CXIV.—*Equilibrium in the Binary Systems : Ethylenediamine–Phenols.*

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Equilibrium diagrams of mixtures of ethylenediamine and phenols have not hitherto been studied, but the thermal analysis of five such systems is now described. For every mixture the following have been determined : (1) the temperature of complete melting of the crystallised mixture; (2) the complete cooling curve; (3) the duration of the eutectic crystallisation.

In the tables, the column headed I under "Temperature" denotes the temperature of first crystallisation (but complete melting in the case of guaiacol), and that headed II refers to the definite (or eutectic) crystallisation. The column headed "Time" shows the duration (in minutes) of the definite crystallisation of 1 g. of substance.

Ethylenediamine–Phenol.—The equilibrium diagram (Fig. 1) is composed of four branches and is characterised by two eutectic points, one open maximum at 66·6 mol. % of phenol, and one transition point at the concentration of 80 mol. % of phenol.   It therefore follows that the open maximum corresponds to the form-

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FIG. 1.
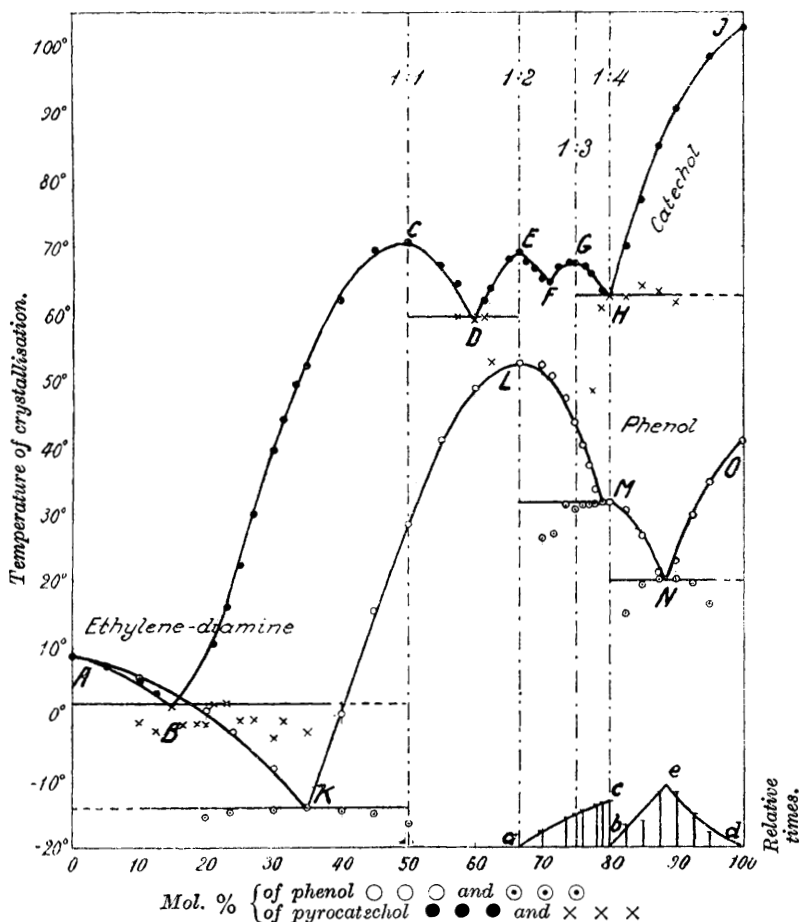
ation of a definite *compound*, $C_2H_4(NH_2)_2, 2C_6H_5 \cdot OH$, melting at 53·5°.

For the determination of the composition of the other compound, the time of duration of crystallisation at the transition point (31·6°) was studied (triangle *abc*).   The maximum was found at 80 mol. % of phenol.   Hence the *compound* is $C_2H_4(NH_2)_2, 4C_6H_5 \cdot OH$.   The

TABLE I.

Ethylenediamine–Phenol.

