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HYDROGEN INTERMEDIATES ON CATALYSTS AND ELECTRODES^{*)}

Part I FUNDAMENTAL

By

JURO HORIUTI

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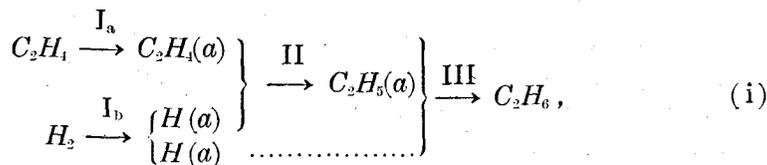
*) The original concept now detailed in the present paper has been presented in an earlier report (HORIUTI: Transaction of 13th Committee of Japan Society for the Promotion of Scientific Research I, 15 (1940), printed in Japanese) laying down the fundamental line of attack since then followed in this laboratory as reviewed in subsequent Parts of this series.

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Introduction

POLANYI¹⁾ has advanced in conjunction with the present author on the basis of experiments of FARKAS, FARKAS and RIDEAL²⁾ and of their own ones¹⁾, the associative mechanism,



as responsible for the catalysed ethylene hydrogenation,



in the presence of nickel as well as of platinum catalyst i. e. that ethylene and hydrogen are first adsorbed by Steps I_a and I_b respectively resulting in adsorbed ethylene C₂H₄(a) and adsorbed hydrogen atom H(a) which combine each other by Step II, and the adsorbed ethyl group C₂H₅(a) thus formed finally picks up H(a) again to complete ethane molecule, the last step III governing the rate of overall reaction (ii).

HORIUTI and OKAMOTO³⁾ later found hydrogen electrodes of different materials of 0.3 volt cathodic polarization at room temperature fell into two groups of electrolytic separation factor of deuterium respectively in the neighbourhood of 7 and of 3: to the former group of separation factor 7 belong the hydrogen electrodes of Ni, Pt, Cu, Au, Ag in acidic solution and Pb in alkaline solution, whereas to the latter group of 3 those of Hg, Sn and Pb in acidic solution.

They have suggested on the basis of this and other experimental facts that the reaction on hydrogen electrodes of the former group proceeded through the intermediary of H(a) whose recombination governed the rate, whereas on those of the latter group through that

of hydrogen-molecule-ion*) $H_2^+(a)$ adsorbed on the electrode, its neutralization being the rate-determining step. These mechanisms were called by them³⁾ the catalytic and electrochemical mechanism respectively.

WOLFENDEN and WALTON conducted an exhaustive experiment on the separation factor over a wide temperature range establishing the experimental facts underlying the above point of view.

These alternative mechanisms were on the other hand confirmed theoretically^{5),6),7)} by deriving conclusions from them on various hydrogen electrode phenomena inclusive of the classical relationship between the current and the electrode potential found by Tafel⁸⁾ and later carefully established by BOWDEN and RIDEAL⁹⁾ with the special reference to those of nickel⁵⁾ and mercury⁷⁾ as representatives of the respective groups. It appeared that the intermediate of neutral hydrogen atom in the case of nickel as well as of platinum was rather established, as might generally accepted to be, throughout the electrode process and the catalysis.

Later experiments with hydrogen electrode of platinum, cathodically polarized less than 0.1 volt, led however IKUSIMA and the present author¹⁰⁾ to the conclusion of the electrochemical mechanism through the intermediary of $H_2^+(a)$ being responsible for the electrode reaction.

In accordance with the above result HORIUTI and KWAN¹¹⁾ have further arrived at the conclusion that the hydrogenation of liquid acetone proceeded through the intermediary of $H(a)$ or of $H_2^+(a)$ when catalysed by nickel or platinum respectively.

Summing up, *Ni* and *Hg* persist respectively in the intermediates of $H(a)$ and $H_2^+(a)$, whereas *Pt* and *Pb* versatily prefer either $H(a)$ or $H_2^+(a)$ according to the condition throughout the electrode process and the catalysis.

The present series of paper is devoted to the development of the theory for understanding the complex features of the above result and to its extension by experimenting on its conclusions. General theory is developed in Chapter 1 of Part I on the effect of the varia-

*) The intermediate originally suggested in Ref. 3 was that consisting of a neutral hydrogen atom and a proton respectively linked to surface metal atom and to a water molecule. It has later been shown (Ref. 7) that both its electronic and the nuclear configuration worked out quantum-mechanically was adequately covered by the words, "hydrogen-molecule-ion adsorbed on the electrode".

tion of different factors, the work function of the catalyst or the electrode, etc., on abundance of hydrogen intermediates, $H^+(a)$ etc. on the catalyst's surface, and in Chapter 2 the above complex features are explained on the basis of the general theory attributing the change of leading intermediate to the difference of the factors.

CHAPTER 1 GENERAL THEORY.

§1 Scope of Theory.

