5. *The Effect of Pressure on the Binary System Monomethylaniline–Dimethylaniline.*

By J. C. SWALLOW and R. O. GIBSON.

THE effect of pressures up to 4000 atm. on the equilibria in binary organic systems of various types has been extensively studied by Puschin and his collaborators (*Z. physikal. Chem.*, 1925, **118**, 276, 447; 1926, **119**, 400; **124**, 16, 217), and by other investigators [Roloff, *ibid.*, 1895, **17**, 325; Kultaschev, Schriften Naturf.-Gesell. Univ. Jurjew (Dorpat), No. 22, 1915]. No work, however, has been done on the system monomethylaniline–dimethylaniline, and it has therefore been studied at pressures up to 2000 atm.

Apparatus.—The apparatus used was designed by Dr. A. Michels of the Physical Laboratory of the University of Amsterdam, and is shown in section in Fig. 1. It consists essentially of a chamber A in which the substance to be examined is placed so that it can be viewed through the windows, B, B', and its temperature measured by means of the internal thermocouple C. Triplex glass screens S, S', were interposed between the observer and the windows. Oil pressure was applied to the surface of the mercury in the pot D and was transmitted by the mercury to the substance in A. The pressure was obtained by means of a screw press of the Cailletet type, also designed by Dr. Michels and built by Dikkers & Co. of Hengelo, Holland, to give pressures up to 3000 atm.

The pressures were measured by means of Bourdon gauges calibrated up to 1000 atm. against a standard pressure balance at Amsterdam.

Difficulty was first experienced in obtaining windows which would withstand the desired pressures, but eventually it was found that the type described by Poulter (*Physical Rev.*, 1930, **35**, 297; see also, *ibid.*, **36**, ii, 3005) was satisfactory. A scale diagram of one of these windows is shown in Fig. 2. The metal disc L was made of Vibrac steel hardened to about 100 tons per sq. in. One surface was ground and polished as flat as possible without optical grinding. The glass disc M was cut from a sheet of Moncrieff's gauge glass, a tough plate-glass. The surfaces of the discs cut from a carefully selected sheet of glass were, as a rule, sufficiently flat and did not require further grinding and polishing. The glass discs were usually stuck on to the steel disc with a little Canada balsam in order to hold them in position until pressure was applied. With a glass disc of the dimensions indicated in Fig. 2, a hole 10 mm. in diameter in the steel disc can be used with safety up to 1500 atm., and an 8 mm. hole up to 2500 atm. One window with a 10 mm. hole failed at 1500 atm. after it had on two previous occasions been tested to 3000 atm. A second window with the same diameter hole cracked at 2200 atm. after it had been in use up to 1800 atm. for several days. A window with an 8 mm. hole failed at 2400 atm. after having been in use on several occasions up to 3000 atm.

Evidence of the limit to which the glass windows can be taken may be obtained by viewing them in a polariscope between crossed Nicol prisms. Before the application of pressure the field is dark; as the pressure is increased, light begins to come through and the dark space contracts to a Maltese cross, the arms of which become thinner as the pressure is further increased. Finally, a few hundred atmospheres before the breakdown of the window, the dark cross almost disappears and colours begin to appear round the edges of the window. A similar phenomenon has been noted by Wahl (*Phil. Trans.*, 1912, **212**, 117) with the apparatus which he built for optical research at high pressures.

Procedure.—Pure substances. Various methods have been used by Tammann (" The States of Aggregation," Constable, 1926), Bridgman (" The Physics of High Pressures," Bell, 1931), Puschin (*Z. physikal. Chem.*, 1924, **113**, 57), and other workers to determine the melting curves of pure substances, depending on either the change of volume or the arrest in the cooling curve during the change of state. The method used with the apparatus described above was to maintain the outside bath at a constant temperature and to raise the pressure until crystals

Fig. 1.

