125. *The Potentiometric Estimation of Hydroxylamine and Hydrazine in Alkaline Solution.*

By H. T. S. BRITTON and MARIANNE KÖNIGSTEIN.

An accurate potentiometric method of estimating hydroxylamine and hydrazine has been devised by titrating either (*a*) alkaline copper tartrate solution or (*b*) ammoniacal copper sulphate solution at 90° with salts of either hydroxylamine or hydrazine. After the end-point has been passed, the platinum electrode functions as a copper electrode in equilibrium with cuprous ions, unlike the behaviour in ordinary " redox " titrations.

DONATH (*Ber.*, 1877, **10**, 766) and Meyeringh (*ibid.*, p. 1940) showed that hydroxylamine is oxidised quantitatively to nitrous oxide by boiling Fehling's solution, and Jones and Carpenter (*Proc. Camb. Phil. Soc.*, 1903, **12**, 218; J., 1903, **83**, 1395) devised a volumetric method of estimating hydroxylamine by allowing the cuprous oxide thus precipitated to reduce an equivalent amount of ferric sulphate in sulphuric acid solution.

Hydrazine is, however, oxidised quantitatively to nitrogen by boiling Fehling's solution with precipitation of cuprous oxide (Petersen, *Z. anorg. Chem.*, 1893, **5**, 1; cf. Browne and Shetterley, *J. Amer. Chem. Soc.*, 1909, **31**, 783) or, with excess of hydrazine, of metallic copper (Jannasch and Biedermann, *Ber.*, 1900, **33**, 631). Ebler (*Z. anorg. Chem.*, 1905, **47**, 371) has also demonstrated that quantitative oxidation to nitrogen occurs with copper sulphate in ammoniacal solution. Titrimetric methods of estimating hydrazine with Fehling's solution do not appear to have been successful, although Petersen showed that measurement of the volume of nitrogen evolved leads to accurate results.

In the present work the oxidation of both hydroxylamine and hydrazine when progressively added to either Fehling's solution or an ammoniacal solution of copper sulphate, maintained at 90°, has been followed potentiometrically, either bright platinum foil or copper being used as the indicator electrode. The complete reduction of the bivalent copper in these two complex solutions to the cuprous state, either by the precipitation of cuprous oxide or by conversion into tetramminocuprous sulphate, is indicated by such a sudden diminution in potential that it serves as an excellent method of estimating hydroxylamine and hydrazine. To obtain accurate results it is desirable, though not absolutely essential, to carry out such potentiometric titrations in an atmosphere of nitrogen in order to prevent oxidation of the cuprous oxide by the air.

EXPERIMENTAL.

The system used was:

— Pt	100 c.c. of Fehling's solution + 0·1M-NH_2OH,HCl (or + 0·1M-N_2H_4,H_2SO_4)	Satd. KCl	N-KCl	N-KCl + Hg_2Cl_2	+ Hg

In order to prevent diffusion, the ends of the saturated potassium chloride salt bridge were plugged with asbestos, and one end was immersed in a vessel containing N-potassium chloride, in which was also inserted the tube leading from the normal calomel electrode. The titration vessel was fitted with an ebonite cap, containing holes for two platinum electrodes, a thermometer, a tube leading from the burette, the end of the salt bridge, a mechanical stirrer, and a tube for the introduction of nitrogen. The whole cell was immersed in a water-bath kept at such a temperature that the solution in the titration vessel was at 90—92°.

Typical titration curves are given in the figure. In each case 100 c.c. of solution containing copper sulphate, sodium tartrate, and sodium hydroxide, in the respective molecular ratios of 1 : 4·6 : 10·8, was titrated with either 0·1M-hydroxylamine hydrochloride (curves *a*) or 0·1M-hydrazine sulphate (curves *b*). The molarity of the copper sulphate in the various solutions titrated is indicated on the curves. For the Fehling solution sodium tartrate was used instead of Rochelle salt, for (see Britton and Phillips, *Analyst*, 1940, **65**, 18) the potassium ion is by no means essential to retain cupric oxide in alkaline solution. Constant potentials were set up at the platinum electrodes in about 2 mins. both with the hydroxylamine and with the hydrazine salt. This was the case during the initial part of the titrations and at the end-points, substantially the same voltages within 2 or 3 mv. being obtained; thereafter the potentials were more slowly attained and tended to become unsteady. The curves show that the positions at which the inflexions denoting the end-points occur correspond exactly with the respective equations :

(i) $4CuO + 2NH_2OH \longrightarrow 2Cu_2O + N_2O + 3H_2O$; (ii) $4CuO + N_2H_4 \longrightarrow 2Cu_2O + N_2 + 2H_2O$.

