results obtained in the absence of magnesium salt are probably the correct ones.

It is hoped to present a later paper which will go into further details concerning the method for urea estimation described above, as applied under various conditions, and which will discuss further the probable value of this method in comparison with that of Folin.

CHICAGO, ILL.

STUDIES IN NITRATION, V. MELTING POINTS OF MIXTURES OF ORTHO- AND PARANITRANILINES.[1]

BY J. BISHOP TINGLE AND H. F. ROLKER.

In the second paper of this series,[2] we gave the results of our determinations of the melting points of mixtures of ortho- and meta- and of meta- and paranitranilines. We also showed that the curves obtained by

TABLE OF THE MELTING POINTS OF MIXTURES OF ORTHO- AND PARANITRANILINE.

Per cent. of ortho.	Per cent of para.	M. P.	M. P. after having been melted and quickly cooled.	Per cent. of ortho.	Per cent. of para.	M. P.	M. P. after having been melted and quickly cooled.
98	2	68.5°	68.0°	48	52	103.0°	102.0°
96	4	67.0°	67.0°	46	54	104.0°	104.0°
94	6	66.0°	67.0°	44	56	109.0°	115.0°
92	8	66.5°	66.0°	42	58	112.0°	113.0°
90	10	64.0°	64.0°	40	60	115.0°	116.0°
88	12	62.5°	63.5°	38	62	109.0°	109.0°
86	14	61.0°	61.5°	36	64	117.0°	121.0°
84	16	63.5°	60.5°	34	66	123.0°	122.0°
82	18	60.5°	60.0°	32	68	129.0°	130.0°
80	20	61.0°	59.5°	30	70	121.0°	122.0°
78	22	62.0°	62.0°	28	72	127.5°	128.0°
76	24	61.0°	60.0°	26	74	127.0°	128.0°
74	26	60.8°	61.0°	24	76	109.5°	114.0°
72	28	61.0°[3]	61.0°	22	78	131.0°	133.0°
70	30	60.0°	72.0°	20	80	132.5°	134.0°
68	32	60.0°	59.0°	18	82	139.0°	142.0°
66	34	61.5°	59.0°	16	84	135.0°	135.0°
64	36	61.5°	86.0°	14	86	135.0°	137.0°
62	38	62.0°	83.0°	12	88	137.0°	139.0°
60	40	61.0°	85.0°	10	90	142.0°	141.5°
58	42	98.0°	96.0°	8	92	141.5°	143.5°
56	44	91.0°	90.0°	6	94	142.0°	144.0°
54	46	104.0°	103.0°	4	96	144.8°	145.5°
52	48	93.0°	95.5°	2	98	147.0°	147.0°
50	50	99.0°	99.0°	..	..	......	......

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[1] Previous papers have appeared as follows: Bishop Tingle and Blanck, *Am. Chem. J.*, 36, 605 (1906); Bishop Tingle and Rolker, THIS JOURNAL, 30, 822; Bishop Tingle and Blanck, *Ibid.*, 30, 1395, 1587 (1908).

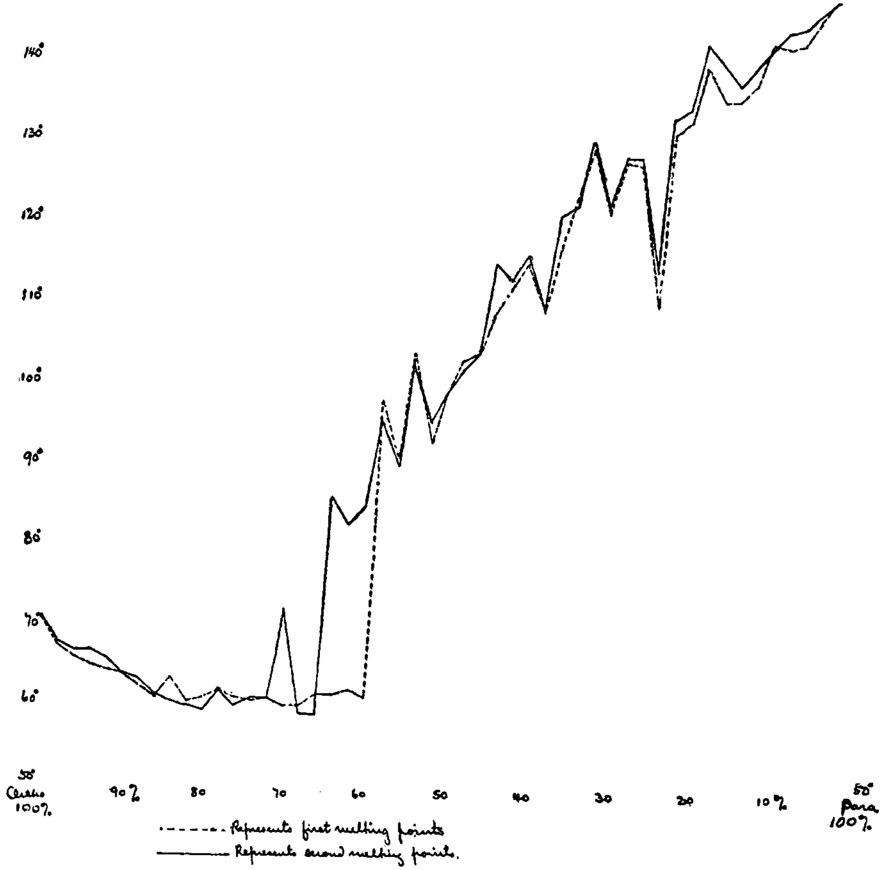
[2] *Loc. cit.* After the proof had been revised the printers changed the name of the junior author to *Roelker*.—J. B. T.