Phenol, mol. %.	Temperature, I.	II.	Time.	Phenol, mol. %.	Temperature, I.	II.	Time.
0	$8.7°$		—	73·5	$+47·1°$	$+31·4°$	1·4
10	$+ 5·6°$	—	—	75	$+43·5$	$+30·9$	1·5
20	$+ 0·6$	$-15·3°$	—	76	$+40·2$	$+31·4$	1·7
23·8	$- 2·4$	$-14·6$	—	77	$+37·2$	$+31·5$	—
30	$- 8·0$	$-14·2$	—	78	$+33·8$	$+31·6$	1·9
35	$-14·0$		—	79	$+31·8$	—	2·0
40	$+ 0·1$	$-14·4$	—	80	$+31·8$	—	2·1
45	$+15·5$	$-14·8$	—	82·5	$+30·6$	$+15$	1·0
50	$+28·6$	$-16·2$	—	85	$+26·8$	$+19·6$	1·2
55	$+41·2$	—	—	87·5	$+21·3$	$+20·1$	2·5
60	$+48·9$	—	—	90	$+23$	$+20·2$	2·3
66·6	$+52·8$	—	—	92·5	$+29·9$	$+19·6$	1·5
70	$+52·3$	$+26·5$	0·8	95	$+34·6$	$+16·5$	0·7
71·5	$+50·6$	$+27$	—	100	$+40·8°$		—

point which corresponds to this compound in the diagram is congruent with the transition point within the limits of the experimental error.

The two eutectic points correspond to (a) 35 mol. % of phenol and $-14°$; (b) 88·5 mol. % of phenol and 20·2°. Triangle *bed* shows the time of crystallisation of the mixture at this second eutectic temperature.

TABLE II.

Ethylenediamine–o-Cresol.

| o-Cresol, mol. %.	Temperature, I.	II.	Time.	o-Cresol, mol. %.	Temperature. I.	II.	Time.
0	$+8·7°$		—	50	$+29°$	—	—
10	$4·5°$	—	—	55	$+37·8$	—	—
15	0	$-19·4°$	1·0	60	$+43·8$	—	—
20	$- 2$	—	—	65	$+47$	—	—
25	$- 8·5$	$-18·2$	2·1	66·6	$+47·2$	—	—
30	$-12·7$	—	—	70	$+45·1$	—	—
32·5	$-17·2$		2·9	75	$+37·6$	$+6·1°$	0·8
37·5	$- 2$	$-17·8$	2·1	80	$+22·9$	$+8$	1·4
40	$+ 5·2$	—	—	85	—	$+8·5$	1·0
42·5	$+ 9·7$	$-18·4$	1·3	90	$+19$	$+6·6$	1·0
45	$+16·3$	—	—	100	$+29·5°$		—

Ethylenediamine-o-Cresol.—The equilibrium diagram (Fig. 2) is characterised by one open maximum at the concentration of 66·6 mol. % o-cresol, and by two eutectic points : one corresponds to 32·5 mol. % of o-cresol and $-17°$, and the other to 85 mol. % and $+8·5°$. The maximum shows the formation of a definite *compound*, $C_2H_4(NH_2)_2,2C_7H_7·OH$, which melts at 48°.

Triangles *abc* and *cde* show the time of crystallisation of the mixtures at the corresponding temperatures and prove the position of the eutectic points on the diagram.

TABLE III.

Ethylenediamine–p-Cresol.

p-Cresol, mol. %.	Temperature, I.	II.	Time.	p-Cresol, mol. %.	Temperature, I.	II.	Time.
0	$8\cdot7°$		—	76·5	$+42\cdot6°$	$+27°$	0·9
10	$-\ 0\cdot3°$	$-14\cdot7°$	1·0	78·5	$+36\cdot6$	$+27\cdot2$	1·0
20	$-\ 8\cdot5$	$-16\cdot6$	1·9	80	$+32\cdot5$	$+28\cdot2$	1·1
25	-13	$-16\cdot4$	2·5	80·5	$+30\cdot6$	$+28\cdot1$	—
30	$-\ 9\cdot5$	$-15\cdot6$	2·9	81·5	—	$+28\cdot0$	1·3
35	$+\ 1\cdot4$	$-15\cdot6$	1·7	83·5	$+29\cdot7$	—	—
40	$+12\cdot2$	$-15\cdot7$	1·4	85	$+30\cdot3$	—	—
45	$+23\cdot5$	-13	1·0	85·7	$+30\cdot1$	—	.
50	$+34\cdot5$	—	—	87·5	$+29\cdot9$	—	—
55	$+44$	—	—	90	$+27\cdot4$	$+23\cdot9$	0·6
60	$+50\cdot6$	—	—	92	—	$+24\cdot0$	1·2
66·6	$+53$	—	—	95	$+27$	—	—
70	$+51$	—	—	100	$+33°$		—
75	$+45\cdot8$	$+26\cdot7$	0·7				

