70. *The Hydrogen–Calomel Cell. Part II. The Calomel Electrode.*

By G. J. Hills and D. J. G. Ives.

The calomel electrode has hitherto been too erratic in behaviour in dilute solutions to be used for measurements of precision with galvanic cells without liquid junction. It is shown that the calomel electrode is capable of a very high degree of reproducibility provided that various sources of error, which have been examined in detail, are eliminated. A theory of the mechanism of operation of the electrode is suggested.

The calomel electrode, introduced by Ostwald in 1890, was widely accepted as a reference electrode in the succeeding twenty years and had its heyday from 1910 to 1920. During this decade, however, the limitations of existing forms of the electrode were discovered and thereafter it fell gradually into disrepute as an instrument of precision.

Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 362) found that the potential of the electrode depended upon the method of preparation and advocated rigid adherence to a given technique. Acree, Loomis, and Myers (*Amer. Chem. J.*, 1911, **46**, 585; 1913, **50**, 396) prepared a large number of calomel half-cells, using potassium chloride and hydrochloric acid solutions in cells with and without liquid junction, but found large deviations in potential from electrode to electrode; only by connecting the electrodes in parallel for long periods could they obtain an ostensibly reproducible potential. Their electrodes varied in sensitivity to mechanical disturbance. Ellis (*J. Amer. Chem. Soc.*, 1916, **38**, 737) used with advantage "electrolytic calomel," a dispersion of mercury and finely-divided calomel introduced by Hulett (*Phys. Reviews*, 1911, **32**, 257; *J. Amer. Chem. Soc.*, 1916, **38**, 20), who employed this type of preparation for mercurous sulphate in connexion with extensive studies of the Weston cell. Ellis chose insensitivity to movement as a criterion of reliability and obtained reproducibility within 0·05 mv., but his electrodes became highly erratic in hydrochloric acid weaker than 0·03N. Ming Chow (*ibid.*, 1920, **42**, 497) largely confirmed Ellis's work. Loomis and Meacham (*ibid.*, 1916, **37**, 2310) studied the hydrogen–calomel cell, standardising each measurement by reference to an aged standard calomel half-cell, but the actual reproducibility of the measurements was poor. Little improvement was shown by Loomis, Essex, and Meacham's work (*ibid.*, 1917, **39**, 1133). Similar rather unsatisfactory results were recorded by Lewis, Brighton, and Sebastian (*ibid.*, 1917, **39**, 2243) and Linhart (*ibid.*, 1919, **41**, 1175), and it was these workers who, with MacInnes and Parker (*ibid.*, 1915, **37**, 1445) and Harned (*ibid.*, 1922, **44**, 2729; 1926, **48**, 326), began to introduce the silver/silver chloride electrode as a more satisfactory alternative. Work on the calomel electrode continued, however, and Harned (*ibid.*, 1920, **41**, 1808), repeating some of Ellis's work, claimed considerable steadiness for his E.M.F.s, but the minimum deviation was no better than 0·20 mv.

All this work was carried out with solutions containing dissolved air; although the reaction $2Hg + 2HCl + \frac{1}{2}O_2 = Hg_2Cl_2 + H_2O$ was known, it was thought to be significant only at low concentrations (Ellis, Ming Chow, *locc. cit.*). This reaction had certainly precluded the determination of the standard E.M.F. of the hydrogen–calomel cell by means of an extrapolation to zero ionic strength and it did, in fact, vitiate nearly all the measurements with the calomel electrode carried out before 1922. This type of reaction is not restricted to hydrochloric acid, for even potassium chloride solutions, in presence of air, will dissolve mercury on long storage (Randall and Young, *ibid.*, 1928, **50**, 989; Gerke, *ibid.*, 1922, **44**, 1684).