The broken curve in section *a* of the figure represents the titration of 100 c.c. of 0·02M-copper sulphate (in Fehling's solution) with 0·1M-hydroxylamine hydrochloride, and that in section *b* is the curve obtained by titrating 100 c.c. of 0·01M-copper sulphate (as Fehling's solution) with 0·1M-hydrazine sulphate, copper electrodes being used against the N-calomel electrode at 90°. The lower curves, marked NH_3, were obtained with platinum electrodes by titrating at 90°, 100 c.c. of 0·02M-copper sulphate solution, saturated with ammonia, with 0·1M-hydroxylamine hydrochloride and 0·1M-hydrazine sulphate respectively. In these two titrations, gaseous ammonia was passed through the solutions instead of nitrogen, thus ensuring an inert atmosphere and keeping the solution saturated. In these titrations the cuprous salt produced was retained in solution.

DISCUSSION.

As the titration graphs show, the end-points are sharply defined by inflexions which represent sudden diminutions in potentials at the platinum electrodes (and also at the copper) of 200—300 mv. The potentials established during the initial stage of the titrations are caused by the varying equilibria between cupric ions and cuprous ions in accordance with the expression

$$E_{Pt} = \varepsilon_{Cu^{\cdot\cdot} \rightleftarrows Cu^{\cdot}} - 0{\cdot}072 \log_{10} [Cu^{\cdot}]/[Cu^{\cdot\cdot}]$$

Thus, by taking $\varepsilon_{Cu^{\cdot\cdot} \rightleftarrows Cu^{\cdot}} = + 0{\cdot}16$ volt (N-H = 0), it being assumed that the normal reduction potential is not greatly affected by temperature and that $[Cu^{\cdot}]$ of the complex tartrate solutions, of which $[OH'] = 10^{-1}$ approx., was determined by the solubility product of the precipitated cuprous oxide, *viz.*, $L_{CuOH} =$ *ca.* 10^{-14} (cf. Allmand, J., 1909, **95**, 2162), it follows that $[Cu^{\cdot}] = 10^{-13}$ approx. Edge (Ph.D. Thesis, London, 1938, p. 54) has shown that the $[Cu^{\cdot\cdot}]$ of such solutions as were here employed is about 10^{-16}. Hence $E_{Pt} = 0{\cdot}16 - 0{\cdot}072 \log 10^{-13}/10^{-16} = - 0{\cdot}06$ volt. Britton and Welford (J., 1937, 1846) have shown that at 91° the potential of the normal calomel electrode (N-H = 0) is + 0·263 volt, whence it follows that the potential of the platinum electrode should be about — 0·32 volt against the normal calomel. The figure shows that this is the case during the reduction process. Incidentally, it is true of the titrations in which copper electrodes were used.

In the ammoniacal copper sulphate titrations less negative potentials were registered at the platinum electrodes. The concentrations of cuprous and cupric ions originate from the dissociation of the complex kations, $Cu(NH_3)_4^{\cdot\cdot}$ and $Cu(NH_3)_4^{\cdot}$. Of these ions, the latter is the more stable, and therefore during the first part of the titrations it is likely that $[Cu^{\cdot\cdot}]$ will be less than in the complex copper tartrate titrations, thus accounting for the lower E.M.F.'s observed.

In an ordinary potentiometric titration in which an oxidising agent is being titrated with a reducing agent, the potential set up at a platinum electrode after the end-point inflexion has been passed is due to equilibria existing in the solution between the added excess of the reductant and its oxidised product or products which remain in the solution. In these titrations, the reductants are hydroxylamine and hydrazine, and in both cases their oxidised forms are gases and at 90° would certainly leave the sphere of action. It was therefore of interest to ascertain the electrodic equilibria that were responsible for the appreciably negative final potentials, and which, indeed, made these potentiometric titrations possible. In the hydrazine titrations of Fehling's solution, it was observed that immediately the end-point had been passed the platinum electrodes began to be coated with a bright adherent mirror of copper, showing that the excess of hydrazine was then reducing the precipitated cuprous oxide to the metal. The potentials were unsteady and tended towards less negative values with time. For instance, the upper curve, 0·01, in section *b* represents readings taken after 2 mins., whereas the lower curve refers to readings taken 10 mins. after each addition of hydrazine. Hence, it appeared that the platinum electrode was then functioning as a copper electrode in equilibrium with cuprous ions originating from the cuprous oxide which had not yet been reduced and therefore

$$\begin{aligned} E_{\text{Pt}} &= \varepsilon_{\text{Cu}^\cdot \rightleftarrows \text{Cu}} + 0{\cdot}072 \log [\text{Cu}^\cdot] \\ &= \varepsilon_{\text{Cu}^\cdot \rightleftarrows \text{Cu}} + 0{\cdot}072 \log L_{\text{CuOH}}/[\text{OH}'] \\ &= +\ 0{\cdot}52 + 0{\cdot}072 \log 10^{-14}/10^{-1} \\ &= -\ 0{\cdot}42\ (\text{N-H} = 0) \\ &= -\ 0{\cdot}68 \text{ volt (against normal calomel at } 90^\circ) \end{aligned}$$

FIG. 1*a*.

