CCXLVI.—*The Effect of Hydrochloric Acid on the Electrode Potential between Mercury and Mercurous Chloride.*

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THE effect of hydrochloric acid on the electrode potential between mercury and calomel has been investigated by Sauer (*Z. physikal. Chem.*, 1904, **47**, 146), who worked with 0·1*N*- and 1·0*N*-solutions of hydrochloric acid. Measurements have also been made by Tolman and Ferguson (*J. Amer. Chem. Soc.*, 1912, **34**, 232), Ellis (*ibid.*, 1916, **38**, 737), and Linhart (*ibid.*, 1917, **39**, 2601), on cells of the type:

$$H_2|xN\text{-}HCl, \text{ solid } Hg_2Cl_2|Hg$$

combined with a similar cell using *N*-hydrochloric acid, the whole forming a concentration cell without transport, reversible with respect to both the chlorine and the hydrogen ions.

Direct measurements of cells of the type :

$$\mathrm{Hg}|\mathrm{Hg_2Cl_2},xN\text{-HCl}|N\text{-HCl}|N\text{-KCl}|N\text{-KCl},\mathrm{Hg_2Cl_2}|\mathrm{Hg}$$

have now been carried out, a correction being applied for the diffusion potential across the boundary xN-HCl|N-HCl on the basis of some earlier results (Carter and Lea, J., 1925, **127**, 487). Measurements of this type have been employed to elucidate certain results which are described in the succeeding communication.

Construction of Cells.—Mercurous chloride was obtained in a state of purity, containing no mercuric chloride and only a trace of free mercury. The mercury used was purified both by electrolytic methods and by distillation. Cell solutions were prepared by grinding calomel, together with a little free mercury, into a paste with hydrochloric acid of a known concentration. The supernatant liquid was decanted repeatedly as in the construction of the normal calomel electrode. The electrode was of mercury, and upon this was placed a thin layer of calomel paste, the vessel being filled with hydrochloric acid solution saturated with calomel. The following chain of solutions was constructed :

$$\underset{\displaystyle\xleftarrow[\qquad\qquad\qquad\qquad\qquad\qquad E_c \qquad\qquad\qquad\qquad\qquad\qquad]{}}{\underset{\xleftarrow[E]{}}{\mathrm{Hg}}|\mathrm{Hg_2Cl_2},xN\text{-HCl}|xN\text{-HCl}\underset{\xrightarrow[\pi]{}}{\overset{A}{|}}N\text{-HCl}\underset{\xrightarrow[0{\cdot}0288]{}}{\overset{B}{|}}N\text{-KCl}|N\text{-KCl},\mathrm{Hg_2Cl_2}|\underset{\xrightarrow[0{\cdot}560]{}}{\mathrm{Hg}}}$$

Special experiments were made in order to ascertain that the diffusion potentials were constant over a considerable period of time and were also reproducible. Several arrangements were tried, but the above was found to be the most satisfactory. Connexion between the solutions at A and B was made by means of inverted U-tubes filled with N-solutions of hydrochloric acid and potassium chloride, respectively, and plugged at both ends with wads of filter paper. The diffusion potential at B can be calculated on the basis of Henderson's formula (*Z. physikal. Chem.*, 1907, **59**, 118) to be 0·0288 volt. That at A has been measured (Carter and Lea, *loc. cit.*) for values of x greater than unity; for values less than unity it may be calculated from the usual formula. Thus if E is the potential of the half-element, Hg|$\mathrm{Hg_2Cl_2}$,xN-HCl, and E_c is the potential of the whole cell, then

$$E = E_c + \pi + 0{\cdot}0288 + 0{\cdot}560 \text{ volt.}$$

All measurements were made at 18°, and the observed *E.M.F.* is regarded as positive if the current flows through the cell from the normal calomel electrode towards the acid solution. An inert atmosphere of nitrogen was maintained in the cells during the experiments.

Results.

The results are given in Table I. The values given under the heading E (obs.) were obtained from the above equation by using the mean of the values given under E_c.

TABLE I.