Here will be treated the effect of varying several factors mentioned below on the abundance of intermediates $H_2^+(a)$ and $H(a)$ concluded of being existent on the catalyst's surface as mentioned in the introduction inclusive of $H^+(a)$ similarly concluded elsewhere¹²⁾. The catalyst will include the hydrogen electrode, the relevant reaction,



where ε is the metal electron in the electrode, being taken of the simplest type of heterogeneous reaction catalysed by the electrode.

The factors considered are the concentration of electrolyte in the medium surrounding the catalyst, which will simply be termed surroundings in what follows, the work function λ of catalyst, the chemical potential $\mu(H^+b)$ of proton or hydrogen ion $H^+(b)$ in the bulk of surroundings, that $\mu(H_2)$ of hydrogen there and the electrode potential of the catalyst, hydrogen ion in the bulk and metal electron in the catalyst being assumed in equilibria,



established either partially, perhaps, by virtue of a certain rate-determining step prevailing or as parts of the total equilibrium.

Such an equilibrium is implied in the mechanism of the hydrogen electrode reaction advanced in the introduction and, although not explicitly in that of the catalysed hydrogenation there, may be additionally assumed without any conflict.

The electrode potential η of catalyst is defined in terms of chemical potentials $\mu(H_2)$ of hydrogen gas, $\mu(H^+b)$ and $\mu(\varepsilon)$ of metal electron in the catalyst as,

$$F\eta = \frac{1}{2} \mu(H_2) - \mu(H^+b) - \mu(\varepsilon), \quad (1.3)$$

where F is Faraday. The η thus defined is the hydrogen overvoltage vanishing at equilibrium of (1.1), when,

$$\frac{1}{2} \mu(H_2) = \mu(H^+b) + \mu(\varepsilon), \quad (1.4)$$

The effect of above mentioned factors will be discussed with reference to the equilibrium relationship (1.2)^{*)} and with Poisson equation to be satisfied simultaneously by the distribution of charged intermediates $H^+(a)$ and $H_2^+(a)$ and ions in the surroundings, after having specified our assembly, in which the reaction of interest is going on, in the subsequent section for affording a concrete basis to the formulation of the above two relations i. e. (1.2) and that of Poisson equation.

§ 2 Specification of Assembly.

Our assembly consists of a heterogeneous catalyst involving metal electrons and of surroundings of any state, gas or liquid, containing hydrogen and possibly some substrate of hydrogenation. The assembly is specified in detail by (A) and (B) below.

(A) Catalyst's surface consists of numerous physically identical sites σ 's, each being empty or occupied by one of hydrogen intermediates $H^+(a)$, $H_2^+(a)$ and $H(a)$ exclusively. The energy $\varepsilon(H^+)$ or $\varepsilon(H_2^+)$ respectively of $H^+(a)$ or $H_2^+(a)$ is the sum of the electrostatic part and the rest $\varepsilon(H^+)_0$ or $\varepsilon(H_2^+)_0$ which depends on the catalyst as well as on the properties of the surroundings^{**)}, except on the concentration of ion, on the chemical potential of hydrogen ion there and on the

*) The (1.2) refers to (1.2. H^+), (1.2. H_2^+) and (1.2. H) together. This manner of notation will be followed below throughout.

***) The energy of $H^+(a)$ will be lowered by the existence of nucleophilic reagent in the neighbourhood of appropriate σ . That of $H_2^+(a)$ will be too, inasmuch as its electronic state or the relevant energy is adequately described just like the original hydrogen-molecule-ion in vacuum as that resonating between two states of alternative occupation of the two hydrogen atomic orbitals by one electron [cf. Ref. 7], energies both of the latter states being lowered by the nucleophilic molecule.

The theory will be developed below regarding $\varepsilon(\delta_i)_0$ as if unique for each δ_i in a given surroundings as far as § 9. The state of δ_i will be discriminated in § 10 with respect to the different kinds of energy depressing molecules in conjunction with an example provided in § 9 showing that the use of unique $\varepsilon(\delta_i)_0$ before implies no lack of generality, if identified with the effective one or "weighted mean" defined there.

population of intermediates on the catalyst^{*)}, whereas that $\epsilon(H)$ of $H(a)$, devoid of the electrostatic part, is definite for a definite catalyst.

(B) Electrostatic potential E is E_0 homogeneously in the catalyst inclusive on its plane surface C varying outside one-dimensionally with distance x along the normal to C toward the bulk of surroundings

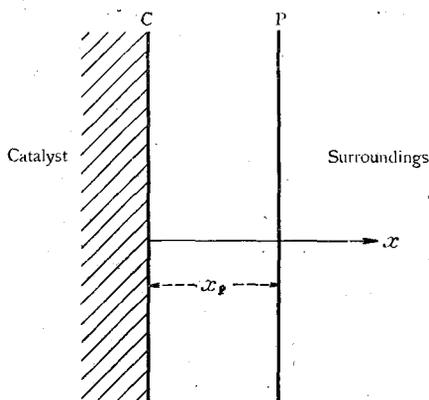


Fig. 1.