FIG. 2.
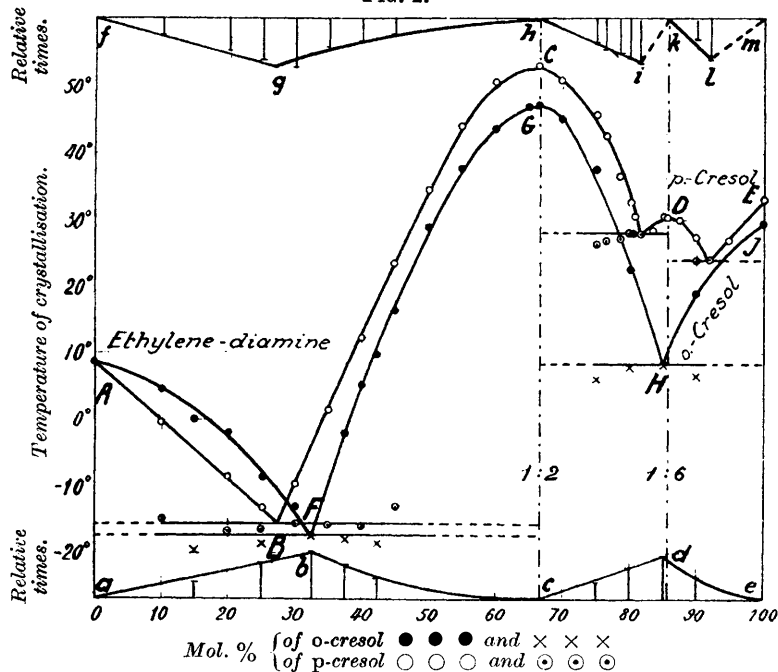
$Ethylenediamine$–p-$Cresol$.—The equilibrium diagram (Fig. 2) is composed of four parts and is characterised by three eutectic points and two open maxima, one of which lies at 66·6 mol. % and the other at 85·7 mol. % of p-cresol. The first maximum shows the formation of the $compound$ $C_2H_4(NH_2)_2,2C_7H_7 \cdot OH$, and the second

of the *compound* $C_2H_4(NH_2)_2,6C_7H_7\cdot OH$. The former compound melts at 54° and the latter at 31°. Between the two maxima lies the eutectic point, which corresponds to 82 mol. % of *p*-cresol and 28·2°. The other two eutectics represent (1) 27 mol. % of *p*-cresol and −13°; (2) 92 mol. % of *p*-cresol and +24°.

Triangles *fgh*, *hik*, and *klm* show the duration of crystallisation at the corresponding eutectic temperatures.

TABLE IV.

Ethylenediamine–Pyrocatechol.

Temp. of crystallisation for 0 mol. % of pyrocatechol, 8·7°; for 100 mol. %, 102·7°.