In 1922 Gerke (*loc. cit.*) carried out the first reliable measurements with the calomel electrode, matching it against the silver/silver chloride electrode in cells containing thoroughly deoxygenated solutions of hydrochloric acid or potassium chloride. The E.M.F.s he obtained were independent of the electrolyte, but not of the method of calomel preparation, and, by using the known standard potential of the silver/silver chloride electrode, he gave the first reliable standard potential of the calomel electrode. In spite of this work, Harned in 1926 (*loc. cit.*) and Randall and Beckenbridge (*ibid.*, 1927, **49**, 1435) continued to record measurements using calomel electrodes in aerated solutions. The situation was clarified by the work of Randall and Young in 1928 (*loc. cit.*), who, using all three combinations of calomel, silver/silver chloride, and hydrogen electrodes in cells without liquid junction, fully established the damaging effects of dissolved air and showed that previous work on the hydrogen–calomel cell was largely worthless. They strongly advocated silver/silver chloride in replacement of calomel and were supported by Mukherjee and Kumar (*ibid.*, 1930, **52**, 2179). No attempt has since been made to use the calomel electrode as an instrument of precision; almost all the important work on cells without liquid junction in the last two decades has employed the silver/silver chloride electrode, which is not, however, entirely free from some of the defects of its predecessor. Thus, it is sensitive to dissolved oxygen (Guntelberg, *Z. physikal. Chem.*, 1926, **123**, 199) and its potential is not independent of its mode of preparation (cf. Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350). No serious attempt has been made to recover the calomel electrode from obsolescence, the only subsequent work of any value being that of Mueller and Reuther (*Z. Elektrochem.*, 1942, **48**, 220; 1943, **49**, 176), who confirmed Randall and Young's work (*loc. cit.*) and measured the E.M.F.s of the hydrogen–calomel cell with very careful technique involving the complete exclusion of oxygen. They claimed a reproducibility of 0·10 mv. and calculated the standard E.M.F. of the cell by making use of the activity coefficients of hydrochloric acid determined by Harned and Ehlers (*loc. cit.*).

As a reference electrode, the calomel half-cell is, of course, widely used in cells with liquid junction, and accuracy has been attained by calibration methods involving buffer solutions (MacInnes, Belcher, and Shedlovsky, *J. Amer. Chem. Soc.*, 1938, **60**, 1094; Hitchcock and Taylor, *ibid.*, 1937, **59**, 1812; 1938, **60**, 2710), although the potential of any one electrode remains somewhat uncertain.

From the considerations mentioned in Part I, and from its rather truncated history, it appeared that the potentialities of the calomel electrode had not been fully realised. The following work, of which a preliminary report has been made (Hills and Ives, *Nature*, 1950, **165**, 530), was undertaken to rectify this situation.

STUDIES OF THE CALOMEL ELECTRODE.

There are five main sources of error affecting the calomel electrode, which, operating simultaneously, may produce deviations and randomness of potential of many millivolts.

(1) *Dissolved Oxygen.*—A cell was set up consisting of two calomel electrodes opposed to each other, containing thoroughly deoxygenated N/10-hydrochloric acid at 25°. The design of calomel half-cell used throughout this work is shown in Fig. 1; no platinum contact is immersed directly in the mercury pool of the electrode, and pure nitrogen from a presaturator may be bubbled through the solution or by-passed over its surface. The effect of passing oxygen for one minute through one half of the cell is shown in Fig. 2; the oxygenated electrode immediately develops a quite large positive potential with respect to the other. Although the reaction between mercury, hydrochloric acid, and oxygen is quite unable, in such a short period, significantly to deplete the bulk concentration of the acid, the effect of this reaction is immediately manifest at the mercury solution interface of the electrode. For short periods of oxygenation, therefore, the effect is reversible, the excess of positive potential falling to zero when the dissolved oxygen is swept out by nitrogen. It is desirable, nevertheless, that mercury should at no stage be brought into contact with oxygen-containing solutions.

FIG. 1.