Model of Boundary

vanishing at infinity; positive charge of $H_2^+(a)$ and $H^+(a)$ is distributed homogeneously on a plane P parallel to C, x_p distant from the latter as illustrated in Fig.1; dielectric constant D is constantly D_p between C and P inclusive of just outside P and D_∞ in the bulk of surroundings, varying in general continuously and one-dimensionally across the interspace; no charge exists between C and P but on them, whereas density ρ of true charge outside P (on the side of surroundings)

is a definite function of electrostatic potential E satisfying the condition,

$$\rho \geq 0 \text{ according as } E \geq 0, \quad (2.1)$$

such as for instance,

$$\rho = (NF/N_A)(\exp(-FE/RT) - \exp(FE/RT)) \quad (2.2)$$

of a uni-uni-valent electrolyte of concentration N in the bulk, where N_A is Avogadro's number.

The function $\rho = \rho(E)$ particular to the concentration and the sort of electrolytes in the surroundings will be called the *space charge function* in what follows.

After deduced some basic conclusions in the subsequent two sections from the above specifications, we proceed to discuss the effect mentioned above in later ones.

*) The dependence of $\epsilon(\delta_i)_0$ on the population of intermediates will be allowed for in later Part of this series.

§ 3 Charge Density Referred to Adsorption Isotherm.

Here will be formulated the abundance of adsorbed intermediates and the charge density on P determined by the latter and thereupon deduced their dependence on E_P at P.

The abundance of any intermediate δ_i , standing for $H^+(a)$, $H_2^+(a)$ and $H(a)$ according as $i=1, 2$ and 3 is proportional, in compliance with (A), § 2, to the probability $\theta(\delta_i)$ that σ is occupied by δ_i , which is generally expressed as^{(13)*}

$$\theta(\delta_i) = (q_\sigma(\delta_i)/p(\delta_i)) \theta(0), \quad (3.1)$$

where $\theta(0)$ is the probability of σ being unoccupied, $q_\sigma(\delta_i)$ the BOLTZMANN factor,

$$q_\sigma(\delta_i) = \exp(-\varepsilon(\delta_i)/RT) \quad (3.1. q)$$

of energy $\varepsilon(\delta_i)$ identified with the reversible work^{**} required to build up δ_i in a specified, unoccupied σ bringing its constituent particles from their respective reference states, and,

$$p(\delta_i) = \exp(-\mu(\delta_i)/RT) \quad (3.1. p)$$

that of chemical potential $\mu(\delta_i)$ or the reversible work required to add a piece of δ_i , reckoned per mol, formed from its constituent particles respectively in the same reference state, to the assembly without such specification however as that for $\varepsilon(\delta_i)$. The $\mu(\delta_i)$ may be expressed for individual δ_i as,

$$\mu(H^+, a) = \mu(H^+, b), \quad (3.2. H^+)$$

$$\mu(H_2^+, a) = 2\mu(H^+, b) + \mu(\varepsilon), \quad (3.2. H_2^+)$$

$$\mu(H, a) = \mu(H^+, b) + \mu(\varepsilon), \quad (3.2. H)$$

in accordance with equilibrium relation (1.2),^{***} whereas $\varepsilon(\delta_i)$ by (A), § 2 as,

$$\begin{aligned} \varepsilon(H^+) &= \varepsilon(H^+)_0 + FE_P, & \varepsilon(H_2^+) &= \varepsilon(H_2^+)_0 + FE_P, \\ \varepsilon(H) &= \varepsilon(H)_0, \end{aligned} \quad (3.3)$$

*) Cf. Eq. (5.1) of Ref. 13. The notations $\theta_{\sigma(\delta_i)}$ and $\theta_{\sigma(0)}$ in the original paper have been replaced by simpler ones $\theta(\delta_i)$ and $\theta(0)$, since the physically identical site of only one kind referred to throughout the present paper needed hardly any detailed notation.

***) The work required to carry out the specified process keeping the whole assembly involved in statistical equilibrium at its every step throughout. Cf. § 7 of Ref. 13.

***) Cf. § 6 of Ref. 13.

where FE_p is the electrostatic part and $\varepsilon(\delta)_0$ the rest as specified in (A) and (B), § 2.

We have from (3.1),

$$\theta(\delta_i) = \exp\left(-\frac{w(\delta_i)}{RT}\right) \cdot \theta(0), \quad (3.4. \theta)$$

where,

$$w(\delta_i) = \varepsilon(\delta_i) - \mu(\delta_i) \quad (3.4. \varepsilon)$$

is, according to the definition of the quantities involved, the reversible work required to fill up a specified, unoccupied σ with δ_i .

