666. *Electrochemical Measurements in Pyridine. Part I.*
The System $Cu-Cu^+-Cu^{++}$.

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A technique for the measurement of electrochemical potentials in anhydrous pyridine has been developed, including the use of a hydrogen electrode as arbitrary zero. Thermodynamic relationships in the system $Cu-Cu^+-Cu^{++}$ in pyridine have been determined, and it has been shown that, in contrast to the state of affairs in water, the equilibrium $2Cu^+ \rightleftharpoons Cu + Cu^{++}$ favours Cu^+ very strongly.

POTENTIOMETRIC measurements with pyridine solutions have been made by a number of workers (Kahlenberg, *J. Phys. Chem.*, 1899, **3**, 379; Neustadt and Abegg, *Z. physikal. Chem.*, 1909, **69**, 492; Müller, *Monatsh.*, 1929, **53—54**, 215; Müller and Schmidt, *ibid.*, p. 224) but in most cases the potentials observed were not shown to be thermodynamically significant. Abegg and Neustadt (*Z. Elektrochem.*, 1909, **15**, 264) and Partington and Skeen (*Trans. Faraday Soc.*, 1934, **30**, 1062) measured the Cu^+-Cu^{++} and $Fe^{++}-Fe^{+++}$ potentials in pyridine at a single temperature, and in both cases showed that approximately reversible potentials were obtained. The present paper describes the measurement of the $Cu-Cu^+$ and Cu^+-Cu^{++} standard potentials in pyridine; values were obtained at 18° and 95°, thus enabling entropy and heat-content changes to be calculated as well as changes in free energies.

EXPERIMENTAL

Materials.—Unless otherwise stated, analytical-reagent quality anhydrous materials were used without further treatment. Crude pyridine, b. p. 115—120°, was refluxed for several hours with some 5% of ferric chloride, to destroy oxidizable impurities. It was then fractionated in a 2-ft. column of the Widmer type with stainless-steel gauze packing, moisture being excluded during distillation by calcium chloride drying tubes. A fraction boiling over a 0·1° range around 115·5°/750 mm. was collected and stored over potassium hydroxide flake. No special precautions were taken to exclude water when handling this purified pyridine, other than exposing it to the air for the shortest possible time, but it was shown to remain satisfactorily dry and to contain less than 0·01% of water.

Cuprous chloride was prepared by reducing an equimolecular aqueous solution of copper sulphate and sodium chloride by sulphur dioxide. It was dried and stored *in vacuo*, and under these conditions remained white for many weeks. Its solutions in pyridine were dark brown,

the solid in contact with saturated solutions being almost black. Anhydrous cupric chloride (B.D.H.) was used, and was stored *in vacuo*. Lithium chloride was dried at 120° and stored *in vacuo*.

Oxygen-free nitrogen was obtained by bubbling gas from a cylinder through a total depth of about 4 feet of a solution of alkaline dithionite (160 g./l. of sodium " hydrosulphite," 150 g./l. of sodium hydroxide, and 8 g./l. of sodium anthraquinone-β-sulphonate) to remove most of the oxygen, drying it with concentrated sulphuric acid and phosphoric oxide, and finally freeing it from oxygen with one or more bubblers containing copper powder and a saturated solution of cuprous chloride in pyridine; as discussed below, this last system has a great affinity for oxygen. All-glass connections were necessary from the first cuprous chloride bubbler onwards.

Apparatus.—Conventional all-glass potentiometric cells were used, fitted with ground sockets for the reference electrode, burettes, etc. Platinum electrodes were of foil about 1 cm. square; they were cleaned in chromic acid, washed with distilled water, and dried at 120° before use. Silver electrodes were made by electroplating platinum electrodes, an aqueous solution of potassium argentocyanide being used. They were washed with water and pyridine and dried at 120°. Copper electrodes were made either from copper foil or by electroplating platinum electrodes from aqueous copper sulphate containing a little alcohol. They were washed first with water, then with pyridine, and were kept under pyridine. No difference in potential was detected between the foil and the plated electrodes.

All the pyridine solutions used were very poor conductors of electricity, and it was consequently necessary to shield all leads carefully and to use a potentiometer with a very high input resistance, such as a Marconi or Cambridge pH meter, allowing readings to $\pm\frac{1}{2}$ mv. Another consequence of the high cell resistances was that an oil thermostat was necessary at temperatures above 18°; erratic results were obtained in a water thermostat, apparently because the water provided a leakage path of resistance comparable with that of the cell itself.

