisation in the bromonaphthalene U-tube were shown to be negligibly small by the fact that the pressure of formaldehyde confined over bromonaphthalene decreased only very slowly. Again, the b. p. obtained from the vapour-pressure curve has been checked by direct determination.

Vapour-pressure of formaldehyde.

Sample.	t.	p, obs.	p, calc.	Diff.	Diff., %.	Sample.	t.	p, obs.	p, calc.	Diff.	Diff., %.
B1	−109·4°	0·95	1·03	−0·08	7·8	A4	−64·6°	61·65	61·87	−0·22	0·4
C2	−104·4	1·85	1·83	+0·02	1·1	A6	−63·7	65·20	65·65	−0·45	0·7
C1	− 98·3	3·60	3·54	+0·06	1·7	C7	−55·8	111·0	110·7	+0·3	0·3
A11	− 95·2	4·85	4·83	+0·02	0·4	A2	−54·0	124·7	123·7	+1·0	0·8
A12, C3	− 89·1	8·68	8·68	0·00	0·0	A7	−49·3	163·1	164·5	−1·4	0·7
C4	− 85·6	12·25	11·96	+0·29	2·4	A8	−40·6	266·6	268·0	−1·4	0·5
A5	− 78·9	21·02	20·97	+0·05	0·2	C8	−39·1	290·6	290·6	0·0	0·0
C5	− 78·3	22·11	22·02	+0·09	0·4	A1	−34·3	368·9	372·6	−3·7	1·0
A10	− 71·9	35·40	36·30	−0·90	2·5	A9	−28·4	496·6	498·8	−2·2	0·4
C6	− 68·5	46·43	46·91	−0·48	1·0	C9	−22·3	664·3	661·3	+3·0	0·5
A3	− 65·3	58·95	58·74	+0·21	0·4						

The calculated pressures have been obtained from the following empirical equation :

$$\log_{10}p_{atm.} = -1429/T + 1·75\log T - 0·0063T + 3·0177,$$

where T represents degrees absolute. The deviation is usually not more than 1%, the average being 1·1%. Four samples of liquid monomeride were used. In the first case, temperature was measured with a pentane thermometer. These results are not shown, but agree very closely with those given in the table. The three remaining samples are represented in col. 1 by A, B, and C, with serial numbers showing the order of the experiment. In Fig. 1, the line represents the above relation between log *p* and $1/T$, but with *p* in mm., and the positions of the experimental points are shown.

Melting Point and Boiling Point.—Pure redistilled formaldehyde was condensed in a tube (10 mm. diameter) containing a large glass bead. The tube was sealed off and suspended in a 3-l. ligroin bath in an inverted sloping position. At the m. p. the bead fell to the bottom, so bringing the tube vertical and making an electrical connexion causing a bell to ring. This occurred at — 118·3°. The range of melting was now investigated. Formaldehyde was frozen in the bottom of a tube (10 mm. diameter) of the type shown in Fig. 2(*a*). This contained a glass weight with a long pointer attached, which was hooked to the tube by a small projection

near the top. When sufficient formaldehyde had collected, the tube was sealed off above the pointer, the hook of which was then released by tapping, and the weight allowed to rest on the surface of the solid. The tube was placed in the 3-l. ligroin bath so that the tip of the pointer protruded about 1 cm. above the mouth of the Dewar flask. Downward movement first became visible at $-118\cdot3°$ and the pointer reached the bottom mark at $-117\cdot6°$. Such a range of melting appeared to be unduly large. Accordingly, another experiment was performed with an m. p. tube only 6 mm. in diameter and with very careful regulation of the bath temperature. The range of melting as indicated by the pointer was now $-118\cdot3°$ to $-117\cdot8°$. The vapour pressure calculated from the equation is $0\cdot35$ mm. at the m. p. Boiling-point determinations were carried out (a) by Smith and Menzies's bulblet method (*J. Amer. Chem. Soc.*, 1910, **32**, 897), and (b) by their isoteniscope method (*ibid.*, p. 1420). The simple form of isoteniscope used is shown in Fig. 2(b). Formaldehyde was condensed in the single limb and in the U by liquid air, and the apparatus sealed off from the main train at A. The wide upper tube was now held by a clamp and the lower portion immersed in a ligroin-bath just above the b. p. When the formaldehyde in the U melted, the capillary tip of the wide tube was broken, admitting air. Formaldehyde vapour bubbled through the liquid in the U. The bath temperature was now gradually
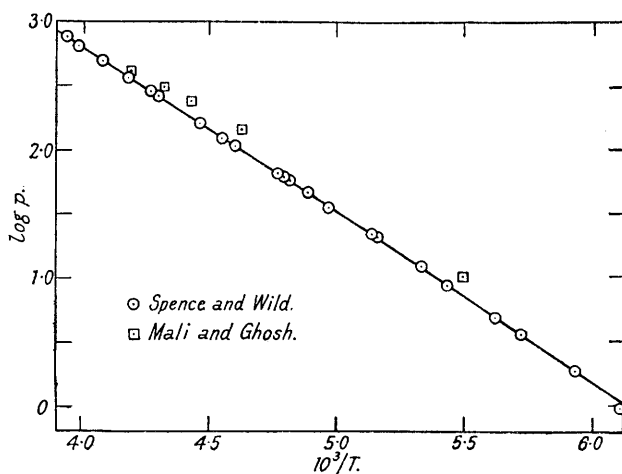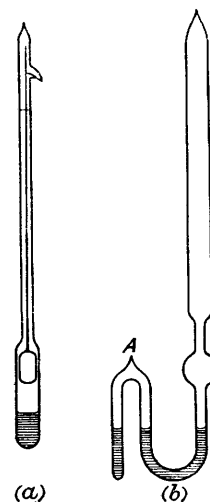
FIG. 1.   FIG. 2.

