CCXLVII.—*The Oxidation–Reduction Potentials of Mercurous and Mercuric Chlorides in Hydrochloric Acid Solution.*

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LITTLE attention has hitherto been devoted to the oxidation–reduction potentials of the chlorides of mercury. Although Drucker (*Z. physikal. Chem.*, 1901, **36**, 195; *Z. Elektrochem.*, 1912, **18**, 236) and Baur (*Z. physikal. Chem.*, 1908, **63**, 687) have made a few measurements in potassium chloride solution, a further investigation of the potentials in hydrochloric acid solution is desirable in view of the complicated behaviour of mercury halides in the presence of halogen acids, and also of the recent investigations of Stewart and Wardlaw (J., 1922, **121**, 1481) on the action of sulphur dioxide on these two chlorides which can be correlated with the electrochemical properties of these systems.

EXPERIMENTAL.

Preliminary experiments indicated that it would be a matter of considerable difficulty to obtain steady reproducible potentials corresponding with the oxidation process $Hg_2^{\cdot\cdot}\longrightarrow 2Hg^{\cdot\cdot}$. In the first place, it was found that a 0·1*M*-solution of mercuric chloride saturated with calomel and containing no acid had so low a conductivity that potential measurements were impossible. Secondly, in solutions of 0·1*N*-hydrochloric acid saturated with calomel and containing mercuric chloride, it was found that no agreement could be obtained between the potentials registered at platinised platinum electrodes; moreover, the potential varied widely with time. In a similar solution containing 0·0005*M*-mercuric chloride, a large fall in potential was observed over several days, but after this a reading was obtained which was fairly constant and almost equal to the electrode potential of mercury and calomel in 0·1*N*-hydrochloric acid. Since the electrodes had become covered with a grey deposit of mercury, it was concluded that an electrode and not an oxidation potential was being measured.

A number of similar experiments were performed with the same result. Shaking the calomel with the solution of hydrochloric acid and mercuric chloride for 12 hours did not give a more constant potential reading. It was noticed, however, that if the electrodes were completely buried to a considerable depth in a paste of calomel instead of being suspended in the solution, and if the dissolved air in the solution were removed by means of a current of purified nitrogen, it was possible to obtain potentials which gave good agreement between different electrodes over considerable periods of time and were reproducible. Moreover, they were distinct from the electrode potentials described in the preceding paper. The necessity for the complete immersion of the electrodes is probably due to the low concentration of mercurous ions, the passage of a very small current in the course of potential measurements being sufficient to exhaust the supply of mercurous ions in the vicinity of the electrode if this is simply suspended in the solution. Complete immersion of the electrode in the paste ensures full saturation in its vicinity.

Cells of the following type were constructed :

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Hg_2Cl_2}\\ xM\text{-}\mathrm{HgCl_2}\\ yN\text{-}\mathrm{HCl}\end{matrix}\right| yN\text{-}\mathrm{HCl} \;\Big|\; N\text{-}\mathrm{HCl} \;\Big|\; N\text{-}\mathrm{KCl} \;\Big|\; N\text{-}\mathrm{KCl,Hg_2Cl_2} \;\Big|\; \mathrm{Hg}.$$

The chain of intermediate solutions has been shown to be sufficient to maintain constant reproducible diffusion junctions (Carter and Lea, J., 1925, **127**, 487; Carter, Lea, and Robinson, preceding paper), and possesses the advantage that the potential at each junction can be determined with the necessary degree of accuracy. The system differs from the previously investigated systems of iron and copper salts (Carter and Clews, J., 1924, **125**, 1880; Carter and Lea, J., 1925, **127**, 499) in that only the mercuric chloride and the hydrochloric acid concentrations in the oxidation cell can be subjected to variation, since the calomel cannot be varied in concentration owing to its low solubility. It is essential, however, to maintain the solution saturated with respect to the calomel in order to obtain a defined system.

The oxidation cell consisted of a glass vessel containing a solution of mercuric chloride and hydrochloric acid in the requisite proportion and saturated with respect to calomel. Experiments showed that platinisation of the electrodes did not increase their sensitivity, nor was the shape or form of the electrodes a factor influencing the potential readings. Three electrodes of polished platinum foil (about 1 sq. cm. in area) were actually employed.

