NOTES.

Volumetric Determination of Semicarbazide and Aminoguanidine. By G. Stanley Smith.

These derivatives of hydrazine may be determined by an adaptation of a method for hydrazine in which potassium iodate and sodium thiosulphate are used (cf. Bray and Cuy, *J. Amer. Chem. Soc.*, 1924, **46**, 859; Kurtenacker and Kubina, *Z. anal. Chem.*, 1924, **64**, 388).

To 0·08 g., accurately weighed, of semicarbazide hydrochloride or of aminoguanidine sulphate monohydrate, dissolved in 50 ml. of water, were added 20 ml. of 5*N*-sulphuric acid, followed by 50·00 ml. of 0·1*N*-potassium iodate. The solution was kept stoppered for 3 minutes, an excess of potassium iodide added, and the total free iodine titrated at once with 0·1*N*-thiosulphate. If the reaction (1) is assumed, then from reaction (2) it follows that the thiosulphate equivalent of the total iodine so formed, deducted from that of the iodate added, gives the " apparent " iodate required. This, multiplied by 1·2, gives the true iodate. Calculated on the difference in the titrations, 1 ml. of 0·1*N*-thiosulphate = 0·0008012 g. of hydrazine or 0·001877 g. of semicarbazide or 0·001852 g. of aminoguanidine.

$$(1)\ 5NRH{\cdot}NH_2 + 4KIO_3 \longrightarrow 2I_2 \qquad (2)\ KIO_3 + 5KI \longrightarrow 3I_2$$

Found, for semicarbazide hydrochloride (m. p. 173°): semicarbazide, 67·4 (Calc.: 67·3%); for aminoguanidine sulphate (m. p. 206°): aminoguanidine, 55·7 (Calc.: 56·1%).

Maselli (*Gazzetta*, 1905, **35**, i, 271) determined semicarbazide by boiling it with dilute sulphuric acid for 15 minutes, oxidising the hydrazine with excess of iodate, boiling off the iodine, and titrating the undecomposed iodate with thiosulphate. This method was found to give high results for semicarbazide hydrochloride (theoretically, 1 ml. of 0·1*N*-potassium iodate = 0·001564 g. of semicarbazide): Found, semicarbazide, 68·9, 69·3, 69·5, 69·5%.

On the other hand, when the solutions obtained by the preliminary boiling with sulphuric acid were treated in the manner first described, the iodine produced in reaction (1) not being boiled off, the results were: Semicarbazide, 67·4%; aminoguanidine, 55·7%.

Acetonesemicarbazone, treated as in the first method, was found to react (0·0542 g., 50 ml. of water, 20 ml. of 5*N*-sulphuric acid, followed immediately in the cold by 25 ml. of 0·1*N*-iodate, required 9·4 ml. of 0·1*N*-thiosulphate). Hence it would not be possible to determine acetone by adding an excess of semicarbazide and determining this excess by direct titration.—166 Wickham Chase, West Wickham, Kent. [*Received, May* 19*th*, 1937.]

The System Potassium Chloride–Potassium Chlorate–Water at 20°, 50°, *and* 75°. By Maxwell B. Donald.

This system was investigated by Winteler (*Z. Elektrochem.*, 1900, **7**, 360) for 20°, and for the conditions where the solution is saturated with chlorate but not with chloride. The results indicate that the solubility of the chlorate decreases very rapidly at first and then is almost constant over a large variation in chloride content; however, they give no indication of the position of the invariant point where the solution is saturated with regard to both chloride and chlorate. The present investigation had as its object the determination of the invariant point, not only at 20°, but also at 50° and 75°. The points were fixed by having excess of the two salts present in solution. The following table shows the degree of accuracy obtained at 50° :

H_2O, %.	KCl, %.	$KClO_3$, %.	*d.*
67·10	28·21	—	1·2111
67·37	28·24	4·32	1·2117

A second determination of the 20° point was made between these two samples.

The chloride was estimated by Mohr's method, the chlorate by Ruff's method (*Z. anal. Chem.*, 1917, **56**, 580), and the water by direct weighing. The results are as follows :

Temp.	H_2O, %.	KCl, %.	$KClO_3$, %.	*d.*
20°	73·4	25·0	1·56	1·177
50	67·4	28·3	4·32	1·211
75	62·6	29·3	8·08	1·244

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The Conductivity of Potassium Chloride Solutions. By CECIL W. DAVIES.

IN a recent paper (this vol., p. 432) some new measurements of the conductivity of potassium chloride solutions at 18°, based on the Jones and Bradshaw standard, were compared with the measurements of Kohlrausch and Maltby. The difference (0·07%) between the figures, it was stated, " gives the difference between the new standard of Jones and Bradshaw and the older standard of Kohlrausch and Holborn for (approximately) 0·01*N*-potassium chloride, on which Kohlrausch and Maltby's measurements depended." This is misleading because, although Kohlrausch and Maltby say that their results were based on Kohlrausch, Holborn, and Diesselhorst's work, their figures are not consistent with the standard quoted by Kohlrausch and Holborn (" Leitvermögen der Elektrolyte," 1898, p. 77). Kohlrausch and Holborn give $10^5 . \kappa = 122{\cdot}5$ for a solution containing 74·59 g. of potassium chloride in 100 litres of solution at 18°, but Kohlrausch and Maltby's mean value is $10^5 . \kappa = 122{\cdot}41_5 \pm 0{\cdot}04_5$ for a solution containing 74·60 g. of the salt in 100 litres of solution at 18° (*Wiss. Abh. Phys. Tech. Reichsanstalt*, 1900, **3**, 199). Consequently, Kohlrausch and Maltby's standard is 0·08% lower than that of Kohlrausch and Holborn, and when allowance is made for this it must be concluded that conductivities based on the quoted Kohlrausch–Holborn standard are 0·15% higher than those based on the new standard of Jones and Bradshaw.

Jones and Prendergast (*J. Amer. Chem. Soc.*, 1937, **59**, 736) have recently made a direct redetermination of the conductivity of the Kohlrausch–Holborn standard solution and find the Kohlrausch value to be $0{\cdot}18_9$% too high. The agreement between these two figures must be regarded as satisfactory when it is remembered that the indirect comparison involves measurements by Shedlovsky at 25°, the data of Kohlrausch and Maltby at 18°, and measurements by the author at 18° and 25°.

It is noteworthy that the difference between the Kohlrausch–Maltby value (which is solvent-corrected) and the Kohlrausch–Holborn value corresponds approximately with the conductivity of the water used by Kohlrausch. A possible explanation of the discrepancy between the two values therefore is that Kohlrausch and Holborn intended no solvent correction to be applied in cell calibrations based on their quoted value. This is the more likely in that no correction is mentioned in Kohlrausch and Holborn's directions, nor could one be accurately calculated for a solution made up by dilution according to these authors' recommendations.

The position then is this. If Jones and Bradshaw's new standard is accepted, any (solvent-corrected) measurements based on the Kohlrausch–Holborn 0·01*N*-standard must be considered to be 0·18% too high; but Kohlrausch's later measurements on dilute salt solutions, and any measurements based on Kohlrausch and Maltby's data, such as those of Kraus and Parker on iodic acid and of Parker on hydrochloric acid, must be regarded as 0·07—0·10% too high.—BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, June* 14*th*, 1937.]