Reference Electrodes.—(i) *Hydrogen electrode in pyridine.* A few experiments were made to explore the possibility of setting up in pyridine a reversible hydrogen electrode of the type established in water. A platinum foil electrode of about 2 sq. cm. surface area was platinized in the usual way in water, then washed well with pyridine and kept under it when not in use. This electrode was immersed in pyridine solutions of pyridine hydrochloride of various concentrations between 0·001 and 0·055M, prepared by absorbing dry hydrogen chloride in anhydrous pyridine. Hydrogen from a cylinder, purified as described for nitrogen, was bubbled through the solutions, and the potential of the platinized electrode was measured relative to the silver–silver nitrate electrode discussed below. It was found essential to use freshly-platinized electrodes, as their efficiency fell rapidly with time. Separate experiments showed that no detectable hydrogenation of the pyridine occurred under these conditions.

The results obtained at 18° and 739 mm. pressure fitted the equation

$$E = E°(\text{H}_2, \text{H}^+) + 51\ \log_{10}[\text{HCl}]$$

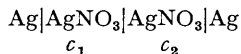which compares reasonably well with the theoretical equation

$$E = E° (\text{H}_2, \text{H}^+) + 58\ \log_{10} a_h$$

where a_h is the hydrogen-ion activity in the solution. As [HCl] $\longrightarrow$ 0, so presumably does $a_h \longrightarrow [\text{H}^+] \longrightarrow [\text{HCl}]$; therefore, using the value of E obtained at the lowest [HCl], and the theoretical factor of 58, we have :

$$E° (\text{H}_2, \text{H}^+) = -534 \text{ mv relative to Ag}|\text{AgNO}_3, 0·048\text{M at } 18° \text{ and } 739 \text{ mm.}$$

However, although it appeared that a hydrogen electrode of the Hildebrandt type did function approximately reversibly in pyridine, it was not such a convenient reference electrode for frequent use as a metal–metal ion one.
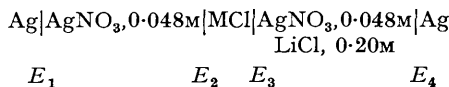
(ii) *Silver–silver nitrate electrode.* The instability in pyridine of mercurous salts rules out the use of a calomel electrode in that solvent, and previous workers (*e.g.*, Abegg and Neustadt, *loc. cit.*) have found the Ag|AgNO$_3$ in pyridine electrode to be the most stable and reproducible of a number of metal electrodes. Sakhanov and Grunbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794) found that the potentials of concentration cells of the type

$$\text{Ag}|\text{AgNO}_3|\text{AgNO}_3|\text{Ag}$$
$$c_1 \qquad\quad c_2$$

obeyed the equation $E = (\boldsymbol{R}T/\boldsymbol{F})\ln c_1/c_2$ at low concentrations. This was confirmed in the present work, a straight line of slope 53 (theoretical 56·8) being obtained by plotting E (at 12°) against $\log_{10} c_1/c_2$ over the concentration range 0·002—0·05M.

The Ag|AgNO₃ half-cell was therefore chosen as a reference electrode, a (purely arbitrary) silver nitrate concentration of 0·048M being used throughout. The form of half-cell used is shown in Fig. 1, contact between the silver nitrate solution inside and the main solution being made by diffusion past the ungreased cap on the reference electrode.

To assess the possibility of reducing the liquid-junction potential by adding a second electrolyte to the reference electrode, the E.M.F. of the cell

$$Ag|AgNO_3,0·048M|MCl|AgNO_3,0·048M|Ag$$
$$LiCl, 0·20M$$
$$E_1 \qquad\qquad E_2 \quad E_3 \qquad\qquad E_4$$