Pyro-catechol, mol. %.	Temperature, I.	II.	Pyro-catechol, mol. %.	Temperature, I.	II.	Pyro-catechol, mol. %.	Temperature, I.	II.
5	7·2°	—	35	52·2°	− 2·7°	71	64·8°	—
10	5	−1·1°	40	62	—	72·5	66·8	—
12·5	3·2	−2·4	45	69·5	—	74	67·6	—
15	—	+1	50	70·7	—	75	67·6	—
16·5	—	−1·4	55	67·3	+53	76·5	67	—
18·5	—	−1·3	57·5	64·5	+59·7	77·5	66	+48·3°
20	—	−1·4	60	—	+59	79	63·4	+60·8
21	10·6	+1·5	61·5	61·5	+59·6	80	—	+62·5
23	16	+1·6	62·5	63·8	+52·9	82·5	70	+62·4
25	22·5	−1	65	68	—	85	77	+64
27	30	−0·7	66·6	69·2	—	87·5	85	+63·2
30	39·6	−3·6	67·5	67·7	—	90	90·5	+61·8
31·5	44·2	−1	69	66·8	—	95	98·2	—
33·3	49·5	—	70	65·2	—			

Ethylenediamine–Pyrocatechol.—The equilibrium diagram (Fig. 1) consists of five parts. Three open maxima are clearly indicated. One corresponds to 50 mol. % of pyrocatechol, *i.e.*, to a *compound* $C_2H_4(NH_2)_2,C_6H_4(OH)_2$, which melts at 73°. The second lies at 66·6 mol. % of pyrocatechol and corresponds to a *compound*

$$C_2H_4(NH_2)_2,2C_6H_4(OH)_2,$$

melting at 71°; and the third to 75 mol. % of pyrocatechol, $C_2H_4(NH_2)_2,3C_6H_4(OH)_2$; this *compound* melts at 69·2°.

Three of the eutectic points are clearly indicated : (*a*) at 15 mol. % of pyrocatechol and 2°; (*b*) at 60 mol. % and 60°; (*c*) at 80 mol. % and 64°. The fourth, *viz.*, that between

$$C_2H_4(NH_2)_2,2C_6H_4(OH)_2 \text{ and } C_2H_4(NH_2)_2,3C_6H_4(OH)_2,$$

could not be accurately determined, and the cooling curves gave indications of the formation of solid solutions between these two compounds.

Ethylenediamine–Guaiacol.—This system resembles the preceding, as might be expected in view of the relation between guaiacol and pyrocatechol. The diagram (Fig. 3) consists of four parts. It looks as if ethylenediamine is not soluble in guaiacol, for the curve

TABLE V.

Ethylenediamine–Guaiacol.

| Guaiacol, mol. %.	Temperature, I.	Temperature, II.	Time.	Guaiacol, mol. %.	Temperature. I.	Temperature. II.
0	9·4°	—	—	60	55·8°	+50°
5	8	+ 3·5°	—	62	56·9	—
7·5	7	+ 3·2	1·1	64	57·5	—
10	6	+ 3·5	—	66·6	57·5	—
12·5	10	+ 4·8	1·9	70	56·8	—
15	15·3	+ 4	—	72·5	59	—
20	23·2	+ 3·2	1·3	75	62·4	+57·2
25	30·2	+ 1·5	1·2	77·5	64·5	+56·7
30	35·8	− 0·4	0·8	80	65·4	+42·6
35	40·7	− 0·5	0·7	82·5	66·3	+41·7
40	45	—	—	85	66·5	—
42·5	46·8	—	—	87·5	66·5	—
45	48·8	—	—	90	65·8	+24
47·5	50·1	—	—	92·5	64·8	+26·5
50	51·5	—	—	95	62·5	+27
52	51·5	—	—	97·5	59	+27·5
54	51·5	—	—	99	51·2	+27
55	52·2	—	—	100	—	+28°
57·5	54·2	+51·3	—			

