862. *Precise Measurements with the Glass Electrode. Part III.*[1] *The Cell: Glass Electrode*|HCl|AgCl|Ag *at* 0°.

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It is shown that low-resistance glass electrodes can be used at 0° in aqueous solutions (pH 1—2) with an accuracy only slightly less than that attainable at 25°. The experimental precautions to be taken to achieve precise measurements are elaborated.

IN Part I [1] it was shown that, provided changes in asymmetry potential with time were taken into account, low-resistance glass electrodes in conjunction with conventional potentiometric equipment and a sensitive moving-coil galvanometer give results comparable with the best work with the hydrogen electrode. That work was restricted to 25°. It was of interest to examine whether, if the temperature of the laboratory is very different from the thermostat temperature, the technique of quickly transferring a glass electrode with washing, between two solutions yields e.m.f.–time graphs which can be reliably extrapolated to the time of transfer of the electrode. The present work at 0° was undertaken to test this, and to investigate if condensation of moisture, which may cause electrical leakage, and the increased resistance of the membrane at the lower temperature make precise electrical measurements difficult or impossible.

EXPERIMENTAL

Each 30-mm. diameter low-resistance glass electrode (Type 9000 of the Jena Glaswerk), mounted in a Polythene bung machined to fit the B45 socket of the electrode vessel, was fitted with a horizontal guard ring of 33 mm. internal diameter formed from 2·5-mm. diameter glass rod sealed to two vertical glass struts. These struts fitted into holes drilled in the Polythene bung and held the ring in position just below the centre of the bulb. The glass ring and supports were painted with paraffin wax to facilitate the washing procedure. By using guard rings, the transference technique [1a] can be performed more quickly and the risk of small undetected cracks in the glass membrane being caused by slight contact with the neck of the electrode vessel is eliminated. The electrodes were soaked for at least one week in water, followed by at least two days in 0·1m-hydrochloric acid to reduce the value of the asymmetry potential and its rate of change with time. This is in accordance with the usual practice of conditioning electrodes in solutions as similar as possible to those in which they are to be used.

The electrical measuring apparatus, experimental technique, and preparation of the silver–silver chloride electrodes (bias potentials <10 μV) have been described.[1a] The galvanometer sensitivity was increased to 5600 mm./μA by using the scale at 2 metres.

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[1] (*a*) Part I, Covington and Prue, *J.*, 1955, 3696; (*b*) Part II, *idem*, *ibid.*, p. 3701.

" Telcon " non-microphonic cable Type PT1GM(MOD) was used for all wiring. This Polythene-insulated copper cable has a low-resistance graphitised coating between the Polythene and the braided screening which successfully eliminates parasitic voltages which may be produced when the cable is bent or twisted while changing connections to the glass electrode before and after transfers. Unless the cable screening, the " equipotential shields," and thermostat (and the earth-line of its heating, stirring, and control circuits) are connected to a good, single, independent earth, accurate and reproducible results are not obtainable. The electrode vessels were held above the thermostat water level by metal clamps with rubber-faced jaws attached to scaffolding constructed independently of the tank, so that the metal parts were above the thermostat temperature and condensation was thereby reduced. Even so, reproducible results were not obtained if excessive condensation of atmospheric moisture occurred on the supporting clamps, and very humid days were avoided.

The thermostat was fitted with a copper cooling-coil through which a water–glycol mixture was circulated from a commercial refrigerator unit. The temperature of the thermostat, which contained water plus a little alcohol, was adjusted to 0·00° ± 0·01° by comparison with the temperature of crushed ice prepared from distilled water.

RESULTS AND DISCUSSION

Before the work at 0° was begun the measurements [1a] at 25° were repeated to test the electrical measuring circuit. It is recommended that some check of this kind be made before undertaking all new precise work with low-resistance electrodes, to ensure that the maximum accuracy and reproducibility are being achieved. The results, analysed as described previously, lead to a value of B in the equation [1a]

$$E^{\circ\prime} = E + 2k \log \mathrm{m} - 2kA\mathrm{m}^{\frac{1}{2}}/(1 + \mathrm{m}^{\frac{1}{2}}) = E^{\circ} - 2kB\mathrm{m}$$

of 0·217 ± 0·003 mole^{-1} kg. in agreement with the value [1a] of 0·214 ± 0·004.

TABLE 1.

