

SOLID STATE INTERACTION, AN IMPORTANT FACTOR IN REVERSIBILITY AND REPRODUCIBILITY OF ELECTRODES OF THE SECOND KIND

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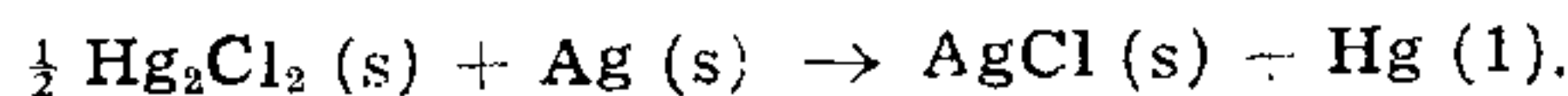
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It has been recently reported¹ that the electromotive force (e.m.f.) of the cell comprising Ag(s)/AgCl(s) KCl_{aq} (c)Hg₂Cl₂(s)/Hg (1) when measured at different concentrations of the KCl solution shows a systematic increase in the value as shown in Table I.

TABLE I
E.m.f. of the cell Ag(s)/AgCl(s)KCl_{aq} (c)
Hg₂Cl₂(s)/Hg(1)

Concentration of KCl	E.m.f.
1 M	0.04552 V
0.1 M	0.04566 V
0.01 M	0.04612 V
0.001 M	0.048 V

The cell reaction of the system is given by



The standard e.m.f. of the cell should therefore have the same value irrespective of the concentration of the common electrolyte, in contrast to what is reported above.

El Constantinescu¹ has taken notice of this and interpreted the observed change as caused by the liquid junction potential arising from the fact that one of the electrodes has a solution saturated with silver chloride whereas the other is having a solution saturated with mercurous chloride. A simple calculation would show that the liquid junction potential in such a system even in the most dilute solution of potassium chloride tried herein would not amount to more than a few microvolts.

The dependence of the potential of the system on the chloride concentration in aqueous phase may be caused by either thermodynamic factors affecting reproducibility or kinetic factors affecting reversibility. Poor reversibility would lead to erratic variation of potential whenever a small current is drawn during measurement; the potential may be also upset in an unsystematic way by the interaction of reducible or oxidisable impurities present with the redox system under study. In view of the fact that the deviations observed are markedly systematic it is our opinion that the thermodynamic factors are playing the main role. This conclusion is rendered further plausible by the facts that (a) the potentials of the electrodes being on the positive side, the normal reducible impurities would not appreciably interfere, (b) with the present measuring techniques, upsetting of potential by any appreciable current being drawn from the system, is not a problem.

SOLID STATE EFFECTS AND REPRODUCIBILITY

The e.m.f. of the cell under consideration is given by the equation

$$E = \frac{1}{F} [\frac{1}{2} G_{\text{Hg}_2\text{Cl}_2} + G_{\text{Ag}} - G_{\text{AgCl}} - G_{\text{Hg}}]. \quad (1)$$

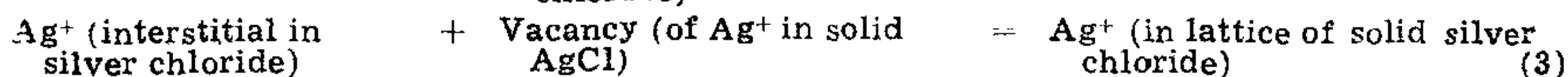
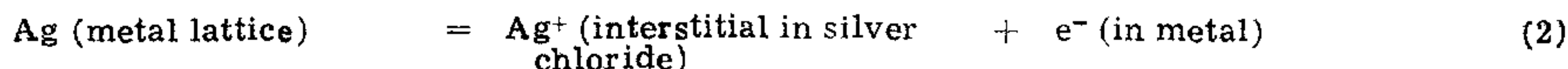
The invariability of the electromotive force of the system is dependent on the invariability of the activities of (a) liquid mercury, (b) solid silver, (c) solid silver chloride and (d) solid mercurous chloride. The increase of electromotive force of the cell as one passes from high concentrations of chloride ion to low concentrations of chloride ion should be caused individually by (a) the increase in the effective activity of silver metal or of mercurous chloride or (b) the decrease of effective activity of mercury metal or silver chloride. The thermodynamic activity of the metallic components are not likely to be affected by the changes in chloride ion concentration in aqueous medium.