Noting the relation,

$$\theta(0) + \theta(H^+) + \theta(H_2^+) + \theta(H) = \sum_{i=0}^{i=3} \theta(\delta_i) = 1, \quad (3.5)$$

stating in accordance with (A), § 2 that σ is either empty or occupied by one of $H^+(a)$, $H_2^+(a)$ and $H(a)$ exclusively, we have from (3.4. θ),

$$\theta(\delta_i) = \exp\left(-\frac{w(\delta_i)}{RT}\right) / \sum_i \exp\left(-\frac{w(\delta_i)}{RT}\right), \quad (3.6)$$

$i=0, 1, 2, 3,$

where $i=0$ refers to none occupying σ , appropriate $w(\delta_i)$ being zero according to the definition.

Charge density s on P-plane is now expressed on the basis of (A) and (B), § 2 as,

$$s = \frac{GF}{N_A} \left(\theta(H^+) + \theta(H_2^+) \right) \quad (3.7)$$

where G is the number of σ per unit area, F Faraday and hence F/N_A the elementary charge.

By varying E_p alone, $\varepsilon(\delta_i)$ of charged δ_i varies according to (3.3), while $\mu(\delta_i)$ remains the same and hence $w(\delta_i)$ of (3.4. ε) as,

$$\frac{\partial w(\delta_i)}{\partial E_p} = c_i F, \quad c_1 = c_2 = 1, \quad c_0 = c_3 = 0. \quad (3.8)$$

We have now from (3.7), (3.6), and (3.8),

$$\left(\frac{\partial s}{\partial E_p} \right)_{Ads.} = -\frac{GF^2}{N_A RT} \left(\theta(H^+) + \theta(H_2^+) \right) \left(\theta(H) + \theta(0) \right), \quad (3.9)$$

suffix *Ads.* denoting appropriate to adsorption isotherm due to (1.2).

Probabilities $\theta(\delta_i)$'s and hence $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ are according to (3.9) essentially positive or s decreases with increasing E_P with reference to the adsorption isotherm, i. e.

$$\left(\frac{\partial s}{\partial E_P}\right)_{Ads.} < 0. \quad (3.10)$$

§ 4 Charge Density Referred to Poisson Equation.

According to (B), § 2 the density of true charge ρ and electric displacement ϑ should satisfy the one-dimensional Poisson equation written in the form,

$$\frac{d\vartheta}{dx} = \rho, \quad (4.1.0)$$

This equation may be integrated as,

$$\vartheta_a - \vartheta_i = \lim_{t \rightarrow +0} \int_{x_P-t}^{x_P+t} \rho dx = s, \quad (4.1.P)$$

$$\frac{1}{2} \vartheta^2 = \int_{\infty}^x \rho \vartheta dx, \quad x > x_P, \quad (4.1.a)$$

remembering that $E=0$ at $x=\infty$ according to (B), § 2 and hence $\frac{\partial E}{\partial x}$ or ϑ vanishes there according to the relation,

$$\vartheta = -\frac{D}{4\pi} \frac{\partial E}{\partial x}, \quad (4.2)$$

where suffix a or i denotes just outside or inside P respectively:

We have now from (4.1) and (4.2),

$$\frac{E_P - E_C}{x_P} - \left(\frac{\partial E}{\partial x}\right)_a = \frac{4\pi s}{D_P}, \quad (4.3.i)$$

$$\frac{\partial E}{\partial x} = \pm \frac{1}{D} \sqrt{-8\pi \int_0^E \rho D dE}, \quad (4.3.a)$$

$$\left(\frac{\partial E}{\partial x}\right)_a = \pm \frac{1}{D_P} \sqrt{-8\pi \int_0^{E_P} \rho D dE}, \quad (4.3.P)$$

where suffix P or C denotes being relevant respectively to plane P or C; plus or minus sign of the square root should be appropriate respectively to negative or positive E or E_P , since otherwise E , different

from zero at $x > x_p$, leads to $+\infty$ or $-\infty$ at $x = \infty$ in contradiction to (B), § 2.

We see on the other hand that the quantity in the square root of (4.3. a) or (4.3. P) is essentially positive according to (2.1) and increases or decreases with E or E_p according as the latter is positive or negative, vanishing when E or $E_p = 0$. It follows from this conclusion and the above relevance of sign of the square root that $\left(\frac{\partial E}{\partial x}\right)_a$ decreases with increasing E_p irrespective of its sign, i. e.

$$\frac{\partial}{\partial E_p} \left(\frac{\partial E}{\partial x} \right)_a < 0. \quad (4.4)$$

We have now from (4.3. i) and (4.4),

$$\left(\frac{\partial s}{\partial E_p} \right)_{Pois.} = \frac{D_p}{4\pi x_p} - \frac{D_p}{4\pi} \frac{\partial}{\partial E_p} \left(\frac{\partial E}{\partial x} \right)_a \quad (4.5. e)$$

and
$$\left(\frac{\partial s}{\partial E_p} \right)_{Pois.} > \frac{D_p}{4\pi x_p} > 0. \quad (4.5. u)$$

As ρ tends to zero, so does $\frac{\partial E}{\partial x}$ inclusive of $\left(\frac{\partial E}{\partial x}\right)_a$ as seen from (4.3)* i. e.

$$\lim_{\rho \rightarrow 0} \frac{\partial E}{\partial x} = 0. \quad (4.6)$$

It follows hence from (4.5. e),

$$\lim_{\rho \rightarrow 0} \left(\frac{\partial s}{\partial E_p} \right)_{Pois.} = D_p / 4\pi x_p. \quad (4.7)$$

In the subsequent sections will be discussed the effect on $w(\delta_i)$'s of different factors mentioned before.