lowered by addition of solid carbon dioxide until bubbling ceased and the levels in the U became the same. Measurement of three different samples by method (a) gave $-19\cdot3°$, and the mean of six readings by method (b) with one sample was $-19\cdot3°$, corrected to 760 mm. The b. p. calculated from the vapour-pressure equation is $-19\cdot1°$, whence the mean of the direct and the indirect determinations is $-19\cdot2°$. Attempts were made to determine the critical temperature of formaldehyde by placing a sealed capillary tube containing the liquid in an oil-bath at a definite temperature. Precise observations were impossible owing to the occurrence of rapid polymerisation. At 147° the liquid expanded and almost filled the tube. As the temperature rose, solid at first separated, but this eventually melted, and the contents of the tube appeared to remain unchanged until the latter burst at 250°.

Thermodynamic Constants.—Differentiation of the above vapour-pressure equation, and combination of the result with the simplified Clausius–Clapeyron equation $d \log_e p/dT = \Delta H/RT^2$, leads to the following expression for the heat of vaporisation : $\Delta H = 6545 + 3\cdot480T - 0\cdot02885T^2$. At the b. p., $-19\cdot2°$ ($253\cdot9°$ K.), $\Delta H = 5570$ cals. The value of Trouton's constant, $\Delta H/T$, is $21\cdot9$ entropy units.

<center>DISCUSSION.</center>

The results of Mali and Ghosh (Fig. 1) show considerable deviation from the curve derived from our table. This may be due to an error in their thermocouple, which was checked only at a single temperature. Furthermore, the b. p. is given as $-21°$, identical with Kekulé's figure (*Ber.*, 1892, **25**, 2435), but the value calculated from their equation is

— 20°. The accuracy of our results appears to be limited chiefly by temperature variation, and it is probable that the difference of 0·2° between the b. p. measured at atmospheric pressure and that calculated from the vapour-pressure equation lies within the limits of experimental error. The results were not considered to be sufficiently accurate to justify correction for the local value of g and for the expansion of mercury (cf. Smith and Menzies, *loc. cit.*). It is evident from the vapour-pressure data and from the value of Trouton's constant, that formaldehyde is a normal liquid. Actually, however, certain measurements (*e.g.*, A12 and C9) were carried out with specimens which had become gelatinous, without any apparent deviation from the curve. Furthermore, the fact that no deviation occurred when fresh specimens were employed initially at widely different temperatures demonstrates the uniform purity of the liquid phase. It must be concluded, therefore, that the polymerisation of monomeric liquid formaldehyde, like that of the gas, occurs only at the surface of the solid polymeride, which is insoluble and possesses negligible vapour pressure. The insolubility of the polyoxymethylene in monomeric formaldehyde is remarkable, although in agreement with the very high molecular weight now attributed to it. The process of gelatinisation probably occurs as follows. Thread-like molecules of polyoxymethylene grow out from the glass walls or from suspended matter into the liquid. As the threads thicken, they become visible locally as faint, woolly formations, which gradually extend until there is a semi-rigid network which retains a relatively large mass of unchanged liquid. The enclosed liquid behaves as if it is entirely pure, and exerts its normal vapour pressure.

SUMMARY.

The vapour-pressure curve of formaldehyde has been traced from the m. p. (— 118·0°) to the b. p. (— 19·2°).

The heat of vaporisation is 5570 cals. at the b. p., and Trouton's constant is 21·9 entropy units, whence it is concluded that formaldehyde is a normal liquid.

Polymerisation occurs only as a heterogeneous or solid phase reaction, leaving the liquid phase unaffected.