	E_c.				E	E (calc.).	
[HCl].				π.	(obs.).	(Conductivity.)	(Activity.)
10·09	−0·2595			0·0809	0·4102	—	0·4106
10·00	−0·2572,	−0·2576,	−0·2580	0·0806	0·4118	—	0·4112
7·60	−0·2121			0·0706	0·4473	—	0·4436
7·20	−0·2036,	−0·2041,	−0·2045	0·0674	0·4521	—	0·4494
4·64	−0·1460,	−0·1462,	−0·1465	0·0465	0·4891	—	0·4877
4·48	−0·1434			0·0450	0·4904	—	0·4900
2·73	−0·0970,	−0·0975,	−0·0975	0·0263	0·5177	—	0·5184
2·29	−0·0823			0·0205	0·5270	—	0·5263
1·00	−0·0348,	−0·0348,	−0·0349	0·0000	0·5540	0·5579	0·5570
0·10	+0·0590,	+0·0593,	+0·0595	−0·0370	0·6111	0·6137	0·6154
0·0106	+0·1528,	+0·1530,	+0·1531	−0·0731	0·6687	(0·6687)	(0·6687)
0·0027	+0·2121			−0·0974	0·7035	0·7032	0·7019

The potential between mercury and any solution in equilibrium with it is given by the equation :

$$E = E_0 + 0{\cdot}029 \log [\mathrm{Hg_2}^{\bullet\bullet}] \quad . \quad . \quad . \quad . \quad (1)$$

Since the solution is saturated with respect to calomel, if the solubility product $[\mathrm{Hg_2}^{\bullet\bullet}]\,[\mathrm{Cl}']^2 = k_1$, then

$$E = E_0 + 0{\cdot}029 \log k_1/[\mathrm{Cl}']^2 =$$

$$E_0 + 0{\cdot}029 \log k_1 - 0{\cdot}058 \log [\mathrm{Cl}'] \quad . \quad . \quad (2)$$

or

$$E = E_0' - 0{\cdot}058 \log [\mathrm{Cl}'] \quad . \quad . \quad . \quad . \quad (3)$$

The calculated values in the last two columns have been obtained from equation (3) by taking the observed value of $E = 0{\cdot}6687$ volt for [HCl] = 0·0106N. In column 5, the chlorine-ion concentration has been deduced from conductivity–viscosity data for concentrations up to N-hydrochloric acid, whilst in column 6 it has been obtained from activity data (Lewis and Randall, " Thermodynamics," 1923, p. 336).

The agreement with the observed *E.M.F.* is satisfactory, but it should be pointed out that the agreement in the case of the activities cannot be regarded as an entirely independent proof, since the activity values have been derived primarily from potential measurements of cells which are virtually the same as those under consideration.

Effect of Mercuric Chloride on the Electrode Potential.—It was thought possible that mercuric chloride in presence of mercury might register a measurable potential. When such a cell was constructed from 0·05N-mercuric chloride in 3·0N-hydrochloric acid, the usual grey film appeared on the surface of the mercury, and the *E.M.F.* measured showed wide fluctuations over several days, but tended towards the same value as the potential of the same cell containing calomel in 3·0*N*-hydrochloric acid. It was therefore concluded that the $Hg-Hg^{\cdot\cdot}$ potential is inaccessible.

The reduction of mercuric chloride by mercury is by no means rapid. Thus two solutions, each containing 13·576 g. of mercuric chloride per litre in 10*N*-hydrochloric acid, were found after 10 days' contact with mercury electrodes to contain 5·648 and 6·558 g. of mercuric chloride per litre, respectively. In more dilute solutions, the reduction is even slower; for instance, a solution of 0·05*M*-mercuric chloride in 7·6*N*-hydrochloric acid contained 12·90 and 12·32 g. of mercuric chloride per litre after 5 and 7 days' contact with mercury, respectively.

It is thus possible to have a considerable quantity of mercuric chloride in contact with mercury and calomel for a long time before equilibrium is reached, and it should therefore be possible to determine the effect of mercuric chloride on the electrode potential $2Hg-Hg_2^{\cdot\cdot}$.

Cells were constructed containing 0·05*M*-mercuric chloride, in varying concentrations of hydrochloric acid saturated with calomel, in contact with mercury. In Table II E_c' is the *E.M.F.* of the cell containing 0·05*M*-mercuric chloride, and E_c that of the cell free from mercuric chloride. Both potentials represent that of the whole cell, including that of the normal calomel electrode. It will be seen that the effect of 0·05*M*-mercuric chloride on the *E.M.F.* is always small and is least in the higher concentrations of acid. The effect of mercuric chloride is to decrease the chlorine-ion concentration owing to the formation of complex ions, and from equation (2) it may be seen that this results in an increase in the *E.M.F.*

TABLE II.

