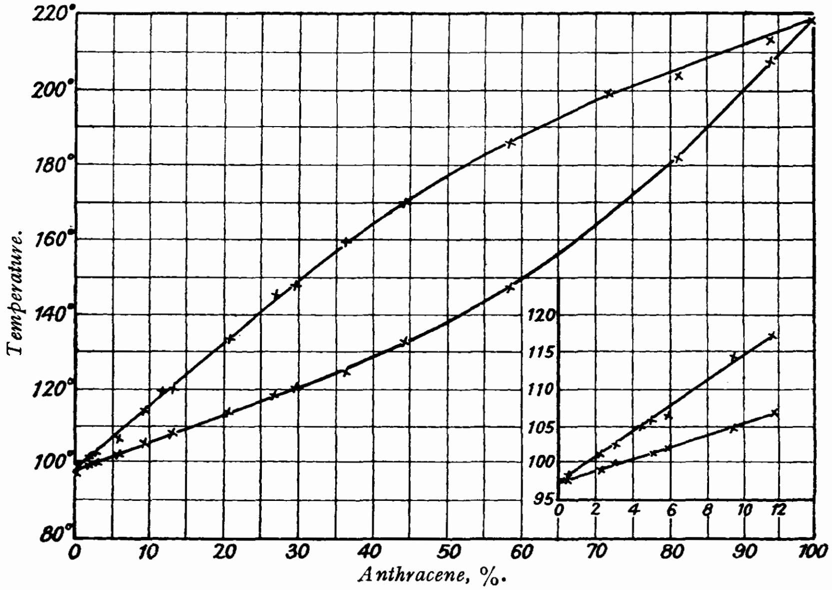
166. *The System Anthracene–Phenanthrene.*

By Gerald Bradley and J. K. Marsh.

Anthracene and phenanthrene form mixed crystals and, as they are both recovered from tar distillate, the more soluble phenanthrene is not obtained pure and the m. p. recorded in the literature shows a wide range.

Vignon (*Bull. Soc. chim.*, 1891, **3**, 387) reported that the addition of anthracene to phenanthrene continuously raised the apparent m. p. of the latter, but he determined very few points on the m. p.–composition curves of these substances and, as Miolati (*Z. physikal. Chem.*, **1892**, **9**, 653) showed, he had thus missed eutectics in other systems. Consequently the form of the anthracene–phenanthrene curve remained doubtful. Cohen and Cormier (*J. Amer. Chem. Soc.*, **1930**, **52**, 4363) noted that the presence of more than 2% of anthracene raises the m. p. of phenanthrene. Marsh and Capper (J., 1926, 726) could not separate the two substances by fractional crystallisation, but were able to do so by polymerising the anthracene with the light of a quartz mercury lamp.

Liquidus–solidus curves now obtained for the anthracene–phenanthrene system indicate that a continuous series of mixed crystals is formed, and that the m. p. of pure phenanthrene is lower than previously recorded. The percentage of anthracene in phenanthrene may be evaluated conveniently by a m. p. determination under the conditions described, in conjunction with the figure.



EXPERIMENTAL.

Anthracene was fractionally crystallised from C_6H_6 till colourless, polymerised by Hg light in boiling C_6H_6 solution, and depolymerised by subsequent boiling in darkness. The product melted at 218°.

Phenanthrene was fractionally crystallised from EtOH. The middle fractions were then treated with Hg light to polymerise the anthracene (Capper and Marsh, *loc. cit.*), but the former efficiency could not be attained. A quantity of material was finally prepared which contained 0·56% of anthracene, as determined by measuring the strength of the anthracene bands in the region λλ 3500—3800, where phenanthrene is diactinic.

The m. p. and f. p. curves of phenanthrene with various proportions of anthracene were then investigated. The f. p.'s were determined by Isaac's method (*Proc. Roy. Soc.*, **1913**, **205**, 88). The material was completely melted in closed glass tubes, and then cooled with a glass rod at one point to start crystn. The tubes were reinserted in a hot bath and the max. temp. was determined at which growth would continue. The same sealed tubes were used for determining the m. p.'s. The mixtures in them were liquefied and then quickly cooled and left for at least 24 hr. Each m. p. was determined by holding the tube in the heating bath so that at the m. p. a trickle of fused substance would flow from the remaining solid. Several determinations of each f. p. and m. p. were made and consistency was usually within 0·2°. The results are recorded in the table and fig. The upper curve of the latter represents m. p. and the lower f. p. For pure phenanthrene the value of both is 97·3°, distinctly lower than in previous determinations. The prepn. of pure phenanthrene is very difficult : the best test for freedom from anthracene is the absence of visible fluorescence of a conc. solution in actinic light.

Composition, % by wt.			
Anthracene.	Phenanthrene.	F. p.	M. p.
0·56	99·44	98·3°	97·8°
2·30	97·70	101·2	99·2
3·13	96·87	102·6	100·0
5·06	94·94	106·2	101·4
5·82	94·18	106·8	102·0
9·54	90·46	114·8	105·0
11·7	88·3	119·2	107·2
13·3	86·7	120·2	107·6
20·5	79·5	134·0	113·5
27·1	72·9	145·4°	118·2°
28·9	71·1	147·8	120·8
36·4	63·4	159·4	126·2
44·4	55·6	170·0	133·2
58·5	41·5	186·4	147·8
72·3	27·7	199·2	170·0
81·2	18·8	204·8	182·2
94·3	5·68	213·2	207·6
100·0	0·00	218·0	218·0

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