

Citation:

A.F. Holleman, On the nitration of benzoic acid and its methylic and ethylic salts, in:
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The preceding tables are obtained by interpolation. Varying quantities of phenol are added to mixtures of water and acetone containing 1.83, 4.24, 7.94, 15.6, 24.6, 31.8, 40.4, 50.2, 59.9 and 64.9 percent of acetone, and the temperature was determined at which the two liquid phases which form are converted into a single phase.

Let us now examine the different connodal lines in figure 1. Below 68° they terminate in two points on the side W-Ph. of the triangle; these two points represent two binary solutions which are in equilibrium with each other. The positions of the conjugate points on the connodal line itself is still unknown. At 68° the connodal line touches the side W. Ph. in a point, at which the two liquid phases of the binary system W. Ph. become identical. As is shown in the figure at 80° , 85° and 87° , the connodal lines at higher temperatures lie wholly within the triangle and approach each other as the temperature rises, disappearing finally at about 92° in the point F. The composition at the point F is approximately 59 % of water, 12 % of acetone and 29 % of phenol.

Above 92° the ζ -surface is convex at every point when regarded from below; as the temperature falls a double plaitpoint therefore appears at the point F, when this temperature of 92° is reached. On further depression of the temperature the point F develops into a plait with two plaitpoints, of which one moves towards the side W. Ph. where it disappears at 68° in the point at which the connodal line of 68° touches the side W. Ph.; at still lower temperatures therefore one point of folding alone remains.

A further investigation will show whether it is possible in some measure to learn the course of the plaitpointcurve.

Mr. SCHREINEMAKERS has thus shown experimentally that connodal lines with two, one or no plaitpoints may appear on the ζ -surface. The first example with two plaitpoints has been communicated in the preceding paper; in previous investigations connodal lines with one and with no plaitpoint were referred to.

Chemistry. — *“On the nitration of benzoic acid and its methylic and ethylic salts.”* By Prof. A. F. HOLLEMAN. (Communicated by Prof. C. A. LOBRY DE BRUYN.)

Some time ago (Recueil 17.335) I described a process for the quantitative determination of the three isomeric mononitrobenzoic acids in mixtures of them. This process has been simplified and improved so that the results obtained by it now attain an accuracy

of about 1 %; by this means an answer to the following questions is obtainable:

1. To what extent does the proportion in which the acids are formed in the nitration of benzoic acid depend on the temperature at which this takes place?

2. How do the methylic and ethylic salts of benzoic acid behave in this respect?

These two questions being answered we find at once, (3). How this proportion is modified by the replacement of the hydrogen of the carboxylgroup by methyl or ethyl.

This appears from the following table:

Nitration at		- 30°	0°	+ 30°
Benzoic acid	{ o	14.4	18.5	22.3
	{ m	85.0	80.2	76.5
	{ p	0.6	1.3	1.2
Methylic benzoate.	{ o	23.6		25.7
	{ m	74.4		69.8
	{ p	2.0		4.5
Ethylic benzoate.	{ o	-40° 25.5	28.3	27.7
	{ m	73.2	68.4	66.4
	{ p	1.3	3.3	5.9

From this it is obvious that the characteristic of the process of nitration, the preponderant formation of the meta-acid, is retained throughout the interval of temperature of 60° and is unaffected by the substitution in the carboxyl group, but that the quantity of secondary products is considerably increased both by raising the temperature and by the substitution.

The details of this investigation will shortly be published in the "Recueil".

Groningen, May, 1899.