Thus, although the existence of dichloro-acetylene has not been proven, it existence seems possible.

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THE LIMITS OF ACCURACY OF HOLLEMAN'S METHOD OF DETERMINING THE COMPOSITION OF A MIXTURE OF TWO OR THREE ISOMERS.

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Holleman[1] gives a method for the quantitative determination of three isomers, depending upon the freezing point. This method is a special application of Bakhuis Roozebooms general method of determing the freezing points of mixed crystals, etc.[2] The purpose of the present experiments is to discover the limits of accuracy of this method, together with the details of the manipulation. While Holleman shows the applications of his method to many compounds, he says nothing of its limit of accuracy. A short résumé of the method will first be given; for a more extended description the reader is referred to Holleman's book, and to the references given therein. It is plain that if the method furnishes accurate enough results, it will save much tedious work formerly required in investigations of isomers of this character, in separating the products to determine the result.

If two isomers are melted together and allowed to cool, unless they form a eutectic mixture, one of the isomers will start to solidify at a definite temperature, depending on the proportion of the substances. This isomer will freeze out until the eutectic point is reached, when the whole mass will solidify together. In this way, after determining a curve for the freezing points of different mixtures of the two substances, the constitution of a binary mixture can be determined from the position on the curve of the freezing point. This curve has two branches, dropping from the freezing point of one pure isomer to the eutectic, and then rising to the freezing point of the second substance. It is always possible, however, to find on what branch of the curve a given point lies, by adding a weighed portion of one of the isomers to the mixture, and observing the position of the freezing point for the resulting mixture.

In most compounds produced by the addition of substituents to the benzene nucleus, two of the isomers occur chiefly, while the third is found in small porportions—from a mere trace to 8 or 10%. In some cases only one isomer is obtained in quantity; this, however, necessitates only changes

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[1] "Die direkte Einfuhrung von Substituenten in den Benzolkern" (Veit & Co., 1910).

[2] *Z. physik. Chem.*, 30, 386 (1899). Reference may be made to Roozeboom's "Die Heterogene gleichgewichte von Standpunkte der Phasenlehre" Vol. II, 1904 for further information on the general theory.

in the details of the method. The effect of the third isomer is to change the position of the freezing point, and also to lower the eutectic. For the small amount which usually occurs, the amount of lowering of the eutectic is directly proportional to the quantity of the third substance present—that is, the curve of the lowering may be considered as a straight line. For arbitrary mixtures of three isomers of any proportion, Holleman gives two methods, by which a quantitative estimation may be made without first determining the entire freezing-point surface of the ternary mixture. These methods are not considered here, but would obviously have about the same degree of accuracy.

The method recommended by Holleman is as follows: The mixture, after suitable purification, containing the three isomers and free from all other substances, is placed in a test tube and melted, and the freezing point approximately determined with an ordinary thermometer. It is then heated to a few degrees above the melting point, and placed inside a second test tube large enough to furnish a small air space. This second tube is immersed in a suitable bath, furnished with a stirrer; or for lower temperatures, in a Dewar flask with a suitable cooling mixture. This bath is provided with a thermometer and is kept from 5 to 10°, according to circumstances, below the temperature of the substance in the tube. A thermometer graduated to 0.10 is immersed in the substance, and is used to stir the mixture. The temperature drops at the same rate as the bath, but is a little higher, as mentioned above. The mixture supercools a little, and then, when the first isomer commences to solidify latent heat is liberated and the temperature rises. The highest point so reached is the primary freezing point: in a binary mixture this is sufficient to determine the composition. The rate of cooling must not be too rapid. It will be noticed that the procedure is essentially the same as that used in determing the lowering of the freezing point by Beckmann's method.

The primary point is determined two or three times and the results averaged together. Then the mixture is allowed to cool, without further stirring, until the second isomer also beings to solidify. This gives the secondary point, or, in a binary mixture, is the eutectic. Three or four determinations are made of this point, also.

The results are calculated by taking a mixture of the two substances appearing in the largest proportions, and observing the lowering of the primary and secondary points on adding a given quantity of the third isomer. A carefully weighed amount of the third isomer is then added to the sample, and the lowering of the two points observed. A simple proportion between the per cent. added and the lowering of the secondary point produced gives the percentage of the third isomer, and subtracting the lowering produced by this amount from the primary point gives the percentage of the second isomer.