Measurements of each of the cells were carried out, in general, over a period of a week, a lapse of 12—24 hours after construction being necessary before a constant potential was registered. Renewal of the liquid boundaries during this period showed that no appreciable change had occurred in the diffusion potentials. All potentials are referred to the absolute scale. A positive sign indicates that the current flows through the cell from the calomel electrode to the oxidation element. All measurements were made at 18°. Concentrations of mercuric chloride are given as g.-mols. per litre.

Potential Measurements.—If E is the potential of the oxidation element, π the diffusion potential between xN- and N-hydrochloric acid (Carter and Lea, *loc. cit.*), 0·0288 volt the diffusion potential between N-hydrochloric acid and N-potassium chloride (calculated on the basis of Henderson's formula, *Z. physikal. Chem.*, 1907, **59**, 118), and E_c the potential of the whole cell, then :

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

The values for one experiment given in Table I are typical of the degree of accuracy attained.

TABLE I.

Cell made up as : [HCl] = 1·00N, [$HgCl_2$] = 0·75M.
Final composition by analysis : [HCl] = 0·96N, [$HgCl_2$] = 0·735M.

Time (days).	0.	1.	2.	3.	4.	5.
Electrode No. 1	(0·2654)	0·3026	0·2974	0·3012	0·2988	0·3006
„ „ 2	(0·2644)	0·3026	0·2966	0·3006	0·2988	0·3006
„ „ 3	(0·2634)	0·3026	0·2970	0·3012	0·2988	0·3006

Average potential (neglecting readings on first day) = 0·3000 volt.
Average error = ±0·0017 volt.

In Table II are given the potentials of a number of cells, showing the effect of varying the mercuric chloride concentration in solutions of hydrochloric acid of the following concentrations : 0·01, 0·1, 0·5, 1·0, 2·7, 4·6, 7·2, and 10·0N.

TABLE II.

[HCl] = 0·01N.

Cell No.	[HCl].	[$HgCl_2$].	E_c.	π.	E.
1	0·0100	0·00013	0·2810	−0·0740	0·7958
2	0·0100	0·00119	0·3258	−0·0740	0·8406
3	0·0100	0·0154	0·3868	−0·0740	0·9016
4	0·0104	0·100	0·4671	−0·0734	0·9825
5	0·0100	0·150	0·4897	−0·0740	1·0045
		[HCl] = 0·10N.			
6	0·0995	0·000256	0·1972	−0·0370	0·7490
7	0·100	0·0018	0·2385	−0·0370	0·7903
8	0·099	0·0103	0·2719	−0·0370	0·8237
9	0·106	0·0199	0·2912	−0·0360	0·8440
10	0·100	0·100	0·3603	−0·0370	0·9121
11	0·096	0·134	0·3735	−0·0375	0·9248
12	0·100	0·213	0·4082	−0·0370	0·9600
		[HCl] = 0·5N.			
13	0·509	0·00057	0·1119	−0·0106	0·6901
14	0·508	0·00193	0·1347	−0·0106	0·7129
15	0·507	0·020	0·1842	−0·0106	0·7624
16	0·500	0·196	0·2750	−0·0106	0·8532
17	0·500	0·470	0·3329	−0·0106	0·9111

TABLE II (*contd.*).

[HCl] = 1·0*N*.

Cell No.	[HCl].	$[HgCl_2]$.	E_c.	π.	E.
18	1·005	0·00053	0·0272	0	0·6160
19*	1·000	0·00099	0·0433	0	0·6321
20	1·050	0·00198	0·0564	+0·0008	0·6460
21	0·964	0·0196	0·1051	−0·0007	0·6932
22	0·960	0·0208	0·1080	−0·0008	0·6960
23	0·980	0·072	0·1543	−0·0004	0·7427
24	0·995	0·096	0·1616	0	0·7504
25	0·991	0·169	0·1911	0	0·7799
26	0·960	0·735	0·3000	−0·0008	0·8880
27	0·920	0·985	0·3207	−0·0014	0·9081
28	1·000	1·010	0·3292	0	0·9180

* Cell No. 19 contained four electrodes, two of polished platinum foil and two of platinised platinum foil. They all gave identical results.

[HCl] = 2·7*N*.