§ 5 Effect of Space Charge Function.

As shown in the foregoing two sections charge density s decreases or increases with increasing E_p according as referred to the adsorption isotherm or to the Poisson equation respectively. Both the relations should of course be satisfied simultaneously at equilibrium (1.2), as

*) The E_p is not necessarily infinitesimal, if $\frac{dE}{dx}$ were so, since it is $-\frac{dE}{dx}$ integrated from $x = x_p$ to $x = \infty$ that gives E_p , according to (B), § 2.

illustrated in Fig. 2 by the intersection of full lines "Adsorption" or "Poisson" relevant respectively to the above two relations.

We will consider below the effect of increasing the absolute value of the space charge function at every E in accordance with (2.1) as for instance effected by increasing N in (2.2), keeping λ , μ (H^+b), η and $\mu(H_2)$ constant.

The constancy of the latter quantities assures now that of $\mu(\varepsilon)$ by (1.3) and henceforth of $\mu(\delta_i)$'s according to (3.2) on one hand and that of E_C on the other hand by the relation,

$$-F(\lambda + E_C) = \mu(\varepsilon), \quad (5.1)$$

which follows from the definition of the quantities involved.

The "Adsorption" remains unshifted by varying the space charge function, $w(\delta_i)$'s and hence $\theta(\delta_i)$'s being now respectively functions solely of E_P by (3.3), (3.4. ε) and (3.6), whereas the "Poisson" shifts upwards for positive E_P due to decrease of $\left(\frac{\partial E}{\partial x}\right)_a$ in (4.3. i), in accordance with (4.3. P) and with the associated relevance of sign.

The dotted lines in Fig.2 shows the new "Poisson" shifted upwards from the original one by Δs i. e.,

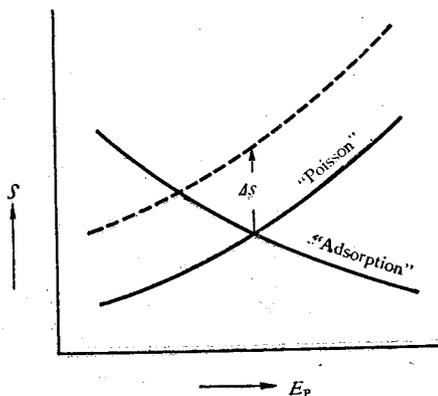


Fig. 2.

Effect of Space Charge Function

$$\Delta s = -\frac{D_P}{4\pi} \Delta \left(\frac{\partial E}{\partial x} \right)_a,$$

according to (4.3. *i*), where $-\Delta \left(\frac{\partial E}{\partial x} \right)_a$ is the decrease of $\left(\frac{\partial E}{\partial x} \right)_a$. The intersection shifts now leftwards or E_P at the equilibrium of (1.2) decreases.

It may similarly be shown that the intersection shifts rightwards or not altogether according as E_P is negative or zero respectively.

It follows that E_P tends to zero, either it be positive or negative by increasing the absolute value of the space charge function, so that at infinity E_P as well as its increment ΔE_P is kept at zero irrespective of any variation of other factors, i.e.,

$$\lim_{\rho \rightarrow \infty} E_P = \lim_{\rho \rightarrow \infty} \Delta E_P = 0. \quad (5.2)$$

The solution of (4.3. *a*) outside P is then $E=0$ in coincidence with the simple model of HELMHOLTZ's double layer.

It may readily be shown that the homogeneous increase of dielectric constant $D=D(x)$ outside P brings about the similar result as that of the space charge function.

In subsequent sections will be deduced the effect of varying one of λ , $\mu(H^+b)$, $\mu(H_2)$ and η in succession with others kept constant assuming that the distribution $D=D(x)$ of dielectric constant and the space charge function $\rho=\rho(E)$ are respectively definite; it follows from the assumption that $\left(\frac{dE}{dx} \right)_a$ is the function solely of E_P , since E_P , besides the condition $E=0$ at $x=\infty$, fixes the solution, $E=E(x)$ of the ordinary differential equation of the second order obtained from (4.1.0) by substituting ϑ from (4.2).

§ 6 Effect of Work Function.

We discuss here the effect of increasing λ on $w(\delta_i)$'s at constant $\mu(H^+b)$, $\mu(H_2)$ and η . This would correspond practically to the replacing of the catalyst alone with such one as having greater λ but the same $\varepsilon(\delta_i)$'s.