was measured, where MCl was HCl or LiCl. The E.M.F. was independent (to within ±1 mv) of the nature of MCl, and varied by only 10 mv when the concentration of MCl was varied from 0·064M to 0·64M. Since the total E.M.F. was the sum of E_1, E_2, E_3, and E_4 of which E_1 and E_4 were independent of the concentration and nature of MCl, it followed that the two liquid-junction potentials E_2 and E_3 were similarly affected by changes in the bridge solution, and there was no advantage in adding lithium chloride to the reference electrode (the mobilities in pyridine of the lithium and chloride ions are not known, and lithium chloride might not be the most suitable salt to use, but solubility considerations limit the choice). The E.M.F. of the above cell was some 150 mv, suggesting that silver ions and chloride ions in pyridine interact so as to reduce the silver-ion activity very considerably. Potentials measured relative to Ag|AgNO₃ and Ag|AgCl will thus not be comparable even when [AgNO₃] = [AgCl].
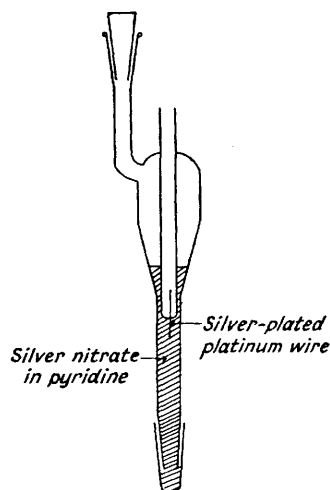
Measurement of the Cu–Cu⁺ Standard Potential, E° (Cu, Cu⁺).—In the system Cu–Cu⁺–Cu⁺⁺ the reaction Cu + Cu⁺⁺ ⇌ 2Cu⁺ is possible, and therefore in general the potential of a copper electrode in a solution containing cuprous and cupric ions will not be stable relatively to a reference electrode if the system is not in equilibrium with respect to the above reaction, unless the velocity of approach to equilibrium is very low, so that a metastable state can persist. It was found that in pyridine the position of the above equilibrium lay so far over on the side of cuprous ion that even the purest cuprous chloride prepared (>99·5%) contained much more cupric ion than the equilibrium amount. Further, the velocity of the reaction Cu + Cu⁺⁺ ⟶ 2Cu⁺ was significant even at low cupric-ion concentration, so that a copper electrode immersed in a cuprous chloride solution containing 0·5% of cupric chloride rapidly became coated with a black film of cuprous salt, and stable potentials were not obtained. Still more rapid changes

Fig. 1. *Reference electrode.*

Silver nitrate in pyridine

Silver-plated platinum wire

were observed when copper was brought into contact with a solution of cupric chloride in pyridine. The copper blackened, and the blue cupric solution became green and finally brown if reduction proceeded sufficiently far. The same colour changes were noted by Partington and Skeen (*loc. cit.*), who did not, however, interpret them and attempted unsuccessfully to use the electrode as a reference one. In order to obtain steady potentials it was therefore necessary to allow the reduction of the excess of cupric ion present in the cuprous chloride used to approach as closely to equilibrium as possible, and this entailed the provision of a large surface of copper and the extremely rigid exclusion of oxygen, since the oxidation of cuprous to cupric proceeds very rapidly, so much so that it provides a very efficient means of removing traces of oxygen.

Nitrogen, purified as described above, was bubbled through a reduction cell containing a cuprous chloride solution of known concentration and a large excess of copper powder, through the potentiometric cell proper, and finally through a copper–cuprous chloride–pyridine bubbler required to prevent back-diffusion of oxygen. The progress of the reduction was followed by measuring the potential of a platinum electrode in the reduction vessel relatively to a silver–silver nitrate reference electrode; this potential difference is approximately given by the equation

$$E = E° (Cu^+, Cu^{++}) + (RT/F)\ln[Cu^{++}]/[Cu^+]$$

[where $E°$ (Cu⁺, Cu⁺⁺) is the cuprous–cupric standard potential] and therefore becomes less positive as [Cu⁺⁺]/[Cu⁺] decreases. After several hours, when reduction had gone as far as

possible, the cuprous chloride solution containing copper powder in suspension was blown over into the cell proper, and the potentials of the platinum and copper electrodes relatively to a silver–silver nitrate reference electrode were measured. These should of course be the same at equilibrium, but in fact equality was never achieved. This discrepancy, however, was not considered serious because it is clear that very small absolute changes in the cupric-ion concentration will have a large effect on the platinum electrode at the minute $[Cu^{++}]/[Cu^{+}]$ fraction established near equilibrium, whereas the copper electrode will be virtually independent of such changes provided that they do not alter the concentration of cuprous ion appreciably, and provided also that the rate of reduction of cupric ion at the copper electrode surface is negligible. The known low initial concentration of cupric ion ensured that the first condition was fulfilled, and the usual stability and reproducibility of the measured E.M.F. showed that the second one was also normally obeyed. The only exception was at the lowest cuprous chloride concentration used; the system was then most sensitive to traces of oxygen and it was correspondingly difficult to approach equilibrium closely. Under these conditions the copper electrode potential became steadily less negative with respect to the reference electrode, and the initial, most negative, value was taken. It was never possible to reduce the cuprous chloride solution in the potentiometric cell proper, because the copper electrodes then became coated with a tenacious layer of cuprous chloride.