[3] Somewhat indefinite

plotting the composition against the melting points could be used to ascertain the proportion of the constituents in mixtures of unknown composition. The curves which we obtained from mixtures of ortho- and paranitranilines were so irregular that we decided to repeat our work on them before publishing the results.

Our revised experiments were carried out in substantially the same manner as those of the first series, certain additional precautions being taken and the work being repeated with various individual mixtures, when necessary, until concordant results were obtained.

Weighed quantities of the nitranilines were dissolved in 95 per cent. alcohol, at the ordinary temperature, the necessary portions of the fairly dilute solutions were run off from a burette and the mixed liquid allowed to volatilize, without heating. The residue was then carefully ground up and dried in a desiccator. After determining the melting point of



Curves showing the melting points of mixtures of ortho- and paranitraniline.

the material in the ordinary manner, the capillary tube was quickly cooled and the melting point redetermined. The results are given in the above table.

The results recorded in the table are given in the above curves, in which the dotted line represents the first and the continuous line the second melting point.

The irregularities shown in the above curves appear to preclude any suggestion of their being due to a constant source of error in our work.

Professor W. J. Pope, of Cambridge, England, has been good enough to suggest that the variations in the melting points are due to polymorphism. Material which melts at one temperature as form *A* may, on heating, change into form *B*, which then melts at a quite different temperature. It will be noticed that the four original mixtures, containing 24, 38, 52 and 56 per cent. of orthonitraniline, respectively, when considered apart from the others, form a fairly regular curve and that the same is true of the remaining 44 mixtures. Regarding the second series of melting points in the same manner, it is found that the nine mixtures containing 16, 24, 38, 52, 56, 60, 62, 66 and 68 per cent. of orthonitraniline, respectively, form *inter se* a fairly regular curve, as do also the remaining 39 mixtures. Moreover, it is evident that the composition of the four original mixtures coincides with that of four of the nine mixtures selected from the second curve.

Additional evidence to test the validity of the suggestion of polymorphism could probably be obtained by the application of crystallographic methods, but we do not propose to pursue the subject further in this direction. As stated in our earlier paper, the object of our investigation was to try to devise an easy and accurate method for determining the composition of binary mixtures of the nitranilines.

In the course of this work we had reason to distrust some of the published data on the solubility of the nitranilines in alcohol. Our own determinations lead to the following results: At 15°, 100 cc. of 95 per cent. alcohol dissolve 15.848 grams of ortho-, 4.960 grams of meta- and 4.030 grams of paranitraniline, respectively.

Summary.

1. Mixtures of ortho- and paranitraniline have been made, the differences in composition between consecutive mixtures being 2 per cent.

2. Curves are given showing (*a*) the melting points of these original mixtures; (*b*) the melting points after the molten mixture had been cooled quickly and then remelted.

3. It is suggested that the irregularities shown by these curves are due to polymorphism.

4. Determinations have been made of the solubility of ortho- and paranitraniline, respectively, in 95 per cent. alcohol.

The general work on nitration is being continued in this laboratory by Mr. C. E. Burke, under the direction of the senior author.

McMaster University, Toronto, Canada,
August, 1908.

FURTHER STUDIES ON THE FORMS OF MILK-SUGAR.

By C. S. Hudson.

Received August 29, 1908.

Contents.—(1) Introduction; (2) The Solubility Relations of Milk-Sugar; (3) The Maximum Rate of Solution of the β-Anhydride; (4) The Transition Temperature between Hydrated and β-Anhydrous Milk-Sugar; (5) The Solubility Curves of Milk-Sugar in Relation to the Transitions of Substances in General; (6) The Vapor-Pressures of Saturated Solutions of Hydrated Milk-Sugar; (7) The Aqueous Vapor-Pressure of Solid Hydrated Milk-Sugar in Contact with the β-Anhydride; (8) The Specific Rotations of the Forms of Milk-Sugar; (9) The Influence of Concentration on the Equilibrium between the Forms of Milk-Sugar; (10) Summary.

1. Introduction.

In a previous publication[1] the writer has called attention to the fact that hydrated milk-sugar crystallizes from aqueous solutions at room temperature but β-anhydrous milk-sugar from solutions above 95°. There must accordingly be a transition temperature within these limits between these forms of milk-sugar. The present investigation was undertaken in order to find the location of this transition temperature; in the course of the investigation it became apparent that the transition from the one form of milk-sugar to the other illustrates to a fulness that has not been experimentally realized before, the general conditions which cause transition temperatures. As the milk-sugar transition becomes thus of general theoretical interest the measurements on it were made very fully and extend to several related phenomena. All of these measurements, which are described below, agree quantitatively with the conclusion that was obtained from the former studies, namely that aqueous solutions of milk-sugar contain two substances in equilibrium and that the mutarotation of milk-sugar results from the slow establishment in cold solutions of the equilibrium of the balanced reaction

$$\underset{\text{(Hydrate.)}}{C_{12}H_{24}O_{12}} \rightleftarrows \underset{(\beta\text{-Anhydride.})}{H_2O + C_{12}H_{22}O_{11}}.$$

In this connection it should be stated that there is no direct evidence that the freshly dissolved hydrate exists in solution in the hydrated condition. It is quite possible that it exists largely as the α-anhydrous modification which is a view that would be similar to the conclusion that

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[1] This Journal, 26, 1067 (1904). Opportunity is here taken to correct an error on pages 1077 and 1081, where common logarithms were employed in calculating the absolute rates of hydration and dehydration. Natural logarithms should have been used and the correct values are 3.36, 17.3, and 51.1 per cent. sugar changed per hour instead of 1.46, 7.52, and 22.2 per cent. respectively.