[HCl].	E_c'.	E_c.
10·09	−0·2551	−0·2595
7·60	−0·2070	−0·2121
5·37	−0·1565	−0·1635
2·29	−0·0676	−0·0823
0·160	+0·0687	+0·0507
0·0137	+0·1625	+0·1514
0·0027	+0·2292	+0·2121

Potentials registered at an Inert Electrode.—Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385) have shown that a definite equilibrium exists between the components of the system

$$Hg-Hg_2Cl_2-HgCl_2,$$

provided that the three are present together; the active masses of the first two are definite but beyond analytical detection, whilst the concentration of mercuric chloride in contact with mercury and calomel has been determined and found to be dependent on the acid concentration. If, therefore, pure mercurous chloride is brought into contact with hydrochloric acid solution, it will not be in a state of equilibrium, but will tend to decompose with separation of metallic mercury and mercuric chloride, the process going on until the equilibrium concentration of mercuric chloride is reached. At this point, as the three components are in equilibrium, the three potentials $E_{2Hg-Hg_2^{\cdot\cdot}}$, $E_{Hg_2^{\cdot\cdot}-2Hg}$, and $E_{Hg-Hg^{\cdot\cdot}}$ will be equal, hence the electrode potential between a mercury electrode and the mercurous ions measured in the above series should be equal to the oxidation potential between mercurous and mercuric ions measured at an inert platinum electrode. Measurements of this nature have been carried out. By the use of hydrochloric acid solutions of 4·6*N*, 7·2*N*, and 10·0*N*, it was found that the potentials at a platinum electrode in a solution saturated with calomel and containing concentrations of mercuric chloride less than the equilibrium concentration were identical with the electrode potentials registered above. Moreover, the mercuric chloride concentration increased until it reached the equilibrium concentration. If, however, the initial mercuric chloride concentration was greater than this, then no further increase occurred, and, moreover, the potential registered —presumably the oxidation potential—was greater than the corresponding electrode potential. Since the oxidation potential is proportional to log [$HgCl_2$], any further increase in the mercuric chloride concentration beyond the equilibrium point will result in a continuous increase in the potential. Thus it was found (compare Fig. 1, following paper) that if the potential were plotted against log [$HgCl_2$], the curve obtained was a straight line parallel to the log [$HgCl_2$] axis for low values of [$HgCl_2$], but it exhibited a definite break at the [$HgCl_2$] value corresponding to the equilibrium point, and then rose sharply.

Table III gives a comparison between the values of the equilibrium concentrations of mercuric chloride which we observed (C., L., and R.) and the values found by Richards and Archibald (R. and A.).

TABLE III.

[HCl]	4·60	5·48	7·20	7·30	10·0*N*
[$HgCl_2$] (R. and A.)	—	0·0020	—	0·0025	0·0025*M*
[$HgCl_2$] (C., L., and R.)	0·0021	—	0·0021	—	0·0019*M*

Thus for [$HgCl_2$] values less than the equilibrium concentration the oxidation potential is less than the electrode potential and the latter is registered both at a mercury electrode and at an inert electrode. At the equilibrium point, they are equal to one another, and for higher concentrations of mercuric chloride the electrode potential is registered at a mercury electrode and the higher oxidation potential at an inert platinum electrode.

In lower acid concentrations (0·01*N*—2·7*N*), this agreement could not be obtained. Richards and Archibald found that the equilibrium concentration of mercuric chloride in 1·0*N*- and 2·7*N*-hydrochloric acid was 0·00017*M* and 0·00076*M*, respectively. Cells constructed containing these concentrations of mercuric chloride were found to yield potentials against platinum electrodes which were, respectively, higher than the corresponding electrode potentials by 0·071 and 0·023 volt. It is probable, therefore, that in solutions which are dilute with respect to both the acid and the mercuric chloride the potential registered at the platinum electrode does not represent the true reversible oxidation potential. It was found that the same potential was registered whether the electrodes were platinised or not. Moreover, the presence of a single platinum electrode did not alter the equilibrium concentration of mercuric chloride which at 18° in *N*-hydrochloric acid was at 0·00022*M*-mercuric chloride. If, however, several electrodes (*e.g.*, four) were placed in the mixture of solution and calomel, an increase in the mercuric chloride concentration to 0·00050*M* occurred, together with the corresponding increase in potential. These phenomena are somewhat obscure and render the measurement of oxidation potentials in very dilute mercuric chloride and hydrochloric acid solutions somewhat uncertain and difficult to interpret.

Summary.

The effect of hydrochloric acid on the electrode potential between mercury and mercurous chloride in hydrochloric acid solution has been investigated over a range of acid concentration from 0·0027*N* to 10·0*N*.

Under the conditions of these experiments, the potential $Hg-Hg^{\cdot\cdot}$ was inaccessible, and the effect of mercuric chloride on the above electrode potential was small.

The equilibrium of the system $Hg-Hg_2Cl_2-HgCl_2$ has been studied in relation to the work of Richards and Archibald, and the potentials registered by this system of platinum electrodes have been described.

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