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ON THE DIFFERENTIAL CAPACITY OF MERCURY HYDROGEN ELECTRODE

By

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HORIUTI and collaborators[1] have proposed the electrochemical mechanism of the hydrogen evolution reaction on mercury electrode, which proceeded through the intermediary of $H_2^+(a)$ with the rate governed by its neutralization, and on its basis accounted for the break of Tafel line observed by MITSUYA[2], where the TAFEL constant changed from 1.5 to 0.5.

FRUMKIN[3] has recently remarked in this regard that, if $H_2^+(a)$ were present on the electrode surface, the differential capacity of a negatively charged mercury surface in acid solutions should be double that in neutral ones by additional electrons required for the formation of $H_2^+(a)$ from H^+ ions which equaled those for charging the electrode surface, hence that no marked difference between the capacities observed in acid and neutral solutions disproved the electrochemical mechanism.

The differential capacity of hydrogen electrode of mercury observed in dilute acid or neutral solutions shows a minimum at the electrocapillary maximum potential and increases monotonously to a constant value with increase of cathodic polarization as found by FRUMKIN[4] *et al.*[5], while that in concentrated acid solutions has similarly a minimum in the neighbourhood of the electrocapillary maximum potential but passes through a distinct maximum with increase of cathodic polarization and then decreases monotonously down to a constant value near that observed in the case of the dilute acid or neutral solutions[2,5]. The latter maximum is not attributable to hydrogen atoms specifically adsorbed on the electrode surface as has already been discussed by FRUMKIN[6].

The present paper is devoted to the explanation of the above behavior of the observed differential capacity of hydrogen electrode of mercury on the basis of the theory of the electrochemical mechanism developed in a previous work[7] with special reference to the above remark of FRUMKIN[3].

§ 1. Formulation of Differential Capacity.

The differential capacity is formulated as below on the basis of the electro-

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chemical mechanism in accordance with the model of mercury electrode described in the previous work[7], where the specific adsorption occurs on a plane P parallel to the electrode surface C and ions in solution are distributed from just outside P towards the bulk of solution in thermal equilibrium under the electrostatic potential of the diffuse layer. The capacity k of the HELMHOLTZ layer is defined as

$$k = \frac{D_P}{4\pi x_P}, \tag{1}$$

where D_P is the dielectric constant of the medium between C and P and x_P the distance of P from C. It is postulated in the present work that $H_2^+(a)$ is the only species specifically adsorbed. The electrostatic potentials at P and C are denoted by E_P and E_C respectively, as referred to that in the bulk of solution in what follows.

The differential capacity of the hydrogen electrode is now the increase of electricity charged on the electrode per unit increase of the electrode potential in the practical absence of Faradic current. The absence of Faradic current is effected by the practical inhibition of the rate-determining step *i.e.*, in the case of the electrochemical mechanism, the neutralization of $H_2^+(a)$, which is in equilibrium with hydrogen ion H^+ in solution and metal electron e, as

$$H_2^+(a) = 2H^+ + e\,. \tag{2}$$

The covered fraction θ of P by $H_2^+(a)$ varies along with the change of electrode potential, which shifts the equilibrium of (2). The quantity of electricity δQ, with which the electrode is charged per unit surface area with increase δE_C of the electrode potential consists of the two parts, *i.e.* that required for charging up the electrode surface and that for the formation of $H_2^+(a)$ according to (2) to increase θ by $\delta\theta$, as

$$\delta Q = C_1 \delta E_C - \frac{GF}{N_A}\delta\theta, \tag{3}$$

where C_1 is the differential coefficient of the charge density q on the electrode surface with respect to E_C, *i.e.*

$$C_1 = \frac{dq}{dE_C}, \tag{4}$$

G the number of adsorption sites per unit area of P-plane, F the Faraday and N_A the AVOGADRO number; negative sign of the second term of (3) accounts for the negative electricity required for the formation of $H_2^+(a)$. The latter term is given in terms of the charge density s on P, *i.e.*

$$s = \frac{GF}{N_A}\theta\,, \tag{5. a}$$

as

$$\frac{GF}{N_A}\delta\theta = \delta s\ . \tag{5. b}$$

The differential capacity $C = \dfrac{dQ}{dE_C}$ is given by (3) and (5), as

$$C = C_1 - \frac{ds}{dE_C}\ . \tag{6. a}$$

Rewriting $\dfrac{ds}{dE_C}$ by (4) as

$$\frac{ds}{dE_C} = \frac{ds}{dq}\,\frac{dq}{dE_C} = C_1\frac{ds}{dq}\,, \tag{6. b}$$