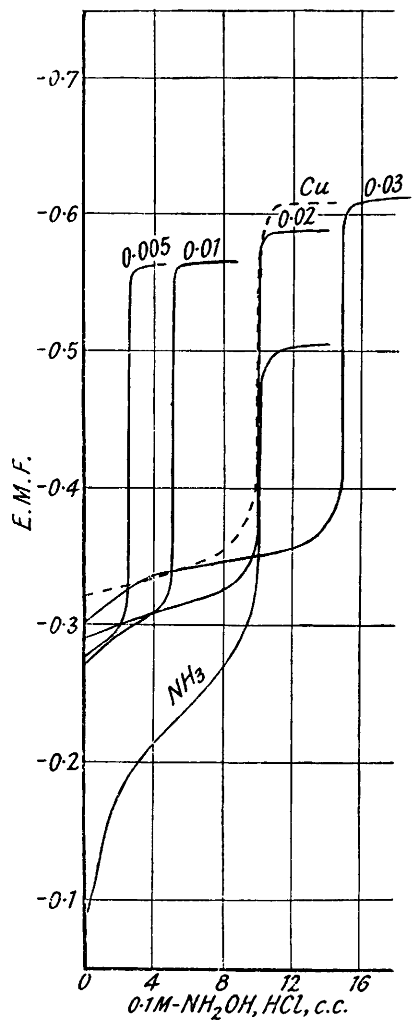
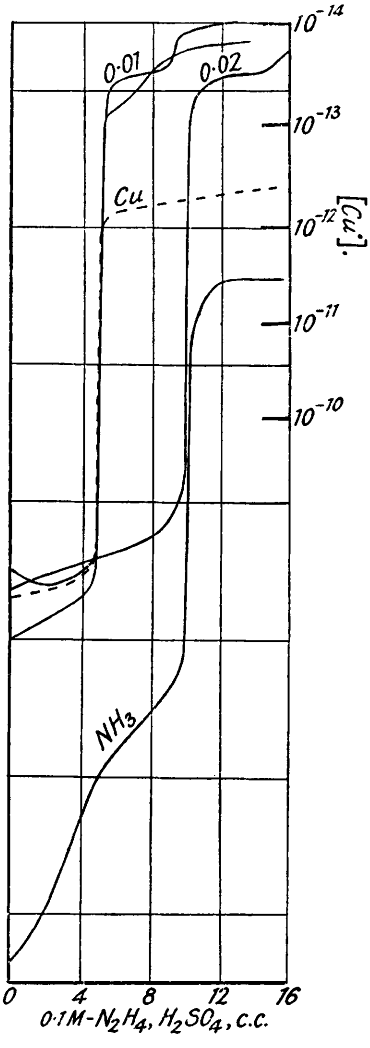


FIG. 1*b*.



which is the order of magnitude of the E.M.F. set up in the final stage of the hydrazine titrations. The approximate scale at the right of the figure, giving the cuprous-ion concentrations, is based on the assumption that the platinum and copper electrodes behaved as copper–cuprous ion electrodes. It will be seen that the cuprous-ion concentrations are of the same order as that computed above. The final stages of the hydroxylamine titrations are marked by somewhat less negative potentials, about — 0·6 volt, and tend to assume more negative values as the alkali content of the Fehling's solutions titrated is increased, apparently owing to the diminished concentration of cuprous ions in equilibrium with the cuprous oxide precipitate. It is significant also that the potential set up at the copper electrode is of similar magnitude. Despite the absence of copper deposits on the platinum electrodes in these titrations, it would appear that the potentials were caused by some slight reduction of cuprous ions to copper, or at least a tendency for such a reduction to occur. It is not clear why the copper electrode did not reach such a negative potential as the platinum electrodes in the hydrazine titrations; on the other hand, it is somewhat surprising that the copper electrodes should have functioned in what appears to be a reversible manner in such alkaline solutions.

Owing to the lower p_H of the ammoniacal copper sulphate solutions, relatively larger concentrations of cuprous ions must have existed in the solutions after passing the end-point than in the alkaline tartrate solutions, and this fact must have led to the lower potentials then prevailing. It may also explain why the platinum electrodes were not visibly covered with a copper film in such hydrazine titrations.

Another point brought out by these titrations is the fact that hydrazine is oxidised to nitrogen whereas hydroxylamine yields nitrous oxide. It appears that the hydrogen atoms attached directly to the nitrogen atoms in both molecules are oxidised, but that the hydroxyl hydrogen in hydroxylamine resists oxidation, thus $2O + 2NH_2{\cdot}OH \longrightarrow 2H_2O + H_2N_2O_2 \longrightarrow 3H_2O + N_2O$; at the temperature at which the titrations were performed hyponitrous acid is decomposed immediately into nitrous oxide.

One of the authors wishes to record her appreciation of the help kindly given by the Exeter Branch of the Federation of University Women and by the Senate of this College which has made collaboration in this work possible.

WASHINGTON SINGER LABORATORIES,
UNIVERSITY COLLEGE, EXETER.

[*Received, March* 21*st*, 1940.]