10^3m (mole kg.$^{-1}$)	E_0 (mv)	δ_0 (mv)	E_{25} (mv)	δ_{25} (mv)	10^3m (mole kg.$^{-1}$)	E_0 (mv)	δ_0 (mv)	E_{25} (mv)	δ_{25} (mv)
$1{\cdot}356_1$	—	—	$96{\cdot}31_5$	$+0{\cdot}02_5$	$3{\cdot}398_8$	47·50	−0·04	—	—
$1{\cdot}438_2$	85·81	+0·04	—	—	$4{\cdot}498_1$	34·94	+0·08	38·19	−0·02
$2{\cdot}086_5$	69·23	−0·05	$75{\cdot}33_5$	$-0{\cdot}02_5$	$6{\cdot}065_0$	21·82	−0·06	$23{\cdot}76_5$	$-0{\cdot}00_5$
$3{\cdot}139_7$	—	—	55·49	+0·04	$7{\cdot}235_1$	13·92	+0·00	15·26	+0·01

The results at 0° are shown in Table 1. The values of $k = (\boldsymbol{RT}/\boldsymbol{F}) \ln 10$ and the Debye–Hückel constant A at 0° were taken as 54·199 mv and 0·488 (mole^{-1} kg.)$^{\frac{1}{2}}$ respectively. The e.m.f.–time extrapolations were as good as those at the higher temperature. An electrode held out of the solution for 30 sec. before being replaced in the same solution changed its potential by only 0·02 mv, showing that any warming of the electrode during the normal removal and washing period of 10 sec. is negligible. The value of B calculated by the method of least squares is 0·223 ± 0·006 mole^{-1} kg. The scatter [$\delta = E^{\circ\prime}$ (exp.) $- E^{\circ\prime}$ (calc.), cf. Table 2 of Part I] of the points from the best straight line is slightly greater than in the work at 25° shown for comparison in Table 1, but this is understandable in terms of the increased resistance of the glass membrane at the lower temperature which results in a loss in sensitivity noticed during the runs (discrimination, 0·01 mv). The values of B obtained by various methods are summarised in Table 2. The present value at 0° is lower than both the previous e.m.f. values [2,3] but the values obtained with the glass electrode at 25° were also lower than the value obtained from hydrogen electrode cells [3] by a similar amount although in agreement with the value from the concentration cells.[1b] The lower values obtained by using the glass electrode might signify a slight deviation from the hydrogen electrode function in solutions of increasing molality of

[2] Covington and Prue, *J.*, 1957, 1930.

[3] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350

hydrochloric acid. A difference of 0·01 in B at m = 0·1 corresponds to 0·1 mv. The present value of B does not help to resolve the discrepancy, which was originally pointed out,[4] between the freezing point and e.m.f. value.[3] The third decimal place in values of B (0·001 in B corresponds to 0·0002 in γ at 0·1 m) is not significant for any other electrolyte yet studied, and it could be concluded from Table 2 that it is only just significant for hydrochloric acid.

TABLE 2.

B (mole^{-1} kg.)			
0°	25°	Method	Workers
0·241	0·228	Hydrogen–silver/silver chloride cells	Harned and Ehlers [3]
0·240	0·217	Silver/silver chloride concentration cells	Covington and Prue [1b, 2]
	0·214	Glass–silver/silver chloride cells	Covington and Prue [1]
0·223	0·217	,, ,,	This work
0·216	—	Freezing point	Randall and Vanselow [4]

Despite the development in recent years of vibrating-reed electrometers with much greater zero stability than valve electrometer d.c. amplifiers, the precision of measurements with such instruments is still limited to 0·1 mv. Only with electrodes of resistance as low as 0·5MΩ can measurements be made with the glass electrode to a precision of 0·01 mv. According to Schwabe [5] and Kordatski,[6] the Jena electrodes are constructed from low-resistance, high-sodium-content glass on which a thin layer of a higher-resistance, pH-sensitive glass of better chemical durability is deposited chemically. It does not seem possible to make electrodes in the laboratory of such low resistance directly from electrode glasses known at present. The manufacturers suggest that 40° is an upper limit for their use because of the increased solubility of the glass at higher temperatures, and the useful pH range is stated to be 1—10. The above authors give warnings about the large release of alkali from these electrodes, and it has been noted in the present work that some electrodes deteriorate slightly after several weeks of use, perhaps for this reason. Frequent tests in a pair of standard solutions (*e.g.*, 0·01, 0·1m-HCl) are therefore suggested for checking the correct functioning of the electrodes.

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[4] Guggenheim and Prue, "Physicochemical Calculations," North Holland Publ. Co., Amsterdam, 1955, p. 226.

[5] Schwabe, "Fortschritte der pH Messtechnik," Verlag Technik, Berlin, 2nd edn., 1958, p. 101.

[6] Kordatski, "Taschenbuch der praktischen pH Messung," Rudolph Müller und Steinicke, Munich, 4th edn., 1949, p. 150.