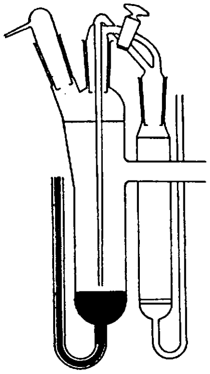
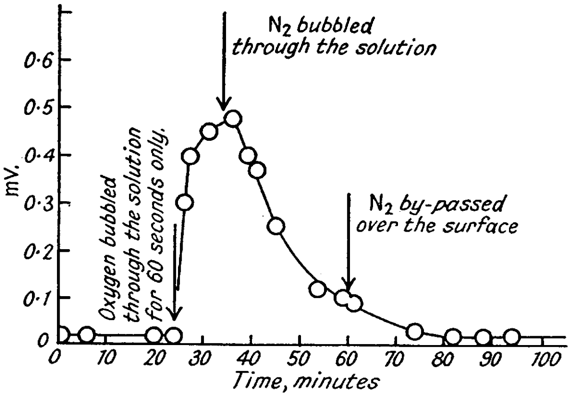
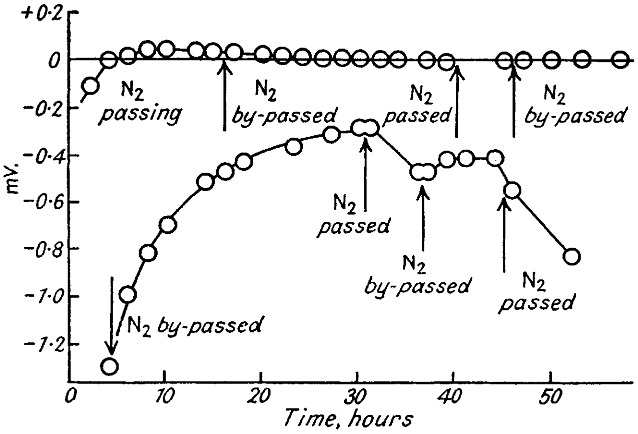


FIG. 2.



(2) *Segregation.*—The classical method of preparing calomel electrodes has been in use for at least fifty years and consists of grinding or shaking mercury, calomel, and solution together to form a wet paste, which is deposited with the solution on a mercury pool. In the absence of specialised anaërobic technique (cf. Mueller and Reuther, *loc. cit.*), this involves a high degree of oxygenation and is further objectionable because the heavy layer of solid segregates a zone of solution close to the mercury surface. In an electrode system truly in equilibrium, this barrier to free exchange between the segregated region and the bulk of the solution might be harmless, but it magnifies the effects of any disequilibrium arising from the calomel and prevents normal response of the electrode to changes in the bulk solution (cf. Fales and Mudge, *J. Amer. Chem. Soc.*, 1920, **42**, 2434). The classical procedure gives an " untidy " electrode with a distorted mercury surface, changing in configuration with mechanical disturbance; the net effect is a highly erratic electrode very sensitive to movement. This point is illustrated in Fig. **3**, in which the upper curve shows the E.M.F. of a symmetrical calomel–calomel cell with a very thin layer of calomel on each electrode; the lower curve relates to a similar cell in which the traditional paste was used for both electrodes. Thoroughly deoxygenated N/10-hydrochloric acid was used in each case, and other conditions were as alike as possible. It has in fact been found that an extremely thin layer of calomel is adequate and that it is unnecessary to equilibrate the calomel with the cell solution or to saturate the cell solution with calomel before use.

FIG. 3.



(3) *Annular Solution Films.*—Many electrodes, prepared identically with avoidance of the two defects already described, still showed considerable differences of potential. These differences could nearly always be reduced by gently rocking the electrodes, but, in time, this treatment produced still larger deviations which could be removed by repeated rocking, and so on. It was obvious that the beneficial effect of this movement was to bring a wetted annulus between the mercury and the walls of the vessel into contact with the bulk of the solution.

Capillary action causes penetration of solution to considerable depths between mercury and the walls of the containing vessel. This occurs to such an extent that the area of the mercury/annular liquid-film interface may largely exceed the area of the interface which the mercury makes with the bulk solution, which alone is intended to be potential-determining. It is not to be expected that the conditions in such a constrained film will be the same as in the free solution. It is clear that, in an attempt to set up a two-phase equilibrium system, it is damaging if one of the phases is allowed partially to segregate into an enclave which cannot freely mix with the rest. When the system also involves a third, solid, phase, as in the calomel electrode, the possibilities of penetration and segregation are still further increased, especially if the solid phase is added in careless excess. This view is substantiated by the fact that the use of hydrophobic electrode vessels effected a very great improvement in the behaviour of the electrodes. This was achieved by treatment of the vessels with silicone fluid, by a method described in the experimental section, under conditions which ensured bonding between the silicone and the glass. With such vessels, no liquid annular film was formed; the solution terminated sharply at a mercury/glass/solution line and there was a marked resistance to annulus formation on mechanical disturbance. The improvement resulting from this device is illustrated by comparing two groups of experiments, each involving a multitude of measurements, in terms of the mean deviation from the mean E.M.F.: these quantities were ± 13 μv. and ± 72 μv. for the hydrophobic and hydrophilic groups, respectively. The difference is an underestimate of the taming of the calomel electrode because many of the wilder vagaries were ignored. The use of " siliconed " glass may benefit many types of mercury electrode and may have virtue in reducing ion exchange between very dilute acid solutions and glass.