FIG. 3.
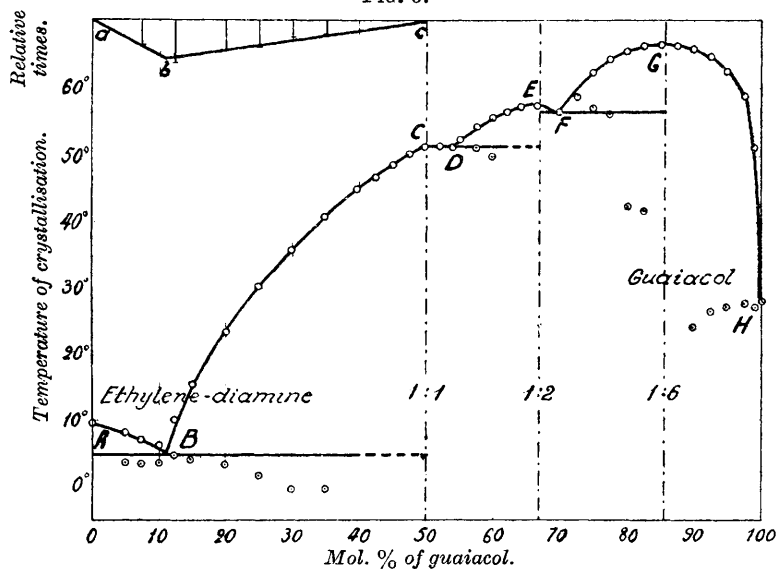
ascends steeply from pure guaiacol, forming an open maximum at 85 mol. % of guaiacol, corresponding to a *compound*

$$C_2H_4(NH_2)_2,6C_6H_4(O\cdot CH_3)(OH).$$
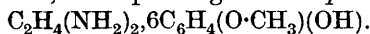
This is the most characteristic of the three compounds formed by these components, and melts at 66·5°. If one bears in mind that

there is but one hydroxyl group in guaiacol, whilst there are two in pyrocatechol, the above-mentioned compound is analogous to $C_2H_4(NH_2)_2,3C_6H_4(OH)_2$. With pure guaiacol this compound forms only mechanical mixtures, since in the interval from 85—100 mol. % of guaiacol the temperature of crystallisation of the latter is clearly noticeable.

The second maximum in the diagram corresponds to 66·6 mol. % of guaiacol, and therefore to $C_2H_4(NH_2)_2,2C_6H_4(O\cdot CH_3)(OH)$, which melts at 57·5°. This *compound* is analogous to
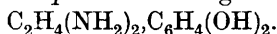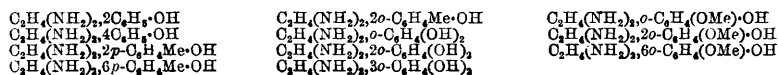
$$C_2H_4(NH_2)_2,C_6H_4(OH)_2.$$

The third maximum lies at 50 mol. % of guaiacol and shows the formation of a *compound*, $C_2H_4(NH_2)_2,C_6H_4(O\cdot CH_3)(OH)$, m. p. 51·5°. The eutectic point between this compound and pure ethylenediamine corresponds to 11 mol. % of guaiacol and 5°.

The triangle *abc* shows the time of crystallisation at this eutectic temperature. Judging by the fact that the eutectic crystallisation is clearly noticeable in the interval of 0—50 mol. % of guaiacol, pure ethylenediamine and its equimolecular compound with guaiacol do not form solid solutions.

Summary.

Equilibrium has been determined in five binary systems composed of ethylenediamine on the one hand and phenol, *o*- and *p*-cresol, pyrocatechol, and guaiacol on the other. The existence has been demonstrated of the following definite compounds, which all melt without decomposition :

$C_2H_4(NH_2)_2,2C_6H_5\cdot OH$ $C_2H_4(NH_2)_2,2o\text{-}C_6H_4Me\cdot OH$ $C_2H_4(NH_2)_2,o\text{-}C_6H_4(OMe)\cdot OH$
$C_2H_4(NH_2)_2,4C_6H_5\cdot OH$ $C_2H_4(NH_2)_2,o\text{-}C_6H_4(OH)_2$ $C_2H_4(NH_2)_2,2o\text{-}C_6H_4(OMe)\cdot OH$
$C_2H_4(NH_2)_2,2p\text{-}C_6H_4Me\cdot OH$ $C_2H_4(NH_2)_2,2o\text{-}C_6H_4(OH)_2$ $C_2H_4(NH_2)_2,6o\text{-}C_6H_4(OMe)\cdot OH$
$C_2H_4(NH_2)_2,6p\text{-}C_6H_4Me\cdot OH$ $C_2H_4(NH_2)_2,3o\text{-}C_6H_4(OH)_2$