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ELECTROCHEMISTRY

HCN ELECTRODES ON NOBLE METALS (*)

(A paper by Ernestina Paglia Dubini and Enrico Padula, presented (**) by Livio Cambi, Member)

/Following is a translation of an article in the Italian-language periodical Rendiconti dell' Accademia Nazionale dei Lincei (Class de Scienze fisiche, matematiche, e naturali) (Reports of the Accademia Nazionale dei Lincei, Classes in the Physical, Mathematical and Natural Sciences), Series VIII, Vol XXVIII, Fasc. 1, Jan 1960, pages 63-68./

1. The research on which we are reporting, as advised by Professor L. Cambi, is an outgrowth of published inquiries into the reactions between HCN and certain noble metals in the presence of oxygen, concentrating chiefly on Au and Hh.(1)

We have already referred to the Au/HCN electrodes that were established in buffered hydrocyanic solutions of a given pH.

We were led to extend our experiments by the relative ease of reproducing these electrodes, and the specificity of the potentials, which differ from metal to metal.

The procedures we shall describe have to do with the following metals: Hg, Au, Ag, Pt, and Pd.

Accurate interpretation of the processes for the electrodes in question involves considerable difficulty. In this paper we shall explain the experimental data which, so far as we know, have not yet been published by other authors. The hypothesis requires further experiment

2. The hydrocyanic electrodes we examined were constituted of the metal under consideration, immersed in the buffered solutions at a given pH, and containing HCN in the concentrations indicated.

(*) Research performed at the Metallurgical Chemistry Center of the National Research Council, Milan University.

(**) At the session of 16 January 1960.

(1) L. Cambi, these "Reports," XXIV, 129 (1958); L. Cambi and E. Paglia, idem, XXVII, 428 (1959)

Most of the tests were performed with HCN at 0.5 moli/l.

Air was excluded. We worked in an Ar atmosphere; even the buffer saturation was performed by means of slow currents of HCN in Ar.

The hydrocyanic electrodes were, in almost every case, placed opposite to the chinidrone electrodes, in the same buffer, and we measured the emf of the pairs.

	HCN x gr/l, buff. pH = n		Chinidrone buffer pH = n	
Me	buff. pH = n	pH = n		Pt

The E_{Me} values we record were the result of subtracting the chinidrone potential from the emf of the couple. Table I shows the E_n potentials of the electrodes, in each of the metals considered, as a function of the pH.

It is generally known that elimination of oxygen from an electrolyte is very difficult to achieve, even with the finest experimental equipment. Therefore, in our work, too, it is probably traces of oxygen that caused the relatively fast establishment of the electrodes, by means of processes that might be diagrammed as follows:

$$2Me + 2HCN + (O) \longrightarrow 2MeCN + H_2O.$$

We observed that the accidental intervention of air, even in minute amounts, can markedly alter the potentials. Gold proved to be most sensitive to oxygen, even in trace amounts; particularly in the buffers with lower pH, the potentials oscillate between extremes on the order of 0.03 to 0.04V, as we shall show later.

The potentials usually were established within 3 hours, and reached sufficiently stable levels. Over long periods of time, they changed.

The diagrams in Figure I show fairly accurately that the hydrocyanic electrodes behave like hydrogen electrodes: they are in practically direct proportion to the pH involved.

The proportionality factor, however, differs with the different metals, and we must introduce a special coefficient for every single metal, which we indicate with γ .

On an empirical basis, the first process considered was:

$$A) \quad MeCN + H^+ + e \longrightarrow Me + HCN.$$

which gives us I) $E_{Me} = E_o + RT \ln \frac{a}{a_{HCN}} - \gamma pH$

with δ as a solubility constant for metallic cyanide. The equation is not satisfactory, because it would imply a directly proportional relationship with the pH at a constant concentration of HCN. The straight lines in the diagrams of Figure I are not parallel.

Therefore we took the expression:

II) $E_{Me} = E_o + RT \ln \frac{\delta}{HCN} - 2RTPh$

which can be simplified to

III) $E_{Me} = E_o - X - 2RTPh$

with HCN being constant.

In conclusion, we find that the potentials act as if they corresponded to a process of type (A) above, but with activity coefficient for the $[H^+]$ different from I and specific for each metal.

From the angle of the straight lines in the diagrams on Figure I, we find the following values:

a 18° C

Hg	0.895
Pt	0.987
Ag	1.110
Pd	1.667
Au	1.710

It is probable that various processes are involved in polarization, and have a cumulative effect on it. We are not able to define these processes at present.