(4) *Calomel.*—Electrodes prepared with different samples of pure calomel continued to show discrepancies as large as 0·70 mv.; this common occurrence led Ellis (*loc. cit.*) to advocate the electrolytic preparation, which could be relied upon to give a product of reproducible properties, already equilibrated with mercury and hydrochloric acid. This material contains minute mercury droplets dispersed in calomel of crystal size 1—5 μ. Commercial " AnalaR " calomel, of uniform crystal size (*ca.* 50 μ.) appears to be unsuitable; it gives an electrode which is positive in potential to the " Ellis electrode," but the excess of positive potential decays asymptotically to zero over the course of days. Exhaustive equilibration with mercury and hydrochloric acid before use produced no improvement. Precipitated calomel of crystal size 1—5 μ., however, gave electrodes in excellent agreement with those prepared from the electrolytic calomel. It became clear that crystal size was the significant factor, but operating in the reverse direction to that expected from the normal solubility–size relationship.

It has been found that electrolytic calomel, on being kept for months, gives electrodes with gradually increasing positive deviations of potential. This is accompanied by the growth in the calomel of a yellow substance, which can be seen under the microscope in the form of yellow crystals much larger than the parent calomel. The yellow colour of old electrolytic calomel becomes apparent when it is ground, as, for example, between the cones of a ground joint. Again, the excess of positive potential of an electrode prepared from this aged material shows a very slow exponential decay.

This has been shown to be due to the formation of basic mercurous chloride, HgO,Hg_2Cl_2, which occurs naturally as the mineral Eglestonite, unequivocal identification being provided by *X*-ray powder photographs of new and old electrolytic calomel and the naturally occurring mineral. The authors are indebted to Dr. F. A. Bannister of the Mineralogy Department of the Natural History Museum for providing this evidence It had been expected that the yellow substance would contain mercuric mercury, in order to account for the positive deviations in potential which it produces, but the formula for Eglestonite is well established (Hillebrande and Schaller, *Amer. J. Science*, 1907, **24**, 272) and there is unassailable *X*-ray crystallographic evidence that it contains only mercurous mercury (Hedlik, *Experientia*, 1948, **4**, 66). The true explanation may therefore be that, by virtue of its oxide content, the " Eglestonite electrode " is reversible to oxide as well as chloride ions, and is therefore sensitive to pH. It may be regarded as the half-way house between the calomel and the mercury/mercurous oxide electrode. Since the latter has a standard potential of the order of 0·95 v. (M. de K. Thompson, *J. Amer. Chem. Soc.*, 1906, **28**, 731), the positive deviations are adequately explained; their decay with time is probably due to dissolution of mercurous oxide following the slow dissociation of Eglestonite into its components. Calomel precipitated chemically by the method described in the experimental section is less susceptible to these changes, which seem to occur when calomel is in contact with mercury, in air, under any but extremely dry conditions. Either electrolytic calomel or chemically precipitated calomel, in absence of this disturbing factor, gives electrodes which are identical in potential.