29	2·73	0·0004	−0·0885	0·0257	0·5260
30	2·74	0·0024	−0·0526	0·0258	0·5620
31	2·74	0·0052	−0·0330	0·0258	0·5816
32	2·72	0·020	−0·0032	0·0256	0·6112
33	2·72	0·051	+0·0253	0·0256	0·6397
34	2·72	0·100	+0·0409	0·0256	0·6553
35	2·70	0·407	+0·1043	0·0250	0·7181
36	2·61	0·910	+0·1641	0·0240	0·7769
37	2·72	2·260	+0·2376	0·0256	0·8520

[HCl] = 4·6*N*.

38	4·68	0·0026	−0·1422	0·0469	0·4935
39	4·66	0·0032	−0·1355	0·0468	0·5001
40	4·67	0·021	−0·0825	0·0467	0·5530
41	4·62	0·024	−0·0791	0·0465	0·5562
42	4·53	0·192	−0·0160	0·0457	0·6185
43	4·63	0·529	+0·0238	0·0466	0·6592
44	4·44	0·966	+0·0480	0·0450	0·6818
45	4·60	1·033	+0·0543	0·0463	0·6894
46	4·60	3·80	+0·1494	0·0463	0·7845

[HCl] = 7·2*N*.

47	7·40	0·0028	−0·1994	0·0667	0·4561
48	7·30	0·0108	−0·1674	0·0680	0·4894
49	7·18	0·0961	−0·1082	0·0673	0·5479
50	7·40	0·977	−0·0322	0·0685	0·6251
51	7·20	3·80	+0·0318	0·0674	0·6880

[HCl] = 10·0*N*.

52	10·05	0·0039	−0·2374	0·0808	0·4322
53	10·19	0·0117	−0·2104	0·0815	0·4599
54	10·19	0·0986	−0·1518	0·0815	0·5185
55	10·05	0·937	−0·0836	0·0808	0·5860
56	10·00	3·80	−0·0314	0·0806	0·6380

Variation of Potential with Concentration of Mercuric Chloride.—In Fig. 1 the potential of the oxidation element is plotted against the logarithm of the mercuric chloride concentration, for each acid concentration. According to the equation :

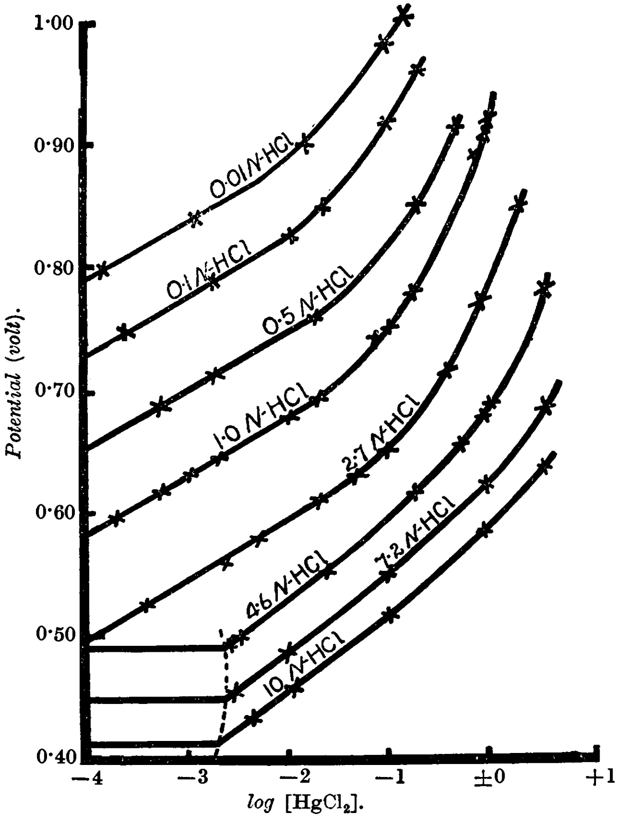
$$E = E_0 + 0{\cdot}029 \log [\text{Hg}^{\cdot\cdot}]^2/[\text{Hg}_2{}^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad (1)$$

since $[\text{Hg}^{\cdot\cdot}] = k_2[\text{HgCl}_2]/[\text{Cl}']^2$ . . . . (2)

and $[\text{Hg}_2{}^{\cdot\cdot}] = k_1/[\text{Cl}']^2$ . . . . (3)

therefore $E = E_0 + 0{\cdot}029 \log k_2{}^2[\text{HgCl}_2]^2/k_1[\text{Cl}']^2$ . . (4)

FIG. 1.