The results obtained are shown in Table 1, which includes two experiments in which lithium chloride was added to obtain a higher ionic strength than was possible with cuprous chloride alone.

TABLE 1.

Temp.	E (Pt),* mv	E (Cu), mv	[CuCl], M	E_0 (Cu, Cu$^+$), mv	Temp.	E (Pt),* mv	E (Cu), mv	[CuCl], M	E_0 (Cu, Cu$^+$), mv
18°	−540	−664	0·0064	−536	95°	−572	−641	0·0051	−475
18	−627	−675	0·0105	−559	95	−583	−617	0·0143	−483
18	−645	−670	0·0117	−558	95	−432	−584	0·0396	−481
18	−563	−630	0·050	−555	95	−503	−571	0·079	−490
18	−670	−685	0·0112 +	−571	95	−651	−661	0·0112+	−518
			[LiCl] = 0·189					[LiCl] = 0·189	

* Lowest Pt potential.

The quantity E_0 (Cu, Cu$^+$) calculated from the equation

$$E = E_0 \text{ (Cu, Cu}^+) + (\boldsymbol{R}T/\boldsymbol{F})\ln[\text{CuCl}]$$

shows a definite drift with [CuCl], so that one or more of the assumptions implicit in the use of the equation are not strictly fulfilled in this case. The two most likely causes of error are incomplete dissociation of the cuprous chloride and variations in the activity coefficient of the cuprous ion, and the fact that a plot of E_0 (Cu, Cu$^+$) against (ionic strength)$^{\frac{1}{2}}$ (see, *e.g.*, Glasstone, " Textbook of Physical Chemistry," MacMillan, 1947, p. 942) gives a reasonably straight line suggests that the second is the main factor here. By extrapolating in this way to [CuCl] = 0, we have :

$$E_0 \text{ (Cu, Cu}^+) = -538 \text{ mv at } 18° = -477 \text{ mv at } 95°$$

relatively to the arbitrary silver–silver nitrate electrode described above.

Measurement of the Cu$^+$–Cu^{++} *Standard Potential* E$_0$ (Cu$^+$, Cu^{++}).—This quantity was determined by measuring the potential relatively to the reference electrode of a platinum electrode in pyridine containing various amounts of cupric and cuprous chlorides. These mixtures were prepared either by direct mixing of cupric and cuprous chloride solutions, or by titration of cuprous chloride solution with ferric chloride solutions in pyridine, the former being the more

TABLE 2.

Temp.	[CuCl], M	[LiCl], M	E_0 (Cu$^+$, Cu^{++}), mv	Temp.	[CuCl], M	[LiCl], M	E_0 (Cu$^+$, Cu^{++}), mv
18°	*ca.* 0·002	—	−25	95°	*ca.* 0·002	—	+26
18	,,	0·2	−53	95	,,	0·2	−20

satisfactory method. The procedure adopted was to weigh the appropriate quantity of cuprous chloride directly into a known volume of pyridine in the potentiometric cell, through which a stream of nitrogen was passing, so that the cuprous chloride solution was protected from contact with air. Then either a cupric chloride solution or a ferric chloride solution of known concentration was added in successive portions from a burette. After each addition the E.M.F. of the cell became steady within a few minutes, and remained constant indefinitely.

