101. *The Effect of Pressure on the Melting Points of* o-, m-, *and* p-*Xylene.*

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This work is a continuation of a study of the effect of pressure on certain binary organic systems (this vol., p. 18), but, owing to the low temperatures required, this contribution has been restricted to the effect of pressure on the m. p.'s of the pure xylenes and of one mixture of *o*- and *p*-xylene.

The xylenes used were obtained from British Drug Houses Ltd. The *p*- and the *m*-compound contained sulphur, which reacted with the mercury in the pressure apparatus, rendering the sample opaque and the visual determination of the m. p.'s difficult. These samples were therefore shaken with clean mercury for 6 hours, and the precipitated sulphide filtered off.

The m. p.'s at atmospheric pressure, as determined by means of cooling curves, were *o*-, — 25·5°; *m*-, — 45·5°; *p*-, 13·4°. Those recorded in the literature are: *o*-, — 25·7° (Nakatsuchi, *J. Soc. Chem. Ind. Japan*, 1929, **32**, 333B), − 25·3° (Parks and Huffmann, *Ind. Eng. Chem.*, 1931, **23**, 1138), − 26° (Bridgman, *Proc. Nat. Acad. Sci.*, 1926, **61**, No. 3); *m*-, − 50·5° and − 49·0° (Nakatsuchi, *J. Soc. Chem. Ind. Japan*, 1926, **29**, 2931; and *loc. cit.*), − 53·5° (Parks and Huffmann, *loc. cit.*), − 50° (Bridgman, *loc. cit.*); *p*-, 13·15° and 13·19° (Nakatsuchi, *locc. cit.*), 13·2° (Tammann, "States of Aggregation," 1926, p. 101), 13·35° (Timmermans, *J. Chim. physique*, 1926, **23**, 733), 13·5° (Bridgman, *loc. cit.*), 13·2° (Parks and Huffmann, *loc. cit.*).

The agreement between the observed and the reported values for *o*- and *p*-xylene is satisfactory. With *m*-xylene there was considerable supercooling; the value given above was the maximum temperature to which the melt rose after crystallisation had commenced during the determination of two cooling curves. This temperature is markedly higher than the highest recorded m. p., and it is significant that it is in agreement with the linear extrapolation of the observed *p*–*T* curve.

The influence of pressure on the m. p.'s of the pure substances was determined by the visual method previously described (*loc. cit.*). With the binary mixture it was difficult to obtain the first crystallisation temperatures by this method: the crystals were transparent and not birefringent, so there was always some doubt as to their presence in the field of view. In order to obtain the eutectic point, the pressure was raised in steps of about 100 kg./cm.², and the changes in the temperature as recorded by the internal thermocouple were noted, the outside bath being maintained at a constant temperature. As there was usually some supercooling, once the eutectic mixture had commenced to crystallise the temperature rose rapidly. As soon as this sudden rise occurred, the pressure was lowered until the internal temperature was about the same as that of the outside bath. The system was allowed to come to equilibrium, and the temperature and pressure were then read. In order to ensure that the invariant eutectic point was being measured, the pressure was then raised by 10—20 kg./cm.², and the system again allowed to come to equilibrium, whereupon the pressure and temperature should have returned to the original values.

The effect of pressure on the m. p. of *p*-xylene has been determined by Tammann (*op. cit.*). His results are given by the equation $T = 13{\cdot}2^\circ + 343{\cdot}8 \times 10^{-4} P - 171 \times 10^{-8} P^2$, where T is the m. p. at a pressure of P kg./cm.². The pressures at which the xylenes solidify at 30° and 75° were determined approximately by Bridgman (*loc. cit.*); both his and our results (denoted respectively by B. and by S. & G.) are given below, together with the values of the m. p.'s of *p*-xylene at the observed pressures calculated from Tammann's equation (denoted by T.).

p-*Xylene.*

Press., kg./cm.².	Melting point. S. & G.	B.	T.
215	+ 20·0°		20·5°
490	—	30·0°	29·6
670	35·0		35·5
870	41·7		42·1
1110	49·0		49·3
1470	60·6		60·0
1625	65·0		64·6
1900	—	75·0	72·4
2130	80·0		78·7

o-*Xylene.*

Press., kg./cm.².	Melting point. S. & G.	B.
715	− 10·1°	
1675	+ 11·6	
2075	20·0	
2400	—	30·0°
2510	30·0	
5500	—	75·0

m-*Xylene.*

Press., kg./cm.².	Melting point. S. & G.	B.
1295	− 20·3°	
1420	− 16·4	
1655	− 12·9	
1780	− 9·1	
2235	− 0·6	
2280	+ 0·4	
2755	9·6	
4000	—	30·0°
>8200	—	75·0

The agreement between the observed and Tammann's values for *p*-xylene is satisfactory, for the pressures were observed on Bourdon gauges calibrated up to 1000 kg./cm.² and are therefore only reliable to 1%.

The values observed for the first crystallisation and eutectic temperatures of a mixture containing 70% *o*- and 30% *p*-xylene are given below.

Pressure, kg./cm.².	First crystalln. temp.	Pressure, kg./cm.².	Eutectic temp.
445	− 16·3°	1135	− 11·5°
530	− 15·4	1380	− 7·5
740	− 9·6	1610	− 2·0
1130	+ 0·2	1685	− 0·5
1605	+ 11·6	2180	+ 10·0

The results for both the pure xylenes and the first crystallisation and eutectic temperatures of the mixture may be represented, within the experimental error, by straight lines drawn on a pressure–temperature diagram. The first crystallisation and eutectic temperatures of the 70% *o*-, 30% *p*-mixture at atmospheric pressure, obtained by linear extrapolation, are in agreement with the values obtained by Nakatsuchi (*loc. cit.*, 1929) in his determination of this binary system.

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