The constancy of $\mu(H^+b)$, $\mu(H_2)$ and η assures again that of $\mu(\varepsilon)$ according to (1.3) so that the increase $\Delta\lambda$ of λ is associated with the decrease of E_C of the same amount according to (5.1).

Whereas the "Adsorption" remains unshifted as deduced similarly

as in the foregoing section from the constancy of $\mu(H^+b)$ and of $u(\epsilon)$, the "Poisson" shifts upwards due to the decrease of E_C in accordance with (4.3. i) by the amount Δs i. e.,

$$\Delta s = \frac{D_P}{4\pi x_P} \Delta\lambda, \quad (6.1)$$

$\left(\frac{dE}{dx}\right)_a$ there being now the function solely of E_P according to §5.

The result is the decrease $-\Delta E_P$ of E_P at the intersection, i. e.

$$-\Delta E_P = \frac{\Delta s}{\left(\frac{\partial s}{\partial E_P}\right)_{Pots.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.}}$$

as illustrated in Fig 3.

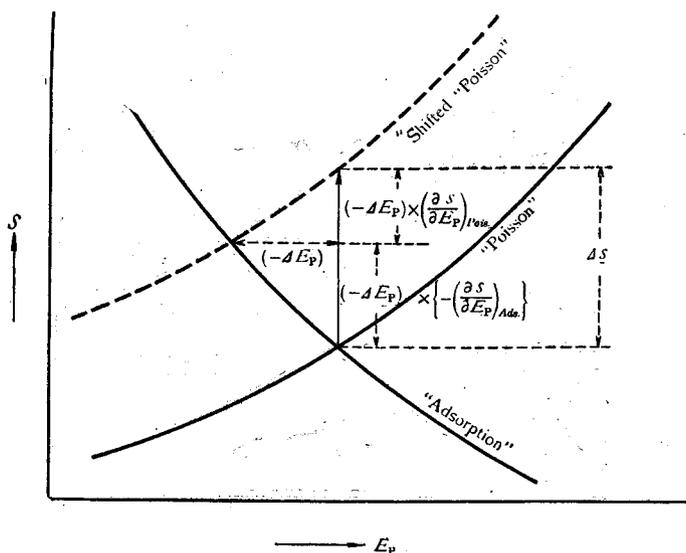


Fig. 3.

Effect of Work Function

We have hence according to (6.1),

$$\Delta E_P = -\alpha_\lambda \Delta\lambda, \quad (6.2. E)$$

where

$$\alpha_\lambda = D_P / \left\{ 4\pi x_P \left(\left(\frac{\partial s}{\partial E_P}\right)_{Pots.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.} \right) \right\}. \quad (6.2. \lambda)$$

is, according to (3.9) and (4.5), a positive proper fraction, i. e.

$$0 < \bar{\alpha}_\lambda < 1. \quad (6.2. \bar{\alpha})$$

The $\bar{\alpha}_\lambda$ tends to $\left(1 - \frac{4\pi x_p}{D_p} \left(\frac{\partial s}{\partial E_p}\right)_{Ads.}\right)^{-1}$ as ρ approaches zero according to (6.2. λ) and (4.7), and moreover to unity as $\left(\frac{\partial s}{\partial E_p}\right)_{Ads.}$ in addition approaches zero, perhaps, along with the factor $\theta(H^+) + \theta(H_2^+)$ of (3.9) tending to zero or unity*.)

In the other extremity of infinite ρ , $\bar{\alpha}_\lambda$ should vanish according to (5.2) and (6.2. E).

The increase $\Delta\lambda$ of λ thus causes that of $\varepsilon(H^+)$ and $\varepsilon(H_2^+)$ by $-F\alpha_\lambda\Delta\lambda$ leaving $\varepsilon(H)$ unaffected. All $\mu(\delta_i)$'s being kept unvaried according to (3.2) because of the constancy of $\mu(H^+b)$ and $\mu(\varepsilon)$, the increase $\Delta w(\delta_i)$'s of $w(\delta_i)$'s of (3.4. ε) are,

$$\Delta w(H^+) = \Delta w(H_2^+) = -F\alpha_\lambda\Delta\lambda, \quad \Delta w(H) = 0. \quad (6.3)$$

The $w(\delta_i)$'s of charged δ_i 's only are thus lowered, while $w(H)$ remains unchanged. The $\Delta w(H^+) = \Delta w(H_2^+)$ approaches $-F\Delta\lambda / \left(1 - \frac{4\pi x_p}{D_p} \left(\frac{\partial s}{\partial E_p}\right)_{Ads.}\right)$ or vanishes as ρ tends to zero or infinity respectively.

§ 7 Effect of Chemical Potential of Hydrogen Ion.

Here is discussed the effect of increasing the chemical potential $\mu(H^+b)$ of hydrogen ion,

$$\mu(H^+b) \equiv Fh \quad (7.1. h)$$

by $\Delta\mu(H^+b) = F\Delta h$ at constant λ , $\mu(H_2)$ and η .