we have from (6. a) and (6. b)

$$C = C_1\left(1 - \frac{ds}{dq}\right)\ . \tag{6. c}$$

The C_1 is developed as follows. The $-q$ equals, on the one hand, the sum of s and the charge density q^d of the diffuse layer,

$$-q = s + q^d \tag{7. a}$$

and is given, on the other hand, as

$$-q = k\,(E_P - E_C)\ . \tag{7. b}$$

We have from (7) on differentiation with respect to q,

$$\frac{dq^d}{dq} = -\left(1 + \frac{ds}{dq}\right)\,, \tag{8. a}$$

$$\frac{dE_C}{dq} = \frac{1}{k} + \frac{dE_P}{dq}\ . \tag{8. b}$$

The $\dfrac{dE_P}{dq}$ in (8. b) is written as

$$\frac{dE_P}{dq} = \frac{dE_P}{dq^d}\,\frac{dq^d}{dq}\,, \tag{8. c}$$

or as

$$\frac{dE_P}{dq} = -\frac{1}{C_2}\,\frac{dq^d}{dq}\,, \tag{8. d}$$

where C_2 is the differential capacity of the diffuse layer, *i.e.*

$$C_2 = -\frac{dq^d}{dE_P} . \tag{8. e}$$

We have from (8. a) and (8. d)

$$\frac{dE_P}{dq} = \frac{1}{C_2}\left(1+\frac{ds}{dq}\right) , \tag{9. a}$$

and from (8. b) and (9. a) referring to (4)

$$\frac{1}{C_1} = \frac{1}{k} + \frac{1}{C_2}\left(1+\frac{ds}{dq}\right) . \tag{9. b}$$

The $\frac{ds}{dq}$ in (6. c) and (9. b) is derived from the adsorption isotherm of H_2^+(a)[7], *i.e.*

$$-RT\ln\frac{\theta}{1-\theta} = \varepsilon^{H_2^+(a)} - \mu^{H_2^+(a)} , \tag{10. a}$$

where $\varepsilon^{H_2^+(a)}$ is the reversible work required to bring up H_2^+(a) to a definite preliminary evacuated adsorption site from the standard state[8),9)]. The $\varepsilon^{H_2^+(a)}$ thus defined is expressed in terms of the electrostatic potential FE_P and the potential $uRT\theta$ due to nonelectrostatic repulsive interaction among H_2^+(a)'s, assumed to be proportional to θ with the proportionality constant uRT, as

$$\varepsilon^{H_2^+(a)} = \varepsilon_0^{H_2^+(a)} + uRT\theta + FE_P , \tag{10. b}$$

where $\varepsilon_0^{H_2^+(a)}$ is the value of $\varepsilon^{H_2^+(a)}$ at $\theta=0$ and $E_P=0$. The chemical potential $\mu^{H_2^+(a)}$ of H_2^+(a) is expressed on account of the equilibrium of (2) as

$$\mu^{H_2^+(a)} = 2\mu^{H^+} + \mu^e , \tag{10. c}$$

where μ^{H^+} and μ^e are the chemical potentials of H^+ ion in solution and metal electron respectively; μ^e is expressed in terms of E_C and the work function λ of mercury, as

$$\mu^e = -F(\lambda + E_C) . \tag{10. d}$$

We have from (10) for constant μ^{H^+} the adsorption isotherm of H_2^+(a) in the differential form, *i.e.*

$$-\delta\theta = \frac{\theta(1-\theta)}{1+u\theta(1-\theta)}\,\frac{F}{RT}\,(\delta E_P + \delta E_C) . \tag{11}$$

The above isotherm is formally equivalent to that advanced by SLYGIN and

FRUMKIN[10)] and TEMKIN and PYZHEV[11)] in the particular case, when $u\theta(1-\theta)$ is sufficiently large compared with unity and δE_P is zero.