It follows that for a given acid concentration, the mercurous-ion concentration is constant, whilst the mercuric-ion concentration will be proportional to $[\text{HgCl}_2]$ since the feeble ionisation of mercuric chloride renders its contribution to the chlorine-ion concentration negligible.

Hence $E = E_0' + 0{\cdot}058 \log [\text{HgCl}_2]$ . . . . . (5)

or the *E.M.F.* is a linear function of the logarithm of the mercuric chloride concentration.

From the graph, it will be seen that the logarithmic law holds in the more dilute solutions of mercuric chloride, but breaks down when the concentrations of mercuric chloride and hydrochloric acid are of the same order. It is noteworthy that in place of the theoretical slope of 0·058 volt for a ten-fold dilution, we obtained slopes of 0·060 volt in the 4·6N-, 7·2N-, and 10·0N-hydrochloric acid solutions, and of 0·047 volt in the lower acid concentrations. The discrepancy in the former case is not serious, but in the latter case is beyond the range of experimental error, and up to the present we have not been able to account for it.

To explain the deviations from the logarithmic law in the more concentrated mercuric chloride solutions, complex-ion formation may be assumed. Complex-ion formation between calomel and hydrochloric acid is unlikely, as calomel is known to form only a few double salts. Sherrill (*Z. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103) and Noyes and Le Blanc (*Z. physikal. Chem.*, 1890, **6**, 389) have brought forward evidence in favour of the existence of the ion $HgCl_4''$, whilst Sand and Breest (*Z. physikal. Chem.*, 1907, **59**, 424) and Drucker (*Z. Elektrochem.*, 1912, **18**, 236) consider that the ion has the formula $HgCl_3'$. As the percentage of mercuric chloride in the form of complex ions is high, it may be seen from the equations $HgCl_2 + 2Cl' = HgCl_4''$ and $HgCl_2 + Cl' = HgCl_3'$ that when the mercuric chloride is present in the same concentration as the acid, a considerable decrease in the acid concentration must occur in order to allow the formation of these complex ions, and hence, according to equation (4), the potential of the cell will be increased. Quantitatively the behaviour of the system is given by equation (4) and an equation determining the equilibrium of the complex ion. According to Sherrill,

$$[HgCl_4'']/[HgCl_2][Cl']^2 = 70 \quad . \quad . \quad . \quad . \quad (6)$$

whilst according to Sand and Breest (if the value of the constant as recalculated by Drucker be used),

$$[HgCl_3']/[HgCl_2][Cl'] = 11{\cdot}5 \quad . \quad . \quad . \quad . \quad (7)$$

These two views have been reconciled by Linhart (*J. Amer. Chem. Soc.*, 1915, **37**, 258; 1916, **38**, 1272) who considers that both the ions $HgCl_3'$ and $HgCl_4''$ are present in solution [together with small quantities of polymerised mercuric chloride, $(HgCl_2)_2$, and the complex ions Hg_2Cl_5 and Hg_2Cl_6''], the equilibrium conditions being given by the equations:

$$[HgCl_3']/[HgCl_2][Cl'] = 9{\cdot}8 \quad . \quad . \quad . \quad . \quad (8)$$

$$[HgCl_4'']/[HgCl_3'][Cl'] = 4{\cdot}9 \quad . \quad . \quad . \quad . \quad (9)$$

and therefore $$[HgCl_4'']/[HgCl_2][Cl']^2 = 48 \quad . \quad . \quad . \quad . \quad (10)$$

From equation (9) it follows that in N-hydrochloric acid solution the complex ion $HgCl_4''$ is predominant, but in 0·01 N-acid solution the $HgCl_3'$ ion is the main constituent, whilst in 0·1N- and 0·5N-acid both ions are present in comparable amounts. We may therefore, as an approximation, apply equation (10) to solutions of mercuric chloride in N-hydrochloric acid. It is difficult to solve this equation to give the amounts of free unbound mercuric chloride in equilibrium with free acid and complex ion, but it is easy to proceed in the reverse manner. Thus, for any given total acid concentration [HCl], if an arbitrary value of the concentration of complex ion $[HgCl_4'']$ be assumed, it follows that the concentration of the free acid is $\{[HCl]-2[HgCl_4'']\}$, and hence the concentration of chlorine ion is $\{[HCl]-2[HgCl_4'']\}\gamma$, where γ is the activity coefficient corresponding with the concentration of the free hydrochloric acid. Hence by substitution in equation (6) we can determine the concentration of free mercuric chloride. The sum of free and combined mercuric chloride gives the total concentration of mercuric chloride, since that of the $Hg^{\cdot\cdot}$ and $HgCl^{\cdot}$ ions is negligible. The concentrations of free mercuric chloride and of chlorine ions may now be substituted in equation (4), together with the values of the constants $E = 1{\cdot}190$ volt, $k_1 = 3{\cdot}5 \times 10^{-18}$, and $k_2 = 10^{-14}$, to give a calculated value of the $E.M.F.$ corresponding with given values of [HCl] and total mercuric chloride.