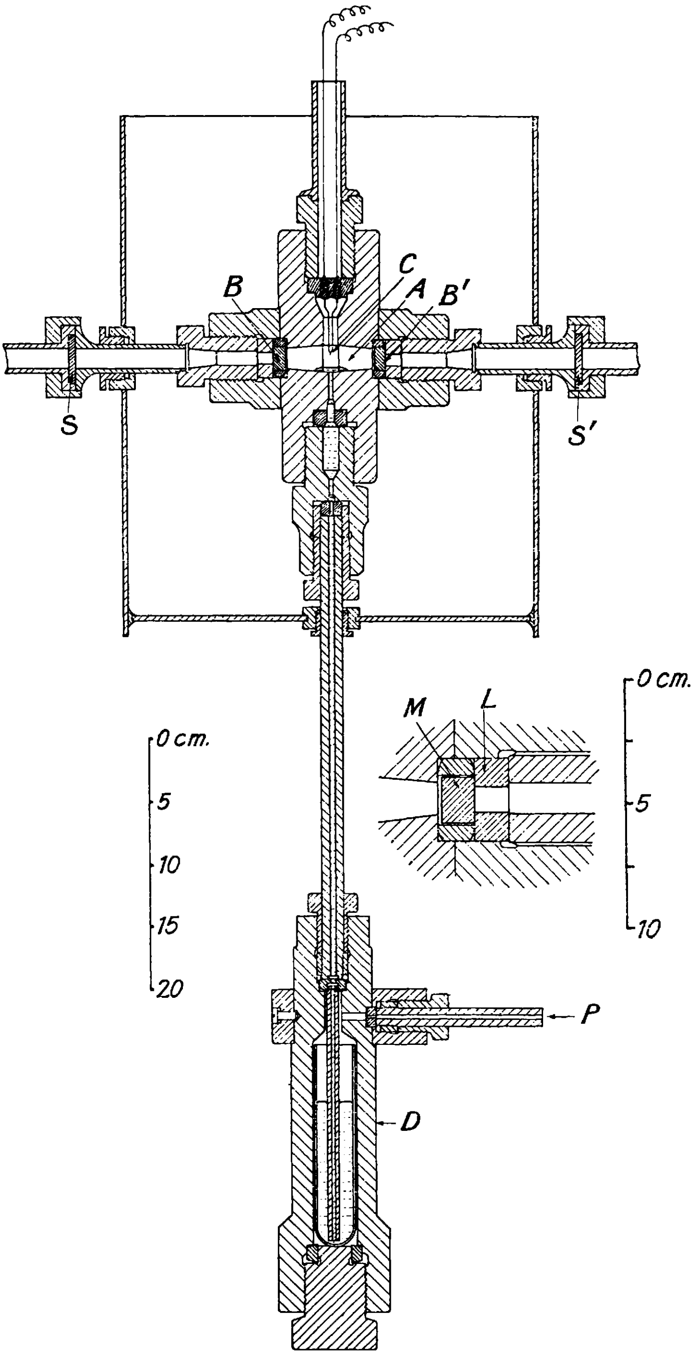
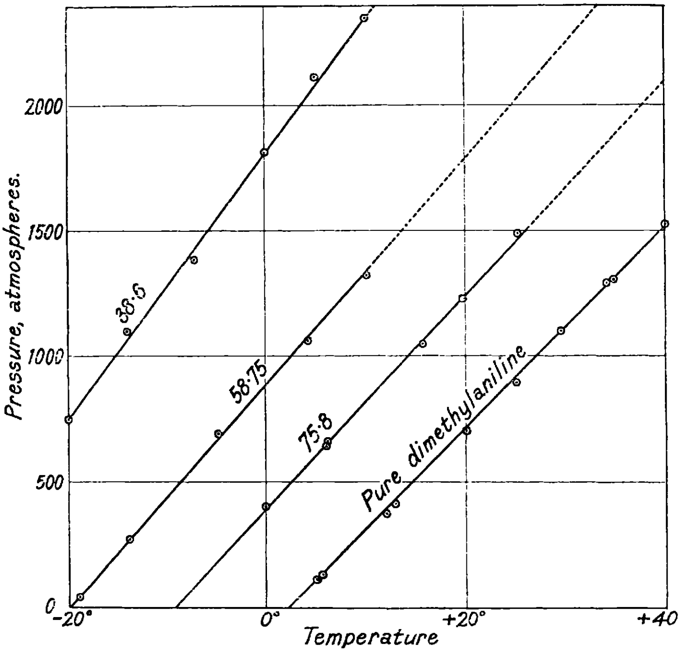


Fig. 2.

began to appear. As 200—300 atm. " over-pressure " usually had to be applied before crystallisation began, the pressure was lowered by this amount as soon as the crystals began to grow rapidly. After allowing sufficient time (about ½ hour) for equilibrium to have been attained, the pressure and temperature were read. The equilibrium pressure could be confirmed by increasing or decreasing the pressure a little and again waiting for equilibrium. It was found advisable to work with only a small quantity of the solid phase present, as the latter tended to form a hard crust on the surface of the mercury which prevented a proper distribution of pressure in the remainder of the substance. It was probably for this reason that attempts to measure the temperature of the thermocouple immersed in the substance at various constant pressures when both liquid and solid were present did not give results having the reproducibility obtained by the visual method already described.

Mixtures. For binary mixtures, the pressures and temperatures at which the *first* crystals appear are required, for only then is the composition of the mixture known. The temperature of the bath was, therefore, kept constant, and the pressure raised until crystallisation had commenced. The pressure was then lowered until just one or two crystals remained floating in the solution. It was arranged that the mercury level was in the field of view in the chamber *A*, and by shaking the whole apparatus efficient agitation was produced in the mixture.

FIG. 3.



Numerals on curves denote mols. % of dimethylaniline.