(5) *The Mercury–Calomel Interaction.*—It has been found essential to allow the mercury and calomel for an electrode to interact under dry conditions before the introduction of the solution. This has been carried out in practice by shaking together dry mercury and calomel for several minutes, whereupon a grey, adherent skin of calomel forms on the mercury. A very small amount of this skin introduced to clean, dry mercury spreads immediately over the whole available surface. Careful addition of solution, after displacement of air by nitrogen, then leads to a satisfactory electrode. This spreading skin is very characteristic in appearance and it seems to be an essential prerequisite for the formation of a completely depolarised calomel electrode. It is not formed if the period of interaction of mercury and calomel in the dry state is too brief, or if the crystal size of the calomel exceeds about 5 μ. (it is not formed by " AnalaR " calomel), or if moisture (let alone solution) is present. Comparative experiments were conducted with the same mercury, calomel, and solution brought together in different ways, and in all cases in absence of the preliminary dry interaction the electrodes were erratic,

positive in potential, and extremely sensitive to small mechanical disturbances, such as those caused by the bubbling of nitrogen. The effects were large, of the order of millivolts, but in all cases the electrodes gradually steadied with time and approached the proper potential. There is therefore strong evidence for the formation of some kind of bonding between the calomel and mercury which is essential for complete reversibility. This point is discussed in a later section.

It has been found that, provided the calomel electrode is prepared on the lines indicated, it is highly satisfactory, even in the most dilute hydrochloric acid solutions. It is simple to set up, reaches constant potential in 2—4 hours, is stable and reproducible to $\pm 10\ \mu$v., and shows no concentration polarisation effects such as those associated with the silver/silver chloride electrode (Smith and Taylor, *J. Amer. Chem. Soc.*, 1942, **64**, 3053).

EXPERIMENTAL.

Silicone Treatment of Electrode Vessels.—The thoroughly cleaned vessels were removed from the drying oven and, at a temperature of about 60°, were filled with a 1% solution of Dow–Corning Silicone Fluid No. 200 in redistilled carbon tetrachloride, emptied, drained, and heated at 165° ± 10° for two hours. After cooling, the vessels were repeatedly rinsed with freshly redistilled carbon tetrachloride, which was shown to remove completely any excess of unbonded silicone. The film so formed was intensely hydrophobic and seemed to be of indefinite life; it was, however, destroyed by successive treatments with nitric–chromic acid cleaning mixture and concentrated sodium hydroxide solution.

Electrolytic Calomel.—An electrolytic cell was set up in a 2·l. beaker, the cathode consisting of a cylinder of bright platinum foil enclosed in a guard tube. The anode consisted of a pool of pure mercury contained in a small beaker centrally placed in the cell, with a centrifugal stirrer arranged over it so as to skim the surface of the mercury and provide a powerful swirling of solution into and out of the small beaker. 2N-Hydrochloric acid was used as electrolyte, and was purified as described in the preceding paper. Electrolysis was carried out with an applied potential difference of 2 v.; on first application, without stirring, the mercury surface become multi-coloured and then formed a dark-grey, metallic-appearing skin. At this instant the current fell to zero (cf. Rothschild, *Proc. Roy. Soc.*, *B*, 1938, **125**, 283), but, on the mercury being stirred rapidly, was re-established at a steady value of *ca.* 0·5 amp., a dark-grey suspension of mercury and calomel being flung out of the anode compartment. After about two hours the electrolysis was stopped, the electrodes removed, and stirring continued for about 12 hours. The precipitate was allowed to settle, the electrolyte decanted off and replaced by fresh 2N-hydrochloric acid, and stirring continued for a further 6 hours. This was repeated and the calomel washed by decantation, first with the same acid and then with water. It was finally filtered at the pump, washed with water until the washings showed no test for chloride, drained, and dried in a vacuum. It was stored in the dark over phosphoric oxide. The hydrochloric acid used in this preparation must not be weaker than N. because of basic-salt formation (cf. Hulett and Gardiner, *Trans. Amer. Electrochem. Soc.*, 1928, **56**, 111, 129, 141).

Precipitated Calomel.—Excess of 2N-hydrochloric acid was added rapidly with vigorous mechanical stirring to a dilute solution of pure mercurous nitrate in dilute nitric acid standing over a pool of mercury. The precipitate was treated in the same way as the electrolytic calomel.

Mercury.—Commercial mercury, under dilute nitric acid, was subjected to aspiration of air for several days, dried, and distilled under reduced pressure of oxygen (delivered beneath the surface by means of a capillary), head and tail fractions being rejected. Batches were redistilled immediately before use in a small, all-glass vacuum still, swept out with nitrogen before evacuation.

