389. *The Potential of the Normal and the Decinormal Calomel Electrodes at Temperatures ranging from 12·5° to 91°.*

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The potentials of the normal and the decinormal calomel electrodes have been determined at a series of temperatures. These electrodes have been standardised with respect to the arbitrary hydrogen standard at the various temperatures. For the

purpose, a specially designed thermostat, in which temperatures were controlled by the vapours of boiling liquids, was used.

ALTHOUGH the potentials of the N/10-calomel electrode at temperatures within the range 0—75° are known (Sørensen, *Ergebn. Physiol.*, 1912, **12**, 393), yet those of the N-calomel half-element above 30° have received but little attention. In the present work, these potentials have been determined with respect to that of the normal hydrogen electrode over the range 12·5—91°, and compared with those of the N/10-calomel electrode. To determine the hydrogen half-elements which are assumed arbitrarily at the various temperatures to be of zero potential, advantage has been taken of Noyes's conductivity data (*J. Amer. Chem. Soc.*, 1908, **30**, 335) of hydrochloric acid solutions, and the degrees of ionisation have accordingly been computed on the basis of Arrhenius's theory. Such a scheme has the advantage that the results so obtained for the two types of calomel electrode can be compared directly.

Furthermore, it is not possible to employ the activity concept over the entire temperature range studied, as Harned and Ehlers's activity data (*ibid.*, 1933, **55**, 2179) for hydrochloric acid extend only to 60°. Despite the empirical nature of the Arrhenius theory and the approximations involved in its use, it is probable that any small discrepancies thereby introduced will not seriously interfere with the usefulness of the data now presented.

The *E.M.F.*'s of the following two cells were measured :

(i) $\overset{-}{\text{Pt}}|\text{H}_2$ (1 atm. — satd. vap. press. of H_2O) ; 0·08N-HCl | Satd. KCl | N-KCl; Hg_2Cl_2 | $\overset{+}{\text{Hg}}$

(ii) $\overset{+}{\text{Hg}}$ | Hg_2Cl_2 ; 0·1N-KCl | 1N-KCl; Hg_2Cl_2 | $\overset{-}{\text{Hg}}$

Contrary to the observations of Kolthoff and Tekelenburg (*Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 766 ; *Rec. trav. chim.*, 1927, **46**, 33), the N-calomel electrode was found to give readily reproducible values at higher temperatures, and therefore to be quite serviceable.

The very small errors involved in the assumption that the saturated water-vapour pressures are equal to those of the dilute hydrochloric acid used are most probably negligible. In the first cell the interposition of a saturated solution of potassium chloride was assumed to eliminate the diffusion potential, and in the second cell such a potential difference was on theoretical grounds considered to be almost non-existent. Col. 2 of Table I gives the *E.M.F.*'s of cell (i) at the temperatures indicated in col. 1. The pressure (P in mm. of Hg) of hydrogen supplied to each electrode, col. 3, is equal to that of the atmosphere less the partial pressure of water vapour at each temperature. The potential of the hydrogen electrode at each temperature, col. 6, was calculated by means of the formula

$$E_{H2} = 0{\cdot}0001984T\,.\log[H^{\cdot}]/\sqrt{P/760}$$

$[H^{\cdot}]$ being equal to α_{HCl} (col. 4), computed from Noyes's data, multiplied by 0·08, this being the normality of the hydrochloric acid used.

TABLE I.

Temp.	*E.M.F.*, volt.	*P*.	α_{HCl}.	$[H^{\cdot}] \times 10^2$.	E_{H2} (N-H = 0).	$E_{N\text{-Cal.}}$ (N-H = 0).
12·5°	0·351	749	0·934	7·47	− 0·064	+ 0·287
25	0·352	736	0·929	7·43	− 0·067	+ 0·285
34	0·352	720	0·925	7·40	− 0·068	+ 0·284
53	0·349	653	0·917	7·34	− 0·071	+ 0·278
63	0·347	589	0·913	7·30	− 0·072	+ 0·275
75	0·342	471	0·908	7·26	− 0·072	+ 0·270
91	0·325	214	0·901	7·21	− 0·062	+ 0·263

In Table II the potentials of the N/10- and the N-calomel electrode are compared, the extent to which the former is the more positive being given in col. 2. Addition of the values of the latter from Table I gives those of the former (col. 4). These data are in excellent agreement with those extrapolated from Sørensen's data, as shown in col. 5.

Incidentally, this agreement points to the accuracy (within 1 mv.) of the *E.M.F.* values given in Table I.

TABLE II.

Temp.	*E.M.F.*, volt.	$E_{N\text{-Cal.}}$ (N-H=0).	$E_{0\cdot1N\text{-Cal.}}$ (N-H=0).	$E_{0\cdot1N\text{-Cal.}}$ (Sørensen).	Temp.	*E.M.F.*, volt.	$E_{N\text{-Cal.}}$ (N-H=0).	$E_{0\cdot1N\text{-Cal.}}$ (N-H=0).	$E_{0\cdot1N\text{-Cal.}}$ (Sørensen).
25°	0·052	+ 0·285	+ 0·337	+ 0·337	63°	0·056	+ 0·275	+ 0·331	+ 0·331
34	0·053	+ 0·284	+ 0·337	+ 0·337	75	0·058	+ 0·270	+ 0·328	+ 0·329
53	0·055	+ 0·278	+ 0·333	+ 0·333	91	0·061	+ 0·263	+ 0·324	—

EXPERIMENTAL.

In order to maintain constant temperatures within the range 12·5—91°, a special type of thermostat was constructed. It consisted of two concentric copper cylinders and, in the space between their walls, were placed liquids boiling at the desired temperatures. The cylinders were covered by means of a copper ring, and a long reflux condenser was inserted in a hole in the top. The apparatus was heated by gas. Water in the central cylinder was mechanically stirred. Around the walls of the inner vessel a copper coil was placed through which hydrogen circulated before passing into the hydrogen electrodes. The cell was almost completely immersed in the water, and the inner tank was covered except for holes for a thermometer and the various tubes employed.

In carrying out *E.M.F.* measurements, it was essential that the hydrogen should be preheated to the correct temperature before being introduced into the hydrogen electrode vessels, and that it should be saturated with water vapour at each particular temperature. This was accomplished by allowing it to bubble very slowly through two bottles of water, placed in the tank, before passing to the electrodes. Had this not been done, serious errors due to evaporation of the solution in the hydrogen electrode chamber would have occurred.

Another source of error lies in the increased diffusion of electrolytes at elevated temperatures. This was most likely to happen by the potassium chloride diffusing from the salt bridge to the N-calomel electrode, and consequently, instead of allowing the tube from this electrode to dip into a saturated solution of potassium chloride, it was dipped into N-potassium chloride solution, which, in turn, was connected with a vessel containing the saturated solution. Diffusion of the salt from the salt bridge into the 0·08N-hydrochloric acid solution in the hydrogen electrode vessel was also likely to occur, and this would have influenced the potential of the electrode (" salt effect "). This was eliminated as far as possible by the interposition of a vessel containing 0·08N-hydrochloric acid between the salt bridge and the hydrogen electrode. The actual lay-out of the cell system used was therefore

$$\overset{-}{H_2}\,|\,0{\cdot}08\text{N-HCl}\,|\,0{\cdot}08\text{N-HCl}\,|\,\text{Satd. KCl}\,|\,\text{N-KCl}\,|\,\text{N-KCl};\ Hg_2Cl_2\,|\,\overset{+}{Hg}$$

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