Let us now consider the thermodynamic activity of solid silver chloride present on the surface of the silver-silver chloride electrode. It is known² that even single crystals of silver chloride contain thermally produced Frenkel defects involving interstitial silver ions and the silver ion vacancies. The Schottky mechanism can also operate in producing silver ion vacancies and surface silver ions. The surface silver ions can enter into solution by hydration. Any increase in chloride ion concentration in solution would naturally affect the concentration of vacancies and interstitials in solid silver chloride particles, not only at the solid-aqueous interface but also in the bulk of the particles in view of the mobile nature of the imperfections. This is particularly possible since the interstitials in solid silver chloride are known to have high mobility.³ This would naturally change the thermodynamic properties of the silver chloride particles. In fact, we may even consider that the crystal would get completely modified into a form having different lattice energy, when it is brought into contact with solution.

In a sense this has indeed been suspected to happen under certain conditions, for example, the passivating film on iron formed by interaction with nitric acid is supposed to be a special oxide not corresponding to any of the known oxides of iron in bulk form. In fact, the solid state effects are shown to play a very important

part in passivation phenomena.⁴ Furthermore, modification of properties of solids by doping from solutions of impurities is often resorted to in solid state work.

The possible effect of chloride ions in solution on the properties of the film gets support from an observation made in this laboratory. A silver chloride film was prepared by anodizing a silver foil in 2 M hydrochloric acid at a current density of 10 mA/cm.² for one hour. The film formed under these conditions could be easily detached from the foil. The surface which was in contact with metal during formation had a dark grey colour presumably due to a high concentration of interstitial silver ions and corresponding electrons and exhibited high conduction. On keeping it under aqueous saturated solution of potassium chloride, the colour changed to a pale grey. The diffuse reflection as measured by means of Beckman Spectrophotometer gave a value of 8% for the original film and 12.5% for the treated film. This confirms the removal of interstitial silver ions by interaction with a high concentration of aqueous chloride ions. The corresponding electrons presumably also got removed by an appropriate interaction. With dilute solution of KCl (0.1 M) there was no perceptible change in colour. It may be mentioned incidentally that a complete modification of the thermodynamic properties of a solid phase by a constituent in solution, is easiest if the solid phase is in the form of a thin film. The conditions of experimentation by Constantinescu appear to be, therefore, particularly advantageous to get this effect in a marked way. It may be of interest to mention in this connection the observation made by Bates *et al.*⁵ as a result



of extremely careful experimentation, with regard to the reproducibility of silver/silver chloride reference electrodes: "The most extensive and careful measurements of e.m.f. of cells $\text{H}_2\text{Pt}/\text{HCl}/\text{AgCl}/\text{Ag}$ have indicated that the observed differences in E° values are to be attributed to small differences in the structure of solid phases since the uncertainty of activity of 0.005 HCl at 0.01 M. is only 0.03 mV."

A similar change in thermodynamic activity of mercurous chloride can be expected with change in the concentration of chloride ion in

aqueous solution. The individual magnitudes of the effects (of chloride ion concentration in the aqueous solution) on the thermodynamic activity of solid mercurous and silver chlorides would be different. It is this differential effect that causes the variation of the electromotive force of the cell under discussion.

SOLID STATE EFFECTS AND REVERSIBILITY

With reference to these solid state effects, it is of interest to examine the question of reversibility. The high reversibility exhibited by the silver-silver chloride electrode has eluded any plausible explanation. It is assumed that the electromotive equilibrium is between the silver metal and the aqueous silver ions in the saturated solution of silver chloride. The concentration of silver ions in a saturated solution of silver chloride in 0.1 M KCl would be of the order of 10^{-9} M. Assuming that the whole of the metal surface is in contact with the solution, it would require a current density as low as 2.5×10^{11} amp./cm.⁻² to completely upset the concentration of silver ions near the electrode and thence the potential of the electrode. The silver/silver chloride electrode however can bear current densities higher than the above by several orders. In order to understand this, it would be necessary to postulate that exhaustion or build up of silver ion concentration is prevented by fast dissolution and precipitation processes combined with fast transport of the silver ions in aqueous solution from the silver chloride surface to the metal surface.

Whereas it is not impossible to make arbitrary postulates which favour a good reversibility by the above mechanism, it appears desirable to examine an alternative picture of reversibility based on solid state interactions, as follows:

The high reversibility of the system implies that all these consecutive steps have a high exchange rate. The very high Faradaic capacity⁶ reported for Ag/AgCl KCl electrode (400 microfarads per square centimetre) appears again to indicate the high exchange rate.

With silver chloride crystals in contact with silver metal on one side and aqueous solution on the other, there would be a high concentration of interstitials near the metal and the corresponding electrons would exhibit high electronic conduction. The portion of the silver

chloride film away from the metal would show mainly ionic conduction. In the intermediate region there would be extensive interlacing of electronic conduction and ionic conduction. The effect would be equivalent to a very large interface between the electronically conducting and ionically conducting regions and appears to play a most important role in causing reversibility.