The results are given in Table 2, the figures quoted each being the average of a number of experiments. Some measurements were again made in the presence of added lithium chloride, and show an effect due either to variations in activity coefficients or to specific interactions
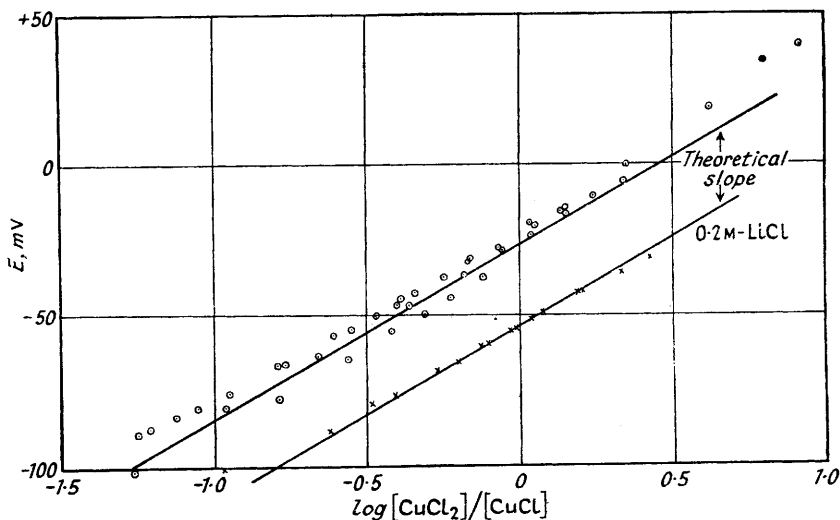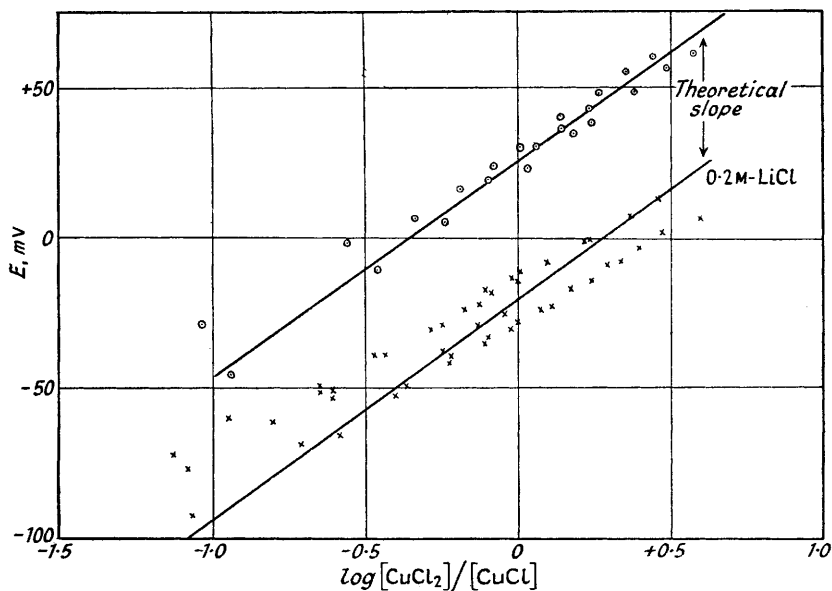
FIG. 2.

FIG. 3.

between chloride and cuprous and cupric ions. The quantity E_0 (Cu$^+$, Cu^{++}) has been calculated from the equation

$$E = E_0 \text{ (Cu}^+\text{, Cu}^{++}\text{)} + (\boldsymbol{RT}/\boldsymbol{F})\ln[\text{CuCl}_2]/[\text{CuCl}]$$

Figs. 2 and 3 show the graphs of log [CuCl$_2$]/[CuCl] against E obtained at 18° and 95°, respectively. Reasonably straight lines were obtained, of slopes close to the theoretical values, particularly in absence of lithium chloride, suggesting that the assumptions implicit in the calculation of E_0 (Cu$^+$, Cu^{++}) are approximately correct at low ionic strengths. We have then

$$E_0 \text{ (Cu}^+\text{, Cu}^{++}\text{)} = -25 \text{ mv at } 18° = +26 \text{ mv at } 95°$$

relatively to the silver–silver nitrate reference electrode.   According to Partington and Skeen (*loc. cit.*), E_0 (Cu$^+$, Cu^{++}) is 86 mv relatively to Ag|AgCl, 0·0265M, which gives 71 mv relatively to Ag|AgCl, 0·048M, it being assumed that the equation $E = E_0 + (\boldsymbol{R}T/\boldsymbol{F})$ ln [AgCl] is obeyed.   As pointed out, however, potentials determined relatively to Ag|AgNO$_3$ and Ag|AgCl, respectively, will not be directly comparable.