We also considered the effect of the formation of cyano-complex negative ions:

$$MeCN + HCN \rightleftharpoons [Me(CN)_2]^- + H^+$$

But here again, the process as such would imply the identity of the proportionality coefficient to pH for such complex anions, and this does not occur, as can be seem from the Au and Ag electrodes.

Even leaving aside the question of complex anion formation, the coefficient is not in relation, at least directly, with the valence the metal takes on as a cyanide. The straight lines for Hg and Pd in the Figure I diagrams are not parallel, although we may assume that both metals become bivalent.

3. Dependence on the HCN concentration was studied particularly for the Hg and Au electrodes. Examination was conducted at 15°C and constant pH. The results are shown in the graphs on Figure 2. We find that the potentials tend towards a limit value, beyond which there is practically no variation in response to increased concentration of HCN.

This behavior is in line with the relatively low sensitivity of the potentials to the HCN concentration.

Although our experiments have so far been limited to mercury and gold, we believe that probably the saturation factor in relation to the potentials is general for all the metals we have examined thus far.

Lastly, the results we show agree with the theory of adsorption and activation of the hydrocyanic acid on mercury and gold, which we adopted in our earlier work.

4. In the case of mercury, we also investigated the influence of the concentration of $Hg(CN)_2$, as shown in Figure 3. We worked at a pH of 4.75, and our HCN concentration was 0.5 moli/l constant.

You note an inverse influence, with reference to the potential signs, of what we observed for HCN (Figure 2), but even in the case of cyanide we find a similar phenomenon of almost total insensitivity to the increase in that concentration, after about 0.03 moli/l.

The process of oxygen cyanization we worked out (Loc. cit.), which shows a quantitative progression with respect to H_2O_2 in an environment of a given pH with Au and Ag, and with a pure hydrocyanic solution with Hg, thus far shows no visible relationship with the potentials mentioned above. Auto-oxidation according to the pattern

$$2\left\{Me^{0}\cdots CNH\right\} + O_2 \rightarrow 2\,Me^{I}CN + H_2O_2$$

would seem to depend on specific inter-reactions between the metal and the adsorbed hydrocyanic acid, rather than on the electromotor activity of the hydrocyanic hydrogen which we found with the electrodes we tested.

The patterns of the E_{Me}/pH diagrams for Au and Hg are quite divergent, while auto-oxidation by H_2O_2 is typical for both.

5. Our measurements were taken at room temperature, with the usual apparatus, with closed electrodes in an argon atmosphere.

The buffering solutions used were the usual familiar ones:

Biphthalate of potassium ..... 0.2 M pH = 4

Tetraoxalate of potassium..... 0.01 M pH = 2.15
Solution of KH_2PO_4 1/15 M and
Na_2HPO_4 1/15M ..... pH from 4.75 to 8
$Na_2B_4O_7 \cdot 10\,H_2O$ ..... 0.01M pH = 9.2

The results are summarized in the following table:

Electrode potential in volts	pH							
	2,15	4	4,75	5	6	6,88	7,5	8,2
E_{Au}	+ 0,1 + 0,11 + 0,12 + 0,13	0,12 0,14	0,17	0,2 0,22	0,20	0,41 0,43 0,45	0,48	0,6
E_{Ag}	— 0,02 + 0,04			0,17 0,18		0,30		0,43 0,44
E_{H_2}	+ 0,11 + 0,12		0,03			0,13 0,14 0,15		0,25
E_{Pd}	+ 0,28 + 0,30		0,03			0,17 0,19		0,38 0,40
E_{Pt}	+ 0,24 + 0,27			+ 0,11		0,02 0,04		0,14