The $\mu(\varepsilon)$ and E_c increases then according to (1.3) and (5.1) respectively as,

$$\Delta\mu(\varepsilon) = -F\Delta h, \quad \Delta E_c = \Delta h, \quad (7.1. \varepsilon), (7.1. E)$$

whereas $\mu(\delta_i)$'s according to (3.2) and (7.1. ε) as,

$$\Delta\mu(H^+a) = \Delta\mu(H_2^+, a) = F\Delta h, \quad \Delta\mu(H, a) = 0. \quad (7.2)$$

The "Poisson" shifts in consequence downwards according to (7.

*) As $\theta(H^+) + \theta(H_2^+)$ tends to unity, the other factor $\theta(0) + \theta(H)$ in (3.9), and in consequence $\left(\frac{\partial s}{\partial E_p}\right)_{Ads.}$ approaches zero according to (3.5).

1. E) and (4.3. i), $\left(\frac{\partial E}{\partial x}\right)_a$ being now the function solely of E_P , whereas the "Adsorption" rightwards by Δh as shown in Fig. 4, inasmuch as the effect of increasing $\mu(\delta_i)$ as given by (7.2) is equivalent, with regard to $w(\delta_i)$ of (3.4. ϵ), which determines "Adsorption" uniquely, to that of decreasing E_P by Δh or of replacing every ordinate at E_P with that at $E_P - \Delta h$.

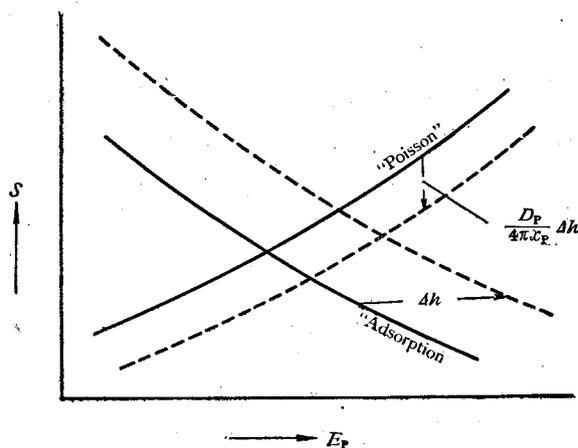


Fig. 4.
Effect of Hydrogen Ion

The downward shift $(D_P/4\pi x_P)\Delta h$ of the "Poisson" causes now the rightward shift,

$$\Delta E_P(P) = D_P \Delta h / \left\{ 4\pi x_P \left(\left(\frac{\partial s}{\partial E_P} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.} \right) \right\} \quad (7.3. P)$$

of the intersection similarly as in Fig. 3 and the rightward one Δh of "Adsorption", corresponding to the upward one $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.} \Delta h$, gives rise to the rightward shift of the intersection,

$$\Delta E_P(A) = - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.} \Delta h / \left(\left(\frac{\partial s}{\partial E_P} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.} \right). \quad (7.3. A)$$

The total rightward shift ΔE_P of the intersection is the sum of $\Delta E_P(P)$ and $\Delta E_P(A)$, i. e.

$$\Delta E_P = \Delta E_P(P) + \Delta E_P(A) = \alpha_n \Delta h, \quad (7.4. E)$$

where,

$$\alpha_h = \left\{ D_p / 4\pi x_p - \left(\frac{\partial s}{\partial E_p} \right)_{Ads.} \right\} / \left\{ \left(\frac{\partial s}{\partial E_p} \right)_{Pots.} - \left(\frac{\partial s}{\partial E_p} \right)_{Ads.} \right\}. \quad (7.4. a)$$

The α_h is a positive proper fraction, i. e.

$$0 < \alpha_h < 1, \quad (7.5)$$

as follows from (4.5) and (3.10), tending to unity or zero according to (4.7), (5.2) and (7.4. E) as ρ approaches respectively zero or infinity.

The total increase $\Delta w(\delta_i)$ of $w(\delta_i)$ is now synthesized from ΔE_p of (7.4) and $\Delta\mu(\delta_i)$ of (7.2) according to (3.4. ϵ) and (3.3) as,

$$\Delta w(H^+) = \Delta w(H_2^+) = -F(1-\alpha_h)\Delta h, \quad \Delta w(H) = 0. \quad (7.6)$$

The decrease of $w(H^+)$ and $w(H_2^+)$ is thus the same negative fraction of $F\Delta h$, tending to zero or to the full amount $F\Delta h$ according as ρ approaches zero or infinity, on the contrary to the case of the work function, when the effect tends to full or nil respectively reversely with respect to the extremity of ρ ; the $w(H)$ remains however unaffected in both the cases.

§ 8 Effect of Hydrogen Overvoltage and of Chemical Potential of Hydrogen.