With regard to step 5 of the mechanism, namely the interaction between silver chloride solid and the aqueous solution, it is likely that there is a strong exchange of chloride ions between the surface of silver chloride solid and the solution, which in turn causes exchange in the other steps in succession, *viz.*, steps 4, 3, 2 and 1. This would naturally make the degree of reversibility a function of concentration of chloride ions.

One can also see from the above mechanism the possible main factor which would bring about a lowering of reversibility. The lowering would be caused by the occurrence of a barrier for the exchange in any of the consecutive interactions (*vide* equations 2-5). The main probable barrier is a thick stoichiometric layer of silver chloride which would bring down the ionic and electronic transport in the solid. In this connection, it is pertinent to note that electrodes with white silver chloride (obviously free from interstitials) show poor reversibility whereas those with violet silver chloride show good reversibility.⁷ It is also known, a long contact between metal and the halide is necessary before proper behaviour can be obtained.⁸ Long intervals of time, of the order of hours and days, are inexplicable in terms of liquid phase diffusion and are presumably connected with the development of stoichiometric barriers. In this connection it is of interest to note that it is usual to give a heat treatment to silver chloride at 350°C. for getting a product showing good electromotive behaviour.⁹ It is known that the fractional concentration of interstitials in such a product may be as high as 10^{-3} . It is again of interest to note that the concentration of interstitials in the electrolytically prepared silver chloride at a current density of 1 mA per cm.² (which is recommended for preparation of reversible electrodes) is of the same order. All the successful efforts made at getting highly reversible electrodes appear to result in making this barrier as thin as possible.

THE CALOMEL ELECTRODE

What is discussed above is also true to a large extent with reference to the calomel electrode. For instance, the capacity of the calomel electrode is known¹⁰ to be as high as 1000 $\mu\text{F}/\text{cm}^2$ Janz

and Ives¹¹ have shown this untenability of the classical mechanism to explain the high reversibility. To quote Janz and Ives, to explain the degree of reversibility it is necessary that "the duty of depolarising about 35 square metres of mercury surface devolve upon each mercurous ion. This is ridiculous....." Furthermore, Hills and Ives¹² by their careful observations have demonstrated the presence of intense solid state interaction between white mercurous chloride and liquid mercury and its consequential "dramatic" effect on electrode reversibility. The product has a grey colour, similar to that of the electrolytic product.¹³ The "highly reactive intermediate" they have rightly postulated to explain this interesting behaviour is obviously connected with the formation of interlacing electronic and ionic conducting regions within the crystals, leading to a remarkable reversibility. The importance of grinding in the dry state¹⁴ can be appreciated from the fact that the solid state interaction between mercury and calomel would be hindered by the hydration layers on calomel and on mercury.

CONCLUSION

It is thus seen that solid state effects play an important role in determining reproducibility and reversibility of the electrodes of the second kind. The extension of these ideas is likely to explain many other mysterious behaviours of these electrodes and would help in designing conditions under which most reproducible and reversible electrodes can be produced.

1. El Constantinescu cited from *Chem. Abs.*, 1964, 60, 14115c.
2. Compton, W. D. and Maurer, R. J., *J. Phys. and Chem. of Solids*, 1956, 1, 191.
3. —, *Phys. Reviews*, 1956, 101, 1209.
4. Pryor, M. J., *J. Electrochem. Soc.*, 1959, 106, 557. Indira, K. S. & Doss, K. S. G., *Seminar in Electrochemistry*, Jodhpur 1966.
5. Bates, R. G., *et al.*, *J. Chem. Physics*, 1956, 25, 361.
6. Fleischman, M and Thirsk, H. R., *Electrochimica Acta*, 1959, 1, 146.
7. Carmody, W. R., *J. Amer. Chem. Soc.*, 1932, 54, 3617; Afanasiev, A. L., *Ibid.*, 1930, 52, 3477.
8. Brown, A. S. *Ibid.*, 1934, 56, 646; Lewis, G. N., *Ibid.*, 1906, 28, 158.
9. Keston, A. S., *Ibid.*, 1935, 57, 1671; Rule, O. K., and Lomer, V. K., *Ibid.*, 1934, 56, 1830.
10. Dibbs, H. P., Ives, D. J. G. and Pittman, R. W., *J. Chem. Soc.*, 1957, p. 3370.
11. Ives, D. J. and Tanz, G. J., *Reference Electrodes—Theory and Practice*, Academic Press, London, 1961, p. 25.
12. Hills, G. J. and Ives, D. J. G., *Nature*, 1960, 165, 530.
13. Ives, D. J. and Tanz, G. J., *Reference Electrodes and Cells*, Academic Press, London, 1961, p. 180.
14. Hills, G. J. and Ives, D. J. G., *J. Chem. Soc.*, 1961, p. 211.