LI. A NOTE ON THE REDUCTION POTENTIAL OF CYSTEINE-CYSTINE MIXTURES.

BY JNANENDRA CHANDRA GHOSH
AND SAILESH CHANDRA GANGULI.

From the Department of Chemistry, University of Dacca.

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GHOSH *et al.* [1932] have shown that in solution of $p_H > 7$, the electrolytic reduction of cystine to cysteine at a mercury electrode sets up a reversible potential system at the electrode. The potential of the system was determined by the concentration of the oxidant and the reductant and agreed with the thermodynamic formula

$$-E_h = E_0 - \frac{RT}{F} p_H - \frac{RT}{F} \log \frac{[\text{Cysteine}]}{\sqrt{[\text{Cystine}]}} \quad \text{.....(1),}$$

where $E_0 = +0.79$.

More recently Green [1933] has shown that the evidence brought forward by Ghosh *et al.* could be substantiated if the potential were measured at the particular mercury surface at which the cystine was reduced. But if the potential were measured at a new mercury surface, introduced into the system by an auxiliary electrode, a difference of about 60 mv. was at once observed and the potential at the auxiliary mercury electrode conformed to Dixon and Quastel's [1923] equation

$$E = E_0 - \frac{RT}{F} p_H - \frac{RT}{F} \log [\text{Cysteine}] \quad \text{.....(2).}$$

Quoting Barron *et al.* [1929] on the possibility of complex formation between cysteine and mercury in absence of oxygen when a galvanic cell is set up, Green confirmed the observation of Ghosh *et al.* that after electroreduction of cystine, H_2S did not give a precipitate, but he did not agree with their conclusion that no complex formation occurred in their experiments, and suggested that such a complex was indeed formed but was confined to the mercury surface.

It is however well known that a mercury surface when exposed to air is covered with an adsorption layer. Reeser and Sissing [1922] found the thickness of the adsorbed layer to be between 22 and 34 Å. McBain [1932] believes this layer to be a film of mercuric oxide, as it is not affected by evacuation for eight hours at room temperature using a Gaede pump.

The present authors in their previous work were guided by the suspicion that a film of adsorbed oxygen or oxide on the surface of the mercury electrode was responsible for the results of Dixon and of Barron *et al.* This film could not be removed by bubbling an inert gas like nitrogen, but could only be destroyed by a cathodic reduction process at the surface. The experimental method of Green with slight modifications is well suited to test directly the accuracy of this hypothesis.

Chemically pure N_2 gas prepared from NH_4Cl and $NaNO_2$ was dispersed into minute bubbles by means of a Jena gas filter and passed up a tower containing about 500 cm. length of a solution of alkaline pyrogallol prepared according to

the method of Haldane and Makgill [1933]. The complete absorption of all traces of oxygen was confirmed by passing the gas over a piece of white phosphorus which did not glow, showing that the oxygen pressure was less than 0.0007 mm.

The cell consisted of two chambers *A* and *B* connected by a stopcock *T* with 8 mm. bore. The inner portion of each chamber consisted of two tubes one within the other. The outer tube served as the nitrogen inlet and the inner tube as the siphon for contact with the calomel electrode. The outer limb of the siphon was filled with agar saturated with KCl. A platinum wire fused into the bottom of the vessel made electrical contact with the mercury electrode.

The chamber *A* was first filled with a buffer solution having the same p_H as the cystine solution. The bore of the stopcock *T* was also filled with buffer solution. The stopcock was then closed and the chamber *B* filled up with the buffered cystine solution. The apparatus was then set up as depicted in Fig. 1

Fig. 1.

and the chambers de-aerated by a vigorous current of nitrogen. A current of 5 milliamperes was passed for 5–10 minutes between the mercury in the chamber *B* as cathode and a platinum anode in the KCl solution beyond the agar bridge. The mercury in the chamber *A* was similarly subjected to cathodic depolarisation for 3–4 hours. It is essential for the success of the experiment that the potential drop at the cathode in chamber *A* shall be sufficient to discharge hydrogen gas but much less than is necessary to discharge the alkali metal ions which were used to prepare the buffer solutions. The results become erratic if alkali metal amalgams are formed at the surface. Hence cathodic depolarisation for sufficiently long periods with very low currents is necessary. The stopcock *T* was now opened; by variation of the height of the mercury columns at the nitrogen outlets from the vessel as well as by passing a vigorous current of nitrogen for 3–4 hours, the solutions in both the chambers were well mixed. The potentials at the mercury surfaces in each chamber were then measured against a decinormal calomel electrode.

The results are given in Table I.

The potentials of the mercury surfaces in chambers *A* and *B* become ultimately the same and are given by the equation (1).

Table I.

p_H	Conc. cystine	Conc. cystine	E_h in mv.		E_0 calc. according to (1)
			Chamber A	Chamber B	
7.00	0.00171 <i>M</i>	0.00099 <i>M</i>	-232	-230	0.082
7.50	—	—	-243	-242	—
8.00	—	—	-307	-308	—
8.50	—	—	-384	-383	—

The experimental results recorded above therefore confirm the hypothesis that an oxygen or oxide film on the mercury surface is responsible for setting up a potential in cystine-cysteine mixtures which follows the equation (2). Elimination of this film and complete removal of oxygen from the solution give rise to potentials which follow the thermodynamic equation (1).

It is well known that in presence of oxygen, complex formation of mercury with —SH compounds takes place rapidly. It is also probable that when a very limited supply of oxygen is available, as is the case in an adsorbed film of oxygen or oxide, mercury forms complexes with —SH compounds in preference to —S—S— compounds. The system $Hg-HgS-H_2S$ gives potentials [Immerwahr, 1901] which would obviously depend only on the concentration of H_2S . The authors are of opinion that the Dixon potentials may be due to a similar system, where HgS has been replaced by a compound formed by interaction of the —SH compound with the oxide film at the mercury surface and H_2S replaced by sulphhydryl compounds.

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