Substituting $\delta\theta$ from (11) into (5.b), we have referring to (4) and (9.a)

$$-\frac{ds}{dq}=fg\left\{\frac{1}{C_1}+\frac{1}{C_2}\left(1+\frac{ds}{dq}\right)\right\}, \tag{12}$$

where

$$f=\frac{\theta(1-\theta)}{1+u\theta(1-\theta)}, \qquad g=\frac{GF^2}{N_A RT}, \qquad \text{(13. a), (13. b)}$$

and solving (9.b) and (12) for C_1 and $\frac{ds}{dq}$

$$\frac{1}{C_1}=\frac{\left(1+\frac{fg}{C_2}\right)\frac{1}{k}+\frac{1}{C_2}}{1+\frac{2fg}{C_2}} \tag{14}$$

$$-\frac{ds}{dq}=\frac{\left(\frac{1}{k}+\frac{2}{C_2}\right)fg}{1+\frac{2fg}{C_2}}, \tag{15}$$

The differential capacity C is now given by (6.c), (14) and (15) in terms of k, C_2 and fg.

§ 2. General Procedure.

It appears to be presupposed in the above remark of FRUMKIN[3)] that $H_2^+(a)$ is, if any, present or absent, respectively in the case of acidic or neutral solution. This presupposition would probably be valid, inasmuch as the chemical potential $\mu^{H_2^+(a)}$ of $H_2^+(a)$ increases with increase of μ^{H^+} by (10.c), although not with certainty. Apart from the question of its validity, the differential capacity of the hydrogen electrode of mercury will be discussed below according to the above formulation both under the premises of the absence and presence of $H_2^+(a)$, assuming in the latter case that s is practically zero at $E_P=0$, *i.e.*

$$s=0 \quad \text{at} \quad E_P=0\,. \tag{16. a}$$

The q^d is expressed as[7)]

$$q^d=\sqrt{\frac{n\bar{D}RT}{2\pi}}\left\{e^{-\frac{FE_P}{2RT}}-e^{\frac{FE_P}{2RT}}\right\}, \tag{16. b}$$

with particular reference to uni-uni-valent electrolyte of concentration n, where

$\bar{D}$ is the mean dielectric constant of the diffuse layer. Since $q^d=0$ at $E_P=0$ by (16.b), we have according to (7) and (16.a)

$$q=0\,,\quad E_C=0 \quad \text{at} \quad E_P=0\,, \tag{16.c}$$

which may duly be attributed to the point of the electrocapillary maximum.

We might first discuss in §3 below the behavior of C at the electrocapillary maximum and then treat in §4 and §5 the cases of absent and present H_2^+(a) for E_C lower than that of the electrocapillary maximum.

§3. Electrocapillary Maximum.

The differential capacity C is given by (14), (15) and (6.c) as

$$C=\frac{kC_2+4kfg+C_2fg}{k+C_2+fg}\,. \tag{17.a}$$

We have $f=0$ by (16.a), (5.a) and (13.a) at the electrocapillary maximum where $E_P=0$ according to §2. The particular value C_0 of C at the electrocapillary maximum is now

$$C_0=\frac{kC_{2,0}}{k+C_{2,0}}\,, \tag{17.b}$$

where $C_{2,0}$ is the appropriate value of C_2. The difference $C-C_0$ is given by (17) as

$$\begin{aligned} C-C_0 &= C-\frac{kC_2}{k+C_2}+\frac{kC_2}{k+C_2}-C_0 \\ &= \frac{(2k+C_2)^2fg}{(k+C_2+fg)(k+C_2)}+\frac{k^2(C_2-C_{2,0})}{(k+C_{2,0})(k+C_2)}\,. \end{aligned} \tag{18}$$

The first term on the third member of the above equation is essentially positive, while the second one positive too, inasmuch as $C_{2,0}$ at the electrocapillary maximum where $E_P=0$ is the smallest value of C_2 as seen from the equation

$$C_2=F\sqrt{\frac{n\bar{D}}{8\pi RT}}\left\{e^{-\frac{FE_P}{2RT}}+e^{\frac{FE_P}{2RT}}\right\} \tag{19}$$

derived readily from (8.e) and (16.b).

In the case of inherent absence of H_2^+(a) the first term of the third member of (18) is constantly zero because $f=0$ by (13.a), whereas the second term contribute a positive value to $C-C_0$ for $E_P\neq 0$ as mentioned above. It follows that C is minimum at the electrocapillary maximum, whether H_2^+(a) is inherently absent or not, in accordance with the experimental results both in the cases of dilute acid or neutral solutions and of concentrated acid solutions.