In the experimental work, nitraniline was chosen as the substance. The freezing points of the three isomers lie far apart, *p* — 166.99°, *m* — 109.0, *o*—71.5. Also, the application of this method to nitraniline is not mentioned by Holleman.

A curve was constructed from the freezing points obtained from mixtures of *m*- and *p*-nitraniline as given below.

Temperature.	*m* %.	*p* %.
146.99	00.00	100.00
145.66	1.47	96.53
144.03	3.91	96.09
143.07	5.55	94.45
141.27	8.34	91.66
140.01	10.07	89.93
135.97	15.44	84.56
134.07	17.66	82.34
126.18	26.44	73.56
117.53	34.44	65.56
110.87	40.23	59.77
97.21	48.90	51.10

This curve, as plotted, was very regular. The difficulty of obtaining consistent points is greater when more than 35% of *m*-nitraniline is present, but by adding a weighed amount of *p*-nitraniline, the percentage of *m* may be made as small as desired. The curve also exhibits irregularities when less than 10% *m*.

After plotting the curve, various mixtures were taken, and the percentages given by the position of the freezing point on the curve compared with the true proportions.

BINARY MIXTURES.

		% *m* with *p*.	
	Temperature.	From curve.	True %.
A	114.43	37.45	37.55
B	119.09	33.48	33.66
C	140.12	9.99	9.12
D	126.74	25.77	25.82
E	131.39	20.80	20.86
F	133.59	18.27	18.24

It will be noticed that the results obtained for A and B are not so close as those for D, E and F. These latter points are very close; this portion of the curve seems to give very accurate results. Also, C is still less accurate; it was noticed above that the portion of the curve below 10% of *m* is very irregular.

The chief points to be noted in the manipulation are that it is best to stir the substance very little until it has supercooled and the temperature has started to rise, when it must be stirred continuously until the point is reached. The stirring, however, must be regular, but not too vigorous. The difference in temperature between the bath and the substance must not be too great, though a few degrees' difference in the temperature of the bath does not affect the freezing point of the mixture appreciably, in the successive determinations. The substance must not be cooled too rapidly. It is very necessary that the substance should be thoroughly melted before taking the freezing points, as a few small crystals remaining solid when the substance is first placed in the bath will greatly affect the result. This precaution is even more important in determining the secondary points; if all the substance is not melted, the point obtained may be two or three degrees lower than it should be. In taking the secondary point, it is also necessary that the mixture be continually stirred until the primary point is reached, and that it then be allowed to cool with no further stirring. Failure to observe these conditions gives successive points varying very widely.

To test the accuracy of the method for three isomers, it is necessary to determine the eutectic point for the binary mixture, and then adding small amounts of *o*-nitraniline to observe the lowering produced. The results of two such experiments are given below.

A. For 20.86% *m* with *p*. Eutectic is 86.63°.

	% *o*.	Temperature.	Lowering.	For 1%, lowering is
1	1.76	82.21	4.42	2.51°
2	3.99	76.44	10.19	2.55
3	6.96	68.27	18.36	2.63
4	8.45	62.59	24.04	2.84
5	11.22	57.04	29.59	2.64

B. For 24.55% *m* with *p*. Eutectic is 86.74°.

	% *o*.	Temperature.	Lowering.	For 1%, lowering is
1	0.86	84.75	1.99	2.31
2	2.78	80.44	6.30	2.26
3	7.33	68.77	17.97	2.45

It is also necessary to observe the effect of the third isomer on the primary point. This is done by observing how closely the freezing point for a given percentage of *o*- plus *m*-nitraniline corresponded to the point for a like percentage of *m*-nitraniline.

Temperature.	Corresponds to % *m*.	% *o* plus *m*.	% *o*.
130.03	22.31	22.29	4.84
129.52	22.90	22.23	5.96
129.57	29.18	29.74	11.22

It will be observed that for 5% or less of *o*—the lowering of both primary and secondary points gives very close results, diverging more widely for larger amounts. However, for as high as 10% of the third isomer it is evident that in the case of nitraniline, at least, the accuracy of the method is all that could be desired.

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