Hence we obtain Table III, which gives the calculated values of the potential corresponding to different total concentrations of mercuric chloride in N-hydrochloric acid on the assumption that $HgCl_4''$ ions are formed.

TABLE III.

[HCl] = 1·0N.

$[HgCl_4'']$.	Free [HCl].	γ.	[Cl′].	Free $[HgCl_2]$.	Total $[HgCl_2]$.	E (calc.).	E (obs.).
0·40	0·2	0·783	0·157	0·338	0·738	0·903	0·883
0·30	0·4	0·763	0·305	0·0672	0·367	0·846	0·825
0·10	0·8	0·796	0·637	0·00513	0·105	0·763	0·752
0·05	0·9	0·811	0·730	0·00195	0·0520	0·735	0·722
0·01	0·98	0·821	0·805	0·000322	0·0103	0·687	0·680

It will be seen that the considerable deviations from the logarithmic law that occur in concentrated solutions of mercuric chloride can be accounted for by assuming the existence of the ion $HgCl_4''$. If it is borne in mind that the values of k_1 and k_2 given above are strictly applicable only at 25° and not at 18°, that there are polymerised molecules $(HgCl_2)_2$, which give rise to Hg_2Cl_5' and Hg_2Cl_6'' ions, also present in solution, and moreover, that the formation of the complex ion $HgCl_4''$ causes a considerable reduction in the chlorine-ion concentration in the more concentrated mercuric chloride solutions, which in turn favours the formation of $HgCl_3'$ ions, it will be seen that the method can only be expected to yield an approximation to the observed values of the potentials. However, the agreement is sufficient to show that the observed potentials can be accounted for on the basis of complex-ion formation.

Since in 0·1*N*- and 0·5*N*-hydrochloric acid both $HgCl_3'$ and $HgCl_4''$ ions are present to about the same extent, it is difficult to calculate the distribution of mercuric chloride between the various complex ions and to obtain calculated values of the potentials in these dilute acid solutions.

In the case of the three highest concentrations of acid, the portions of the curves parallel to the log $[HgCl_2]$ axis represent the potentials registered in solutions in which the mercuric chloride concentration is not high enough for equilibrium between $Hg–Hg_2Cl_2–HgCl_2$ to obtain. Under these conditions it was found that an oxidation potential was not registered, since it was independent of the mercuric chloride concentration, but a potential identical with the electrode potential of mercury and calomel described in the previous paper, and the data for the latter were used for plotting the horizontal portions of the curves. Such systems were found to be unstable since mercurous chloride decomposed into mercury and mercuric chloride until the concentration of the latter corresponded with the equilibrium value for the acid concentration under consideration.

Variation of Potential with Acid Concentration.—By drawing a line perpendicular to the abscissa and cutting it at the desired value of the mercuric chloride concentrations, we have read off from the curves in Fig. 1 the values of the potential of a cell in which the mercuric chloride concentration is constant and the hydrochloric acid concentration is varied between 0·01*N* and 10*N*. This has been done for five values of the former, namely, 1·0, 0·1, 0·01, 0·001, and 0·0001*N*. The results are in Table IV.

TABLE IV.

	$[HgCl_2]$, *M*.					
	0·0001	0·001	0·01	0·1	1·0	4·0.
[HCl].			Potential (volt).			
0·01	0·7910	0·8375	0·8885	0·9820	—	—
0·10	0·7295	0·7775	0·8260	0·9130	—	—
0·5	0·6530	0·7005	0·7475	0·8155	—	—
1·0	0·5840	0·6325	0·6795	0·7500	0·9110	—
2·7	0·4960	0·5455	0·5960	0·6550	0·7850	—
4·6	—	—	0·5305	0·5945	0·6860	0·7960
7·2	—	—	0·4890	0·5500	0·6240	0·6925
10·0	—	—	0·4560	0·5180	0·5875	0·6400

These results have been plotted in Fig. 2, which shows the relation between potential and hydrochloric acid concentration. This graph also contains the curve of the electrode potential $2Hg\text{–}Hg_2^{\cdot\cdot}$ against acid concentration, based upon data given in the preceding paper.