Hydrochloric Acid Solutions.—These were prepared as described in the preceding paper.

Nitrogen.—The better grade of commercial nitrogen was fully deoxygenated by passing it over reduced copper in an electrically heated silica tube. Connections were made in the same way as for the hydrogen supply (described in Part I).

The potentiometric apparatus and general procedure are fully described in Part III (succeeding paper).

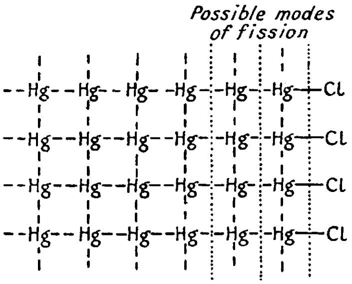
DISCUSSION.

The calomel electrode is traditionally regarded as a mercury/mercurous-ion electrode at which the activity of mercurous ions is reciprocally linked to that of chloride ions by the presence of solid mercurous chloride, with which the solution is saturated. The standard potential of the calomel electrode is related to that of the mercury/mercurous-ion electrode by $E^0_{\text{calomel}} = E^0_{\text{Hg, Hg}_2^{2+}} + \frac{RT}{2F} \log_e K_s$, where K_s is the thermodynamic solubility product of calomel. This relationship is thermodynamically rigid, but it does not necessarily define the mechanism by which the calomel electrode works: all that can be said is that the true mechanism, whatever it may be, must fit into this thermodynamic framework. The idea that the calomel electrode works by the charge and discharge of mercurous ions leads to difficulties. The values of the standard electrode potentials of 0·2680 v. and 0·7896 v. being taken for the calomel and mercury/mercurous-ion electrodes respectively, it follows that the activity of mercurous ions in equilibrium with the standard calomel electrode is of the order 10^{-18} g.-ion/l., or about

600 mercurous ions/c.c. If it be assumed that a mercurous ion needs to be within 10 A. of a mercury surface before it can discharge upon it, it further follows that the duty of depolarising about 35 *square metres* of mercury surface devolves upon each mercurous ion. Even with due regard to the provision of mercurous ions by a mobile equilibrium, it seems evident that the calomel electrode can hardly operate to any significant extent by means of the classical mechanism, and it becomes necessary to consider what ions are present in sufficient quantity to depolarise the electrode. Since it is probable that calomel is not highly dissociated and the second dissociation will be much less than the first, and since chloride ions are present in overriding excess, the chloromercurous ion, Hg_2Cl^+, will be present in significant amount. Jonsson, Qvarfort, and Sillén (*Acta Chem. Scand.*, 1947, **1**, 461) could not experimentally confirm the existence of the chloromercurous ion and concluded that the equilibrium constant for the reaction Hg_2Cl_2(solid) + $Hg_2^{2+} \rightleftharpoons 2Hg_2Cl^+$ must be less than 0·5 × 10^{-6} g.-ion/l. But even if this constant is as low as 10^{-12}, a solution containing 0·001 g.-ion/l. of chloride, in equilibrium with solid calomel, will contain a concentration of chloromercurous ions at least equalling that of mercurous ions and becoming very much greater for higher values of the above equilibrium constant or of the chloride-ion concentration. It can readily be shown that although the system at equilibrium must contain mercuric ions, their concentration is infinitesimal and cannot be mechanistically significant, but, as shown by Jonsson, Qvarfort, and Sillén (*loc. cit.*), they are greatly exceeded in concentration by chloromercuric ions, $HgCl^+$. It may be concluded that the main ionic entities in equilibrium with the calomel electrode are chloride, chloromercurous, and chloromercuric ions.

It is now suggested that one or more of these ions comes into equilibrium with mercury by means of an intermediary which may be called "chloromercury," consisting of a monolayer of chlorine atoms covalently bound to the mercury surface: Fig. 4 indicates formally how alternative modes of fission might allow such a system to come into equilibrium with the appropriate solution ions. It is further suggested that it is this chloromercury structure, which is not spontaneously formed except under special conditions, which is the essential prerequisite for the formation of a fully depolarised, reversible calomel electrode. Some points of evidence may be presented.