§ 4. H_2^+(a) absent.

If H_2^+(a) is practically absent throughout the whole range of the electrode potential, we have from (13.a) and (15) $f=0$ and $\frac{ds}{dq}=0$, hence C_1 and C are given by (14) and (6.c) as

$$\frac{1}{C_1}=\frac{1}{k}+\frac{1}{C_2}\,, \tag{20.a}$$

$$C=C_1\,. \tag{20.b}$$

The C_2 increases now rapidly with increase of $|E_P|$ according to (19) as shown in Table I, while $|E_P|$ increases monotonously with decrease of E_C in this case according to the equation

$$\delta E_P=\frac{k}{k+C_2}\,\delta E_C\,, \tag{21}$$

as derived below.

TABLE I. C_2 $\mu\phi/\text{cm}^2$ of 1-1-valent electrolyte solutions.

E_P mv \ n	0.1 N	10^{-3} N
0	53	5.3
100	200	20
200	1450	145
300	10660	1066

It follows from (19), (20) and (21) that C_1 or C increases monotonously to tend to a constant value k with decrease of E_C. Experimentally it has been found in dilute acidic or neutral solutions in accordance with the above theoretical conclusion that C increases monotonously to approach *ca.* 18 $\mu\phi/\text{cm}^2$ from the minimum value at the electrocapillary maximum[4]. Identifying k with the constant value 18 $\mu\phi/\text{cm}^2$ on the ground of the above accordance, we see from Table I that C_2 is smaller than k at $E_P=0$ in a solution of 10^{-3}N electrolyte concentration, which corresponds to that of dilute acid or neutral solutions referred to above[4]. It follows now from (20) that C is appreciablly lower than k at $E_C=0$, where $E_P=0$ by (16.c), tending monotonously to k with decrease of E_C. This accounts for the observations in dilute acid or neutral solutions, as has already been shown by FRUMKIN *et al*[4].

Eq. (21) is derived as follows. The increment δE_P of E_P was given in a previous work[7][9], in accordance with the model referred to in § 1 as

$$F\delta E_{\mathrm{P}} = \alpha_h \delta h - \alpha_l \delta l , \qquad (22.\mathrm{a})$$

where

$$h = \mu^{\mathrm{H}^+} , \qquad l = \mu^{\mathrm{H}^+} + \mu^{e} \qquad (22.\mathrm{b})\,(22.\mathrm{c})$$

$$\alpha_l \equiv \frac{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} - F\left(\dfrac{\partial s}{\partial l}\right)_{h,\,E_{\mathrm{P}}}}{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} - \dfrac{D_{\mathrm{P}}}{4\pi}\dfrac{\partial}{\partial E_{\mathrm{P}}}\left(\dfrac{\partial E}{\partial x}\right)_a - \left(\dfrac{\partial s}{\partial E_{\mathrm{P}}}\right)_{h,\,l}} , \qquad (22.\mathrm{d})$$

x is the distance from C.

The $-\dfrac{D_{\mathrm{P}}}{4\pi}\dfrac{\partial}{\partial E_{\mathrm{P}}}\left(\dfrac{\partial E}{\partial x}\right)_a$ is the capacity C_2 of the diffuse layer*), *i.e.*

$$-\frac{D_{\mathrm{P}}}{4\pi}\frac{\partial}{\partial E_{\mathrm{P}}}\left(\frac{\partial E}{\partial x}\right)_a = C_2 . \qquad (23)$$

We have from (5.b), (11) and (13)

$$-\delta s = fg(\delta E_{\mathrm{P}} + \delta E_{\mathrm{C}}) ,$$

and from (10.d), (22.b) and (22.c)

$$F\delta E_{\mathrm{C}} = \delta h - \delta l , \qquad (24)$$

hence

$$-F\delta s = fg(F\delta E_{\mathrm{P}} + \delta h - \delta l) ,$$

or

$$F\left(\frac{\partial s}{\partial l}\right)_{h,\,E_{\mathrm{P}}} = fg , \qquad (25.\mathrm{a})$$

$$\left(\frac{\partial s}{\partial E_{\mathrm{P}}}\right)_{h,\,l} = -fg . \qquad (25.\mathrm{b})$$

Substituting now (1), (23) and (25) into (22.d), α_l is expressed as

$$\alpha_l = \frac{k - fg}{k + C_2 + fg} , \qquad (26.\mathrm{a})$$

hence δE_{P} is given for a definite solution of constant h, according to (22.a), (24) and (26.a), as

$$\delta E_{\mathrm{P}} = \frac{k - fg}{k + C_2 + fg}\,\delta E_{\mathrm{C}} . \qquad (26.\mathrm{b})$$

Since $\theta = 0$ in the absence of H_2^+(a), we have $f = 0$ by (13.a), hence (21) above**).