The System Cu–Cu$^+$–Cu^{++} *in Pyridine.*—From the measured values of E_0 (Cu, Cu$^+$) and E_0 (Cu$^+$, Cu^{++}) further quantities can be calculated; *e.g.*, E_0 (Cu, Cu^{++}), the copper–cupric standard potential, given by

$$E_0 \text{ (Cu, Cu}^{++}) = \tfrac{1}{2}[E_0 \text{ (Cu, Cu}^+) + E_0 \text{ (Cu}^+, \text{Cu}^{++})]$$

and K, *i.e.*, [Cu^{++}]/[Cu$^+$]^2, the equilibrium constant of the reaction 2Cu$^+ \rightleftharpoons$ Cu + Cu^{++}, given by $(\boldsymbol{R}T/\boldsymbol{F})$ ln $K = E_0$ (Cu, Cu$^+$) $- E_0$ (Cu$^+$, Cu^{++}). ΔH, the heat absorbed in the reaction 2Cu$^+ \longrightarrow$ Cu + Cu^{++} in pyridine, can also be calculated in the usual way, and hence the approximate heats and entropies of the various cell reactions.   Table 3 summarizes the measured and some calculated quantities for the system in pyridine at 18° and 95°, and values calculated from the literature data for the same system in water at 25° are given for comparison; all potentials are relative to Ag|AgNO$_3$, 0·048M.

TABLE 3.   *The system* Cu–Cu$^+$–Cu^{++} *in pyridine and in water.*

	18°	95°	25° (water)
E_0 (Cu, Cu$^+$), mv	−538	−477	−192
E_0 (Cu$^+$, Cu^{++}), mv	−25	+ 26	−560
E_0 (Cu, Cu^{++}), mv	−281	−225	−376
K, l. mole^{-1}	$1·4 \times 10^{-9}$	$1·3 \times 10^{-7}$	$1·5 \times 10^6$
ΔH		12,600 cals./mole	—

DISCUSSION

It appears that pyridine is not a medium which lends itself to potentiometric measurements of the highest accuracy, partly because of the very low conductivity of pyridine solutions of ionic compounds, and partly because the potentials of redox systems, even simple ones such as Cu$^+$–Cu^{++}, are far less firmly " poised " in pyridine than in water. Presumably both these drawbacks are mainly due to the same cause, *viz.*, the comparatively low dielectric constant of pyridine, and the consequent existence of ion pairs to a much greater extent than in water.   The reproducibility of the results obtained in the present work was of the order of ± 5 mv, but their absolute accuracy is very much harder to estimate.   The liquid-junction potential has been neglected; though it may well be large, it does not appear to vary much with electrolyte concentration, as judged from the experiments described on p. 3475, and will therefore scarcely affect quantities such as K which are calculated from the difference of two measured potentials.

Activity coefficients of ions in pyridine may be expected to depart from unity at much lower ionic strengths than in water, and the present measurements show anomalies [*e.g.*, the drift in E_0 (Cu, Cu$^+$)] which seem to be caused by such variations, but there may also be a specific effect of chloride ions due to the formation of (CuCl$_n$)$^{(n-1)-}$ complexes, as in water.   The effect of increasing chloride-ion concentration on E_0 (Cu, Cu$^+$) is not, however, large, so that complex formation can only occur to a small extent if at all.   In contrast, increasing chloride-ion concentration causes the apparent activity of silver ions in pyridine to fall markedly, presumably because of complex-ion formation.

A comparison of the thermodynamic relationships of the system Cu–Cu$^+$–Cu^{++} in pyridine with the corresponding quantities in water is interesting.   Clearly, the relative stability of cuprous and cupric ions in the presence of copper metal is completely reversed by the change of solvent, and this change must be due to the difference in the relative free energies of solvation of the two ions.   Numerous pyridine–copper complexes are of course known, including pyridine–cupric ones, but from the above figures the latter must be less stable than the pyridine–cuprous complexes.   This strong solvation of the cuprous ion is presumably responsible for the relatively small formation of cuprous ion–chloride ion complexes in pyridine.   Since silver ion–chloride ion complex formation is apparently more marked, silver ions in pyridine must be less strongly solvated.

The experiments with a hydrogen electrode in pyridine indicate the possibility of

expressing potentials in pyridine on the hydrogen scale, as is conventional for aqueous systems, but for most purposes no advantage would be gained by doing so. A more important application of the hydrogen electrode in pyridine would be for the measurement of pyridinium-ion concentrations, making possible acid–base titrations and dissociation-constant measurements as in water.

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