THE FREEZING POINT CURVE OF THE SYSTEM: ORTHO-CRESOL: NAPHTHALENE¹

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Some time ago there was completed some preliminary experimental work on the approximate freezing points of mixtures of ortho-cresol and naphthalene. In this previous work, which was done under the direction of one of us at the H. W. Jayne Laboratory of the Barrett Company, it was found that ortho-cresol and naphthalene form a eutectic mixture which melts at approximately 20°C, and which contains about 22 percent of naphthalene. Moreover, it was observed that mixtures containing relatively large amounts of ortho-cresol are very easily supercooled; and that in some cases the supercooling can be carried so far that crystals of naphthalene may be caused to separate from mixtures containing very considerably more than the eutectic amount of ortho-cresol. Thus, many such mixtures apparently possess two freezing points—one freezing point corresponding to the temperature at which solid ortho-cresol is in stable equilibrium with mother liquor, and the second and lower freezing point corresponding to the temperature at which solid naphthalene is in metastable equilibrium with a supercooled cresol-rich mother liquor.

Since the study of the freezing points of mixtures of ortho-cresol and naphthalene affords a very good experimental demonstration of the fact that the freezing point curve of a system of this type consists simply of two intersecting solubility curves, it was thought advisable to make a more careful investigation of the freezing point curve for the system ortho-cresol: naphthalene. The results of this work are described in this present article.

The materials used in this work were prepared from refined naphthalene and technically pure ortho-cresol, both of

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The ortho-cresol was further purified by dissolving it in an excess of a solution of caustic soda, steam-distilling the carbolate solution to remove traces of pyridine and hydrocarbons, liberating the cresol again by acidifying the solution with sulphuric acid, and finally purifying the ortho-cresol by repeated fractional distillation through an efficient fractionating column. The final purified ortho-cresol had a melting point of 30.4°C .

The naphthalene was further purified by dissolving it in pure benzene and shaking the solution with successive portions of concentrated sulphuric acid, water, sodium hydroxide solution, and water, respectively. After distilling off the solvent the naphthalene was distilled. The resulting product was recrystallized from benzene and redistilled through a fractionating column. The final purified naphthalene had a melting point of 80.2°C .

The apparatus used in determining the freezing points of the various mixtures consisted essentially of a large test tube ($7'' \times 3/4''$) provided with a tightly fitting cork stopper through which were inserted the thermometer and the stirrer. This tube was surrounded by a larger glass tube, which was immersed in the cold water used as a cooling medium. The thermometer used in this work was a standardized "Tycos" thermometer, graduated from 0°C to 100°C in $1/10^{\circ}\text{C}$.

In making a determination accurately weighed amounts of naphthalene and ortho-cresol were placed in the tube, and the mixture was then melted and then cooled slowly and with constant and regular stirring. As the freezing point of the mixture was approached, the charge was "seeded" by adding small crystals of naphthalene or of ortho-cresol. In each case the temperature taken as the freezing point of the mixture was the temperature at which permanent crystals first appeared.

The results obtained in these determinations are given in the following table:

% Cresol	% Naphthalene	Freezing Point	
		Stable	Metastable
100	0.0	30.4	—
99.5	0.5	30.2	—
99	1	29.9	—
98	2	29.4	—
97	3	29.0	—
96	4	28.45	—
95	5	28.2	—
90	10	25.9	—
85	15	23.6	5.0
80	20	21.9	15.94
79	21	21.2	17.54
78	22	20.8	19.1
77	23	21.3	—
76.5	23.5	21.8	—
75	25	24.3	—
70	30	32.3	—
60	40	43.3	—
50	50	50.1	—
25	75	65.65	—
10	90	74.56	—
0	100	80.2	—

These results are shown by the accompanying graph. One branch, AC, of the curve represents the (stable) equilibria be-

Fig. 1

tween solid and ortho-cresol and solution, while the other branch, CD, represents the equilibria between solid naphtha-

lene and solution. The eutectic, C, contains 22.5% naphthalene and melts at 20.6° C. Line CB represents the continuation of branch DC beyond the eutectic point—i. e., the metastable equilibrium between solid naphthalene and supercooled cresol-rich solutions.

Because of the extent to which supercooling occurs in the cresol-rich mixtures, and because of the ease with which points on the metastable curve CB can be determined, the study of the freezing point curve of the system ortho-cresol:naphthalene affords an excellent experimental illustration of the fact that the freezing point curve of a system of this type is composed of the two intersecting mutual solubility curves.

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