In concentrated acid solutions, C in the absence of H_2^+(a) should remain approximately constant at k throughout the whole range of E_{C} according to (20), inasmuch as C_2 is sufficiently large compared with k at any value of E_{P} as seen from Table I. The observed peak of capacity-potential curves in concentrated acid solutions does not follow from this premise. Neither is the theoretical conclusion of constant C experimentally verified.

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*) Cf. Appendix (xiv) of Ref. 7.

**) If adsorbed hydrogen ion H^+(a) were present instead of H_2^+(a), we have $\delta E_{\mathrm{P}} = \dfrac{k}{k + c_2 + fg}\delta E_{\mathrm{C}}$, *i.e.* Eq. (4.14.$l$) of Ref. 7, which leads to the same conclusion that $|E_{\mathrm{P}}|$ increases monotonously from zero at the electrocapillary maximum with decrease of E_{C}.

§ 5. $H_2^+(a)$ Present.

Eq. (21) holds at the electrocapillary maximum potential, where $fg=0$ by (16.a), (5.a) and (13). It follows that E_P decreases initially from zero with decrease of E_C. The θ increases on the other hand monotonously with decrease of E_C according to the equation which follows from (11) and (26.b), *i.e.*

$$-\delta\theta = \frac{F}{RT}\,\frac{\theta(1-\theta)}{1+u\theta(1-\theta)}\,\frac{2k+C_2}{k+C_2+fg}\,\delta E_C\,. \tag{27}$$

Along with increase of θ, fg increases by (13) until it equals k*), when $\delta E_P=0$ by (26.b) and from there on E_P increases with further decrease of E_C. The θ then increases until fg decreases for $\theta>1/2$, since fg has a single maximum at $\theta=1/2$ as readily be deduced from (13). When fg equals k again with increase of θ, E_P attains to maximum and from there on decreases tending to a constant negative value with further decrease of E_C, inasmuch as α_t is then positive and tends to zero according to (26.a) with increase of $|E_P|$, which causes C_2 rapidly to increase by (19). The E_P cannot then tend to a constant positive value, since positive α_t increases with decrease of positive E_P by (19) and (26.a) to decrease E_P more rapidly. The minimum and the maximum of E_P are thus situated at $\theta<1/2$ and $\theta>1/2$ respectively and E_P tends to a constant negative value at extremely low E_C, where θ tends to unity, hence fg to zero by (13) and C_2 becomes very large to approach α_t to zero by (26.a), *i.e.*

$$\theta\to 1\,,\quad fg\to 0\,,\quad C_2\gg k\,,\quad \alpha_t\to 0\,. \qquad \text{(28. a), (28. b), (28. c), (28. d)}$$

We have at the minimum and the maximum of E_P, putting $fg=k$ in (14) and (15)

$$C_1 = k\,, \tag{29. a}$$

$$-\frac{ds}{dq} = 1\,, \tag{29. b}$$

irrespective of the value of C_2. Substituting C_1 and $\frac{ds}{dq}$ from (29) into (6.c), we have

$$C = 2k\,. \tag{29. c}$$

Eq. (29) is interpreted with reference to (8.a) that the HELMHOLTZ layer alone,

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*) The fg amounts to $93\,\mu\phi/\text{cm}^2$ at $\theta=1/2$ by (13) on the base of the value $G=10^{15}$ and $u=65$[12]) [the highest value of those estimated for $H_2^+(a)$'s on mercury electrode[1]) and hydrogen atoms adsorbed on nickel[13]) or on tungsten[12])]. The fg at $\theta=1/2$ is still larger for a smaller value of u. The fg may hence be taken amply to exceed $k=18\,\mu\phi/\text{cm}^2$ along with increase of θ.

but not the diffuse layer, behaves as a condenser at these points, while electrons required for the formation of H_2^+(a) double the capacity to make up $2k$. This corresponds to the case remarked by FRUMKIN[3], which is realized at the minimum and the maximum of E_P, but not at the extremity of low E_C as seen below. It is shown in Appendix that $\frac{dC}{dE_C}$ is negative or positive respectively at the minimum or maximum of E_P. It follows that C should have at least a maximum higher than $2k$ between these extrema of E_P.