FIG. 4.



The behaviour of mercury on anodic polarisation in hydrochloric acid is very characteristic and stands in strong contrast to that of silver. With mercury, after the passage of a few hundred millicoulombs/sq. cm., a sudden, blocking polarisation takes place and the current falls to zero (cf. Rothschild, *loc. cit.*, and, in the experimental section, the preparation of electrolytic calomel) and is only restored by mechanical disruption of the surface. On the other hand, metallic silver may, under the same conditions, be smoothly converted into silver chloride. Since silver is univalent, every discharged chloride ion removes a silver atom from its place in the metal lattice, leaving a fresh site at which further discharge can occur. For mercury, however, every discharged chloride ion does not saturate the valency of the metal atom to which it attaches itself; the metal atom is not removed, no fresh site is generated, and complete polarisation occurs when the mercury surface is covered by a monolayer of chlorine atoms. No doubt this picture is idealised; local disruptions of the film may occur and competing charging processes for mercurous and chloromercurous (or chloromercuric) ions may take place, leading to the formation of the macroscopic, if small, quantities of calomel which are in fact observed. Nevertheless, the anodic current suddenly falls to a vanishingly small magnitude, and this could not occur if the disruptions or charging processes took place readily.

If this chloromercury film is to be advanced as the essential intermediary in the operation of the calomel electrode, it must be shown capable of satisfying the demands which this electrode in fact meets; this is clearly a very critical question in relation to a proposed "monolayer electrode." The number of atoms per sq. cm. of a mercury surface is of the order of 10^{15} and a half-populated monolayer of chlorine atoms residing thereon would contain about 8 × 10^{-10} g.-atoms of chlorine, which, on charge or discharge, would involve the transfer of about 8 × 10^{-5} coulomb, which is ample to satisfy the demands of normal potentiometry. The calomel electrode will in fact satisfy without permanent damage much heavier demands (but not in the course of accurate potentiometric measurements), and this must involve monolayer repair with the aid of crystalline calomel which is always present. It is suggested that a partially populated monolayer is in thermodynamic equilibrium with solid calomel, but that, under the conditions prevailing in the calomel electrode, this equilibrium is not rapidly established and, unless it is established either by long storage or by suitable preliminary treatment, the electrodes shows unsatisfactory behaviour.

A further aspect of the proposed electrode mechanism that requires comment is that, since it involves the making and breaking of covalent bonds, some transition process of low activation energy must be found. Such a process is illustrated in Fig. 5, showing a chloride ion in the close vicinity of a mercury surface. Two potential-energy curves are shown, that on the right relating to a hydrated chloride ion and that on the left to a discharged chloride ion which has become a chlorine atom covalently bound to the mercury surface. The minima of these curves are defined on the energy scale by, respectively, the electron affinity of chlorine plus the hydration energy of the chloride ion and the thermionic work function of mercury plus the energy of the surface covalent binding. The magnitudes of these quantities, as far as they are known, do not exclude the possibility that, when the equilibrium potential difference has been established between the mercury and the solution, these two minima are at approximately equal energy levels and are separated by only a small energy barrier at the point of intersection of the two curves. The argument is similar to that relating to the hydrogen electrode (cf. Part I, preceding paper), but has the important difference that the metal surface is homogeneous and the energy of binding of the discharged atom to the surface should be fixed, unless repuslion between attached atoms leads to a non-constant differential binding energy.

FIG. 5.

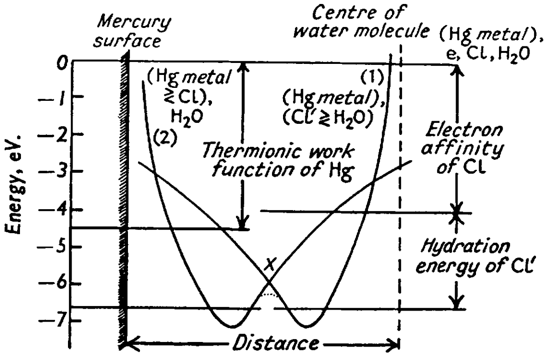
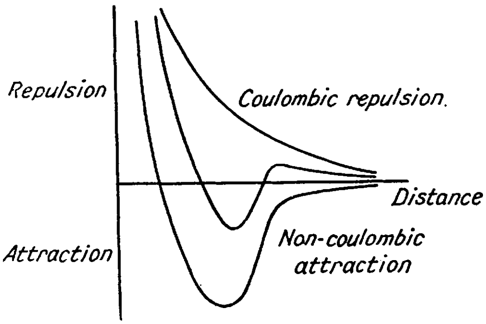


FIG. 6.