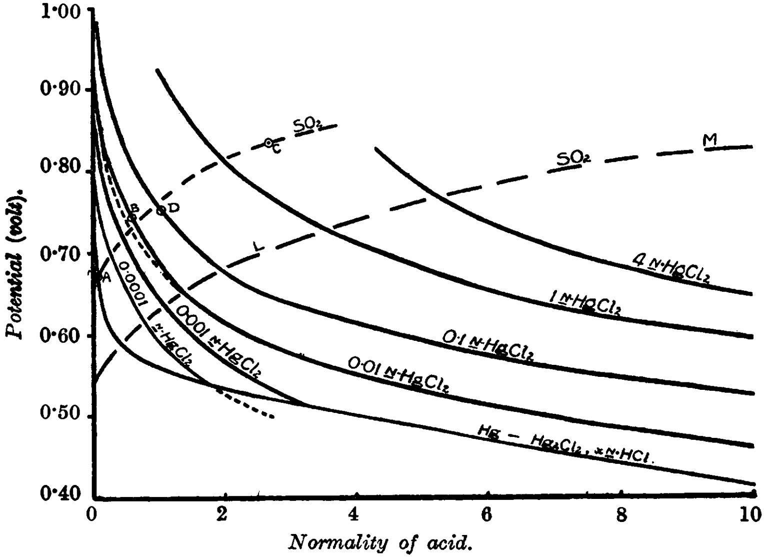
On the assumption that the ions $HgCl_3'$ and $HgCl_4''$ are formed according to equations (8) and (10), and since

$$[HgCl_4''] + [HgCl_3'] + [HgCl_2] = [HgCl_2]_{total}$$

then $$[HgCl_2]_{total} = [HgCl_2]\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$[HgCl_2] = [HgCl_2]_{total}/\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

FIG. 2.



Hence from equation (4)

$$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} / [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} - 0{\cdot}058 \log [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

In $0{\cdot}01M$-mercuric chloride, as the concentration of this salt is so low that the formation of these complex ions does not affect the concentration of acid appreciably, then for a constant value of $[HgCl_2]_{total}$ values of E corresponding to different concentrations of hydrochloric acid may be calculated.

In Fig. 2, the dotted curve indicates the potentials calculated in this manner, compared with the observed potentials, which are indicated by a continuous line. It is evident that good agreement has been obtained for concentrations of hydrochloric acid between $0{\cdot}01N$ and $1{\cdot}0N$; for higher concentrations, however, the calculated potentials decrease much more rapidly than the observed. It is difficult to account for this behaviour, partly because the activities of the different complex ions may vary in an unknown manner in concentrated acid solution, partly because the actual nature of these ions is unknown, and partly because the complex acids may not be completely dissociated. It may be pointed out, however, that in the most concentrated acid solutions the oxidation potential varies in the same way as the $Hg|Hg_2Cl_2,xN$-HCl potential, *i.e.*, it is proportional to $-0{\cdot}058 \log [Cl']$, the chlorine-ion concentration being calculated on the basis of activity data. This indicates that the system is behaving as if complex-ion formation ceased in the high acid concentrations and as if it conformed to its normal behaviour according to equation (4). Although there is no theoretical reason for this supposition, it is interesting to notice that Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385; compare preceding paper) found that the amount of mercuric chloride in equilibrium with mercury and calomel was independent of the acid concentration provided this was above 5*N*. As almost all the mercuric chloride is present as complex ion, this is equivalent to saying that above 5*N*-hydrochloric acid complex-ion formation is not increased by increasing the acid concentration.

The Action of Sulphur Dioxide on the Chlorides of Mercury.—In Fig. 2, we have indicated the variation of the oxidation–reduction potential of sulphur dioxide by the curve LM (Carter and James, J., 1924, **125**, 2234). Stewart and Wardlaw (*loc. cit.*) have studied the action of sulphur dioxide on the two chlorides of mercury, and in considering their results we have been guided by the principle that the system possessing the higher potential will oxidise the other system, being itself reduced.