In the extremity of low E_C we have from (17.a), (28.b) and (28.c)

$$C = k\,. \tag{30}$$

This conclusion may be interpreted as follows. As θ approaches unity, $\delta\theta$ or the contribution to the differential capacity from the formation of H_2^+(a) tends to vanish, hence by (5.b) and (6.a), $C = C_1$. The C_1 is now given by (13) and (14) as $\frac{1}{C_1} = \frac{1}{k} + \frac{1}{C_2}$ at the present condition where $\theta \doteqdot 1$, *i.e.* as the capacity of the HELMHOLTZ layer and that of diffuse layer connected in series. But since C_2 is very large, the connected capacities operate as if they were a single capacity of the HELMHOLTZ layer of the magnitude k or we have (30).

The differential capacity of the mercury electrode thus increases with decrease of E_C to pass through a maximum higher than $2k$ and decreases to approach k, instead of $2k$ as concluded by FRUMKIN. This theoretical conclusion is confirmed by the observations of PHILPOT[5], MITSUYA[2] and PAST and JOFA[14].

§ 6. Conclusion.

We see from the foregoing sections that the present theory accounts for the minimum on C, E_C-curve at the electrocapillary maximum and that the premise of the absence or presence of H_2^+(a) leads respectively to the disappearance or appearance of maximum and to the value of C tending to k at extremely low E_C commonly both in the cases. The existence of H_2^+(a) is now verified by the maximum observed with concentrated acid solution accompanied by the minimum observed at the electrocapillary maximum and the limiting value of k observed at low E_C.

It is further shown that the above limiting value k of C at lower E_C is attained on the basis of the electrochemical mechanism at the same condition, in accordance with the experiment, as that which gives rise to the value near 0.5 of TAFEL constant of mercury electrode. TAFEL constant τ was derived in a previous work[7] as

$$\tau = 2(1-\alpha) + \frac{\alpha - \theta}{1 + u\theta(1-\theta)}(1 + \alpha_l)\,, \tag{31}$$

where α is a constant near 0.5. At the above condition where C tends to k, we have from (28.a), (28.d) and (31) $\tau=1-\alpha\doteqdot 0.5$.

Summary

The differential capacity C of hydrogen electrode of mercury was derived in extension of the previous theory (Ref. 7) on the basis of the electrochemical mechanism, which presupposes hydrogen molecule ion $H_2^+(a)$ on the electrode surface in equilibrium with hydrogen ion in solution and metal electron. It was thus deduced that (I) C is minimum at the electrocapillary maximum with respect to the electrode potential E_C and (II) C approaches with decrease of E_C the capacity k of the HELMHOLTZ layer either in the presence or absence of $H_2^+(a)$, but not to $2k$ as remarked by FRUMKIN (Ref. 3). It was inferred further that (III.a) in the presence of $H_2^+(a)$, C passes through at least one maximum higher than $2k$ intermediately with decrease of E_C before tending to k, whereas (III.b) in its absence C increases from a value smaller than k monotonously with decrease of E_C to approach k. The theoretical conclusion (I) and (II) are concordant with experimental results either of concentrated acid solution or of dilute or neutral solution, whereas (III.a) fits in with those of the former solution and (III.b) with those of the latter, verifying the presence of $H_2^+(a)$ in the former case.

The TAFEL constant was shown on the same basis to be *ca.* 0.5 at the same condition where C tends to k in accordance with the experimental results.

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Appendix

Sign of $\frac{dC}{dE_C}$.