With dimethylaniline, the crystals of which are birefringent, the otherwise invisible thin plates were shown up in polarisation colours by viewing the mixture between crossed Nicol prisms.

*Results.—Pure monomethylaniline.** Monomethylaniline does not appear to have a definite f. p. Beilstein reports that it solidifies to a glassy solid at about —80°, and Jaeger (*Z. anorg. Chem.*, 1917, **101**, 146) states that it solidifies with considerable supercooling and remelts at — 57°. The fact that it cooled to a glassy solid was confirmed, but the remelting did not appear to occur at any definite temperature. No signs of crystallisation were obtained under a pressure of 3000 atm. with the outside bath containing ice and salt at — 15°.

*Pure dimethylaniline.** Dimethylaniline crystallises readily, and the f. p. has been reported by various observers (cf. Beilstein; Landolt–Börnstein; Jaeger, *loc. cit.*) to lie between 0·5° and 2·5°. The measurement of the cooling curve of a carefully fractionated sample gave f. p. 1·5°, and the sample used in making up the mixtures had f. p. 1·0°. Under pressure, it crystallised readily with about 200 atm. over-pressure, in the form of thin transparent plates which, when

---

* Pure samples of mono- and di-methylaniline were prepared for this investigation by I.C.I. (Dyestuffs), Ltd.

growing slowly, were regular hexagons. The crystals sank readily to the bottom of the chamber. The relevant data are :

Pressure, atm.	123	140	385	420	708	900	1105	1295	1305	1530	1755
M. p.	5·0°	5·5°	12·0°	12·8°	20·0°	25·0°	29·4°	34·0°	34·6°	40·0°	45·3°

Mixtures. Four mixtures were made up by weight, and their compositions are given in the following table as mols. %. The detailed behaviour of each mixture is recorded below.

(I) About 200 atm. over-pressure were required to start the crystallisation; the crystals had the form of diamonds and no hexagons were seen.

	Mixture I : $NPhMe_2$, 75·8%.						Mixture II : $NPhMe_2$, 58·75%.				
Press., atm.	410	655	670	1060	1240	1500	49	280	700	1070	1335
M. p.	0·0°	6·1°	6·2°	15·8°	19·7°	25·2°	− 18·7°	− 13·6°	− 4·7°	4·2°	10·1°

	Mixture III : $NPhMe_2$, 38·6%.					
Press., atm.	755	1105	1395	1820	2120	2360
M. p.	− 19·8°	− 13·9°	− 7·1°	0·0°	5·0°	10·0°

(II) Similar behaviour to mixture (I), although rather more over-pressure was required to start the crystallisation. The crystals seemed to have much the same density as the solution and did not settle readily.

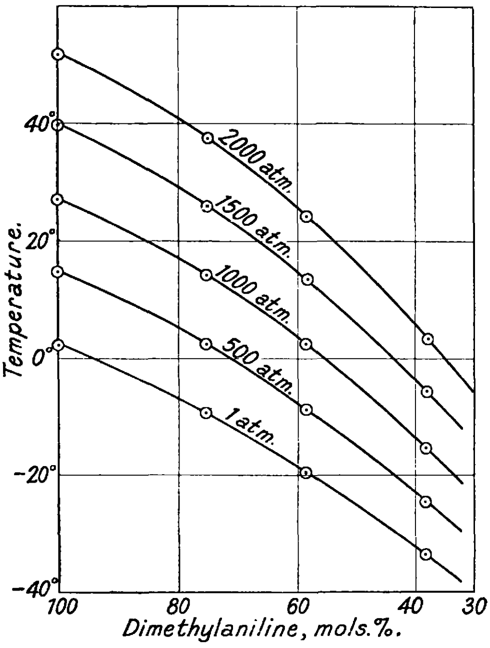
(III) About 1000 atm. over-pressure were required to start the crystallisation, which, however, proceeded very slowly. It was more difficult to obtain the exact pressure of the first crystallisation.

(IV) No signs of crystallisation in this mixture ($NPhMe_2$, 24·7%) were obtained with pressures up to 3000 atm. and at −20°.

DISCUSSION.

The experimental points have been plotted on a pressure–temperature diagram in Fig. 3, and straight lines drawn through them. The temperatures corresponding to a series of even pressures have been interpolated and plotted against composition in Fig. 4, from which it will be seen that the curves at constant pressure tend to approach each other as the proportion of monomethylaniline increases. Puschin (*loc. cit.*) concluded from the systems that he had investigated that these curves ran approximately parallel to one another, although he recognised that they deviated more and more from this parallel direction as the pressure was increased.

FIG. 4.



The authors express their gratitude to the Directors of Imperial Chemical Industries Limited for permission to publish this work.

RESEARCH DEPARTMENT, I.C.I. (ALKALI), LTD.,
NORTHWICH.

[*Received, October* 28*th*, 1933.]