An alternative, and perhaps more probable, mechanism may involve chloromercurous (or even chloromercuric) ions rather than chloride, but no direct means can be seen of distinguishing between these possibilities, each of which, however, involves chloromercury.

Discussion of the theory may be concluded with the following ancillary evidence.

(1) It has been shown that special techniques of preparation are necessary to obtain a completely depolarised calomel electrode, and this points circumstantially to the need for some special relationship between mercury and calomel which is not established spontaneously in all circumstances. In particular, there is no doubt at all about the very profound effect of preliminary dry interaction, which, it is believed, results in the formation of chloromercury. It has been pointed out by Gurney (*J. Physical Chem.*, 1938, **6**, 499) that the force–distance curve for the atoms in the mercurous ion must be compounded from coulombic repulsion between like-charged atoms and the non-coulombic exchange forces of covalent binding and will be of the form shown in Fig. 6. The mercurous ion may therefore undergo ready fission (cf. Pauling's adjacent charge rule), although the electrostatic repulsion will be greatly weakened by hydration. Similar considerations may apply to the calomel molecule. If such a molecule be imagined situated close to, and parallel with, a mercury surface, interactions may occur as a result of the tendency of the calomel mercury atoms to form metallic bonds. If the intramolecular bond between the mercury atoms is sufficiently weak, fission may occur, allowing the mercury atoms to enter the bulk phase and leading to two chlorine atoms covalently bound to the mercury surface. It is for this process that water may be inhibitory, virtually eliminating the electrostatic (dipole–dipole) repulsion on which the fission depends. It must be admitted, on the other hand, that preferential adsorption of water at the mercury surface may play a contributory or decisive rôle. It has been found that fine subdivision of the

calomel is necessary for this interaction: if some special orientation of calomel molecules with respect to the surface is necessary and if only one crystal plane will supply molecules in suitable array, then very fine subdivision will ensure, statistically, satisfaction of the special geometrical requirement.

(2) It has been found experimentally that the anomalous positive increment in potential of faulty calomel electrodes can be removed by small anodic or cathodic polarisations. This is striking evidence in favour of the chloromercury structure, which is the only conceivable single product of the discharge of oppositely charged ions (chloride or chloromercurous, respectively).

(3) The classical method of preparation of the calomel electrode, involving grinding the components together in air, has been condemned, but the fact remains that it is satisfactory, within limits, for many purposes. It seems probable that the aeration in the grinding technique may have one beneficial effect: that the mercury–hydrochloric acid–oxygen reaction proceeds at the mercury surface to give the chloromercury film. Certainly the immediate result of excluding oxygen from the electrode, without attending to any of the other requirements, is a marked deterioration, the wildest variations in electrode potential being observed.

(4) There is much evidence in the literature for the specific adsorption of halide ions on mercury, which may have its root in the tendency to form covalent bonds (Grahame, *Chem. Reviews*, 1947, **41**, 283). The dropping-mercury electrode has often been studied in halide-containing solutions (Kolthoff and Lingane, " Polarography," Interscience, 1946, p. 322) and, when acting as anode, it shows marked dependence, both in current–voltage relationship and in mechanical behaviour, on the halide present (Bockris and Parsons, *Nature*, 1947, **160**, 232), which suggests a more intimate participation of the anion in the electrode reaction than the mere precipitation of the insoluble mercurous salt by reaction with mercurous ions formed by charging (cf. Heyrovsky, *Discussions Faraday Soc.*, 1947, **1**, 212; Haul and Scholtz, *Angew. Chem.*, 1948, **60**, *A*, 65).

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