The $\frac{dC}{dE_C}$ is given by (6.a) in the text as

$$\frac{dC}{dE_C}=\frac{dC_1}{dE_C}-\frac{d^2s}{dE_C^2}. \qquad \text{(i)}$$

We have from (14) by differentiation

$$\frac{1}{k}\,\frac{dC_1}{dE_C}=\frac{(k-fg)\dfrac{dC_2}{dE_C}+(2k+C_2)\dfrac{dfg}{dE_C}}{(k+C_2+fg)^2}\,, \tag{ii}$$

and from (5.b) and (11)

$$-\delta s=fg(\delta E_C+\delta E_P)\,, \tag{iii}$$

hence

$$-\frac{ds}{dE_C}=fg\left(1+\frac{dE_P}{dE_C}\right). \tag{iv. a}$$

The $\frac{dE_P}{dE_C}$ is given by (7.b) on differentiation with respect to E_C with reference to (4), as

$$\frac{dE_P}{dE_C}=1-\frac{C_1}{k}\,. \tag{iv. b}$$

Substituting $\frac{dE_P}{dE_C}$ from (iv.b) into (iv.a,) we have

$$-\frac{ds}{dE_C}=fg\left(2-\frac{C_1}{k}\right), \tag{iv. c}$$

hence

$$-\frac{d^2s}{dE_C^2}=\left(2-\frac{C_1}{k}\right)\frac{dfg}{dE_C}-\frac{fg}{k}\,\frac{dC_1}{dE_C}\,. \tag{v}$$

The $\frac{dC}{dE_C}$ is given by eliminating $\frac{dC_1}{dE_C}$, $\frac{d^2s}{dE_C^2}$ and C_1 from (i), (ii), (v) and (14), as

$$\frac{dC}{dE_C}=\left(\frac{k-fg}{k+C_2+fg}\right)^2\frac{dC_2}{dE_C}+\left(\frac{2k+C_2}{k+C_2+fg}\right)^2\frac{dfg}{dE_C}\,. \tag{vi}$$

The $\frac{dC_2}{dE_C}$ in the above equation is expressed by (19) and (iv.b) as

$$\frac{dC_2}{dE_C}=\frac{F^2}{2RT}\sqrt{\frac{n\bar{D}}{8\pi RT}}\left(1-\frac{C_1}{k}\right)\left(e^{\frac{FE_P}{2RT}}-e^{-\frac{FE_P}{2RT}}\right),$$

or substituting C_1 from (14)

$$\frac{dC_2}{dE_C}=A\,\frac{k-fg}{k+C_2+fg}\left(e^{\frac{FE_P}{2RT}}-e^{-\frac{FE_P}{2RT}}\right), \tag{vii. a}$$

where

$$A \equiv \frac{F^2}{2RT}\sqrt{\frac{n\bar{D}}{8\pi RT}}\,.$$

The $\dfrac{dfg}{dE_C}$ in (vi) is given by (13) as

$$\frac{dfg}{dE_C} = \frac{GF^2}{N_A RT}\,\frac{1-2\theta}{\{1+u\theta(1-\theta)\}^2}\,\frac{d\theta}{dE_C}\,, \tag{vii. b}$$

and $\dfrac{d\theta}{dE_C}$ in the above equation by (11), (iv. b) and (14) as

$$\frac{d\theta}{dE_C} = -\frac{N_A fg}{GF}\,\frac{2k+C_2}{k+C_2+fg}\,, \tag{vii. c}$$

hence

$$\frac{dfg}{dE_C} = -\frac{F}{RT}\,\frac{fg(1-2\theta)}{\{1+u\theta(1-\theta)\}^2}\,\frac{2k+C_2}{k+C_2+fg}\,. \tag{vii. d}$$

We have now from (vi), (vii. a) and (vii. d)

$$\frac{dC}{dE_C} = A\left(e^{\frac{FE_P}{2RT}} - e^{-\frac{FE_P}{2RT}}\right)\left(\frac{k-fg}{k+C_2+fg}\right)^3 - \frac{F}{RT}\,\frac{fg(1-2\theta)}{\{1+u\theta(1-\theta)\}^2}\left(\frac{2k+C_2}{k+C_2+fg}\right)^3. \tag{viii}$$

As E_C decreases from zero at the electrocapillary maximum, E_P passes through a minimum at $\theta<1/2$ and then a maximum at $\theta>1/2$, where $fg=k$, $C_1=k$ and $\delta E_P=0$ both in the cases as shown in §5. The first term in (viii) is zero at the minimum and the maximum of E_P, while the second term in (viii) is $-\dfrac{F}{RT}\,\dfrac{k(1-2\theta)}{\{1+u\theta(1-\theta)\}^2}$, which is negative or positive according as $\theta<1/2$ or $\theta>1/2$. The $\dfrac{dC}{dE_C}$ is in consequence negative at the minimum and positive at the maximum.

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