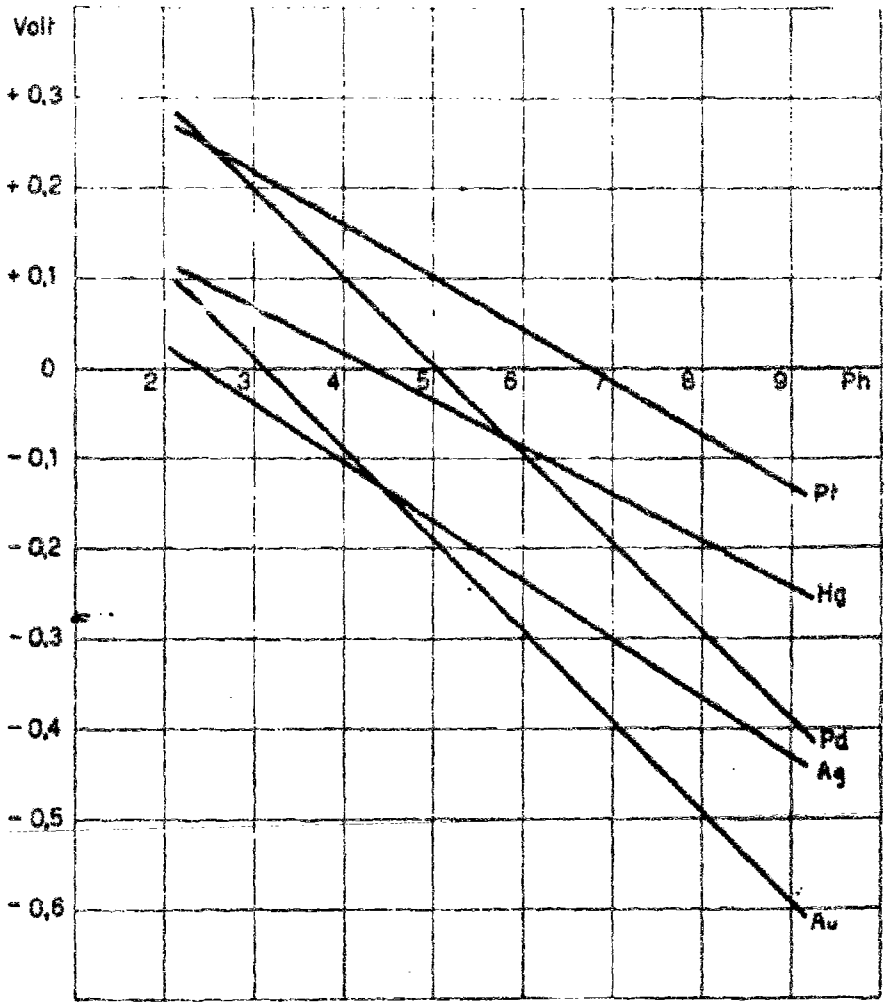

Figure 1.

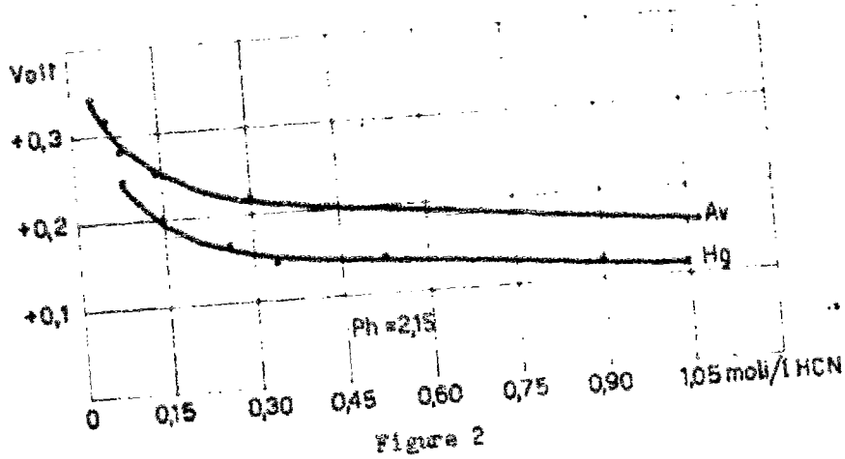

Figure 2

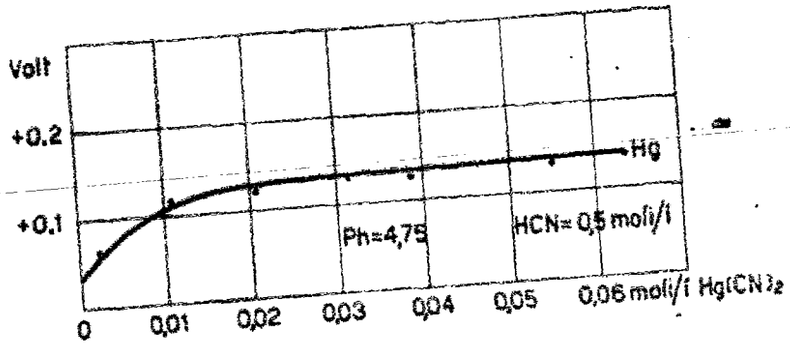

Figure 3