The various reactions between mercury salts, hydrochloric acid, and sulphur dioxide were found to be extremely sensitive to small changes in acid concentration, and this is in agreement with the steepness of the potential curves, particularly in the region of low acid concentration.

(a) *Action of sulphur dioxide on calomel.* At 95°, Stewart and Wardlaw found that sulphur dioxide acted on calomel suspended in hydrochloric acid, in four ways, depending on the concentration of acid:

(1) 8*N*- to 2*N*-acid. Oxidation of calomel to mercuric chloride occurs, being complete only in the most concentrated acid and slight in 2*N*-acid.

(2) 2*N*- to 0·16*N*-acid. Decomposition of calomel and darkening of the solution, according to the equation: $Hg_2Cl_2 \longrightarrow Hg + HgCl_2$. We have confirmed the fact that this reaction is independent of the

sulphur dioxide; moreover, it ceases at approximately 0·16*N*-acid, because calomel could be boiled for several hours in 0·10*N*-acid without the slightest darkening.

(3) 0·16*N*- to 0·07*N*-acid. Inert region—calomel unaffected.

(4) 0·02*N*- to zero acid. Calomel is reduced to mercury by sulphur dioxide.

According to our graph, for acid concentrations between zero and 0·2*N*, the sulphur dioxide potential is lower than the Hg–Hg_2Cl_2 potential and hence reduction of the calomel is to be expected corresponding to (4).

Between 0·2*N*- and *N*-hydrochloric acid, it is to be expected that the oxidising action of sulphur dioxide on calomel will be slight, because the amount of mercuric chloride that must be formed to raise the oxidation potential as high as the sulphur dioxide potential is very small. Observation in this region is hindered by the fact that simultaneous decomposition of the calomel occurs into mercury and mercuric chloride. Above 2*N*-acid the oxidation of calomel becomes considerable and, according to our graph, should proceed almost to completion. It seems probable that equilibrium was not attained in all the experiments of Stewart and Wardlaw.

The point A on Fig. 2 represents the point on the Hg–Hg_2Cl_2 electrode potential curve (at 0·02*N*-HCl) where it intersects the sulphur dioxide curve.

(b) *Action of sulphur dioxide on mercuric chloride.* Stewart and Wardlaw found that if sulphur dioxide was passed for 12 hours through a solution of mercuric chloride in 0·48*N*-hydrochloric acid at 95°, calomel was formed, the amount decreasing with lowering of the mercuric chloride concentration, so that when $[HgCl_2] = 0{\cdot}0094M$ the amount of calomel formed by reduction was very small. It therefore follows that the oxidation potential of sulphur dioxide in acid of this concentration is less than the oxidation of the mercury system when $[HgCl_2]$ is greater than 0·0094*M*, and greater than the oxidation potential when $[HgCl_2]$ is less than 0·0094*M*. This gives the point B in Fig. 2.

In 2·64*N*-hydrochloric acid, Stewart and Wardlaw found that mercuric chloride was not reduced until its concentration reached 1·92*M*. This gives the point C. In 1·0*N*-acid, the extent of reduction was very small when $[HgCl_2] = 0{\cdot}1M$. This is the point D.

It will be seen that the line AC drawn through these four points gives a curve for the oxidation potential of sulphur dioxide which is similar in form to the curve LM based on direct potential measurements, but it is displaced upwards by about 0·2 volt. The discrepancy may be partly attributed to the different temperatures at which our experiments and those of Stewart and Wardlaw were carried out, *viz.*, 18° and 95°, respectively.

Summary.

The conditions necessary for obtaining reproducible oxidation potentials of mercurous and mercuric chlorides in hydrochloric acid solution at 18° have been examined. The influence on potential of various concentrations of both the mercuric chloride and the hydrochloric acid has been determined over a wide range.

The departures from the logarithmic law that have been observed have been attributed to a large extent to the formation of complex ions.

Evidence has been adduced in favour of the existence of complex ions, especially $HgCl_4''$, in hydrochloric acid solutions of mercuric chloride.

The abnormal effect of hydrochloric acid stronger than 5*N* on the complex-ion formation, noticed by Richards and Archibald, has been confirmed.

The reactions of sulphur dioxide on the chlorides of mercury have been studied in the light of the electrochemistry of these systems.

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