The hydrogen overvoltage η and the chemical potential $\mu(H_2)$ of hydrogen appear in (1.3) only but nowhere else throughout the set of equations determining $w(\delta_i)$'s. Introducing l by the definition,

$$Fl \equiv F\eta - \frac{1}{2}\mu(H_2) \quad (8.1. a)$$

and hence writing (1.3) in the form,

$$Fl + \mu(H^+b) + \mu(\epsilon) = 0, \quad (8.1. b)$$

the effect of the individual variation of η or of $\mu(H_2)$ may be adequately taken into account through that of l .

The increase Δl now of l at constant λ and h accompanies that $\Delta\mu(\epsilon)$ or ΔE_c of $\mu(\epsilon)$ or E_c respectively according to (8.1. b), (7.1. h) and (5.1) as,

$$\Delta\mu(\epsilon) = -F\Delta l, \quad \Delta E_c = \Delta l, \quad (8.2. \epsilon), (8.2. C)$$

which causes in turn that $\Delta\mu(\delta_i)$ of $\mu(\delta_i)$ according to (3.2) as,

$$\Delta\mu(H^+) = 0, \quad \Delta\mu(H_2^+) = \Delta\mu(H) = -F\Delta l. \quad (8.3)$$

The corresponding increase of s at constant E_P or the upward shift of "Adsorption" is, as worked out from (3.7), (3.6), (3.4. ϵ) and (8.3),

$$\Delta s = \frac{GF^2}{N_A RT} (\theta(H^+)\theta(H) - \theta(H_2^+)\theta(0)) \Delta l, \quad (8.4)$$

which results in, similarly as in the foregoing sections, the rightward shift $\Delta E_P(A)$ of the intersection,

$$\Delta E_P(A) = \frac{GF^2}{N_A RT} \frac{\theta(H^+)\theta(H) - \theta(H_2^+)\theta(0)}{\left(\frac{\partial s}{\partial E_P}\right)_{Pois.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.}} \cdot \Delta l. \quad (8.5. A)$$

The E_C increase of (8.2. C) causes on the other hand the downward shift $-\frac{D_P}{4\pi x_P} \cdot \Delta l$ of "Poisson" as deduced similarly as in § 7 and the appropriate rightward one $\Delta E_P(P)$ of the intersection i. e.,

$$\Delta E_P(P) = D_P \Delta l / \left\{ 4\pi x_P \left(\left(\frac{\partial s}{\partial E_P}\right)_{Pois.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.} \right) \right\}. \quad (8.5. P)$$

The total shift ΔE_P rightwards of E_P is now,

$$\Delta E_P = \Delta E_P(P) + \Delta E_P(A) = \alpha_i \Delta l, \quad (8.6. E)$$

where,

$$\alpha_i = \frac{D_P / 4\pi x_P + (\theta(H^+)\theta(H) - \theta(H_2^+)\theta(0)) GF^2 / N_A RT}{\left(\frac{\partial s}{\partial E_P}\right)_{Pois.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.}} \quad (8.6. \alpha)$$

lies between -1 and 1 i. e.,

$$-1 < \alpha_i < 1, \quad (8.7)$$

inasmuch as both $\left(\frac{\partial s}{\partial E_P}\right)_{Pois.}$ and $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ in the denominator of (8.6. α) are positive and respectively greater in absolute value than the first and the second term in the numerator according to (3.9) and (4.5). The α_i approaches zero, as ρ tends to infinity when ΔE_P vanishes according to (8.6. E) and (5.2). As ρ tends to zero, α_i approaches unity or possibly negative proper fraction according as both $\theta(H_2^+)$ and $\theta(0)$ simultaneously approximate zero as seen from (3.9) or $\theta(H_2^+)\theta(0)$ becomes sufficiently large.

Synthesizing ΔE_P and $\Delta\mu(\delta_i)$ according to (3.4. ϵ), (3.3) (8.6. E) and (8.3) we have finally,

$$\Delta w(H^+) = F\alpha_i \Delta l, \quad \Delta w(H_2^+) = F(1 + \alpha_i) \Delta l, \quad \Delta w(H) = F \Delta l, \quad (8.8)$$

of which it may be noted,

$$\Delta w(H_2^+) = \Delta w(H^+) + \Delta w(H). \quad (8.9)$$

§9 Analytic Derivation of Effects.

So far we have graphically derived the dependence of E_P or of $w(\delta_i)$ on ρ , λ , h and l . We might give below an analytic derivation colligating the conclusion arrived at in foregoing sections for the sake of better insight into the effects inclusive of the rather involved ones of non-dissociative base and acid in subsequent sections.

We have from (8.1. *b*) and (7.1. *h*),

$$\mu(\varepsilon) = -F(l+h) \quad (9.1. \varepsilon)$$

and hence from (5.1),

$$E_C = l+h-\lambda, \quad (9.1. E)$$

which gives, substituted into (4.3. *i*),

$$\frac{E_P + \lambda - h - l}{x_P} - \left(\frac{dE}{dx} \right)_a = \frac{4\pi s}{D_P}. \quad (9.2)$$

Expressing $\mu(\varepsilon)$ and $\mu(H^+b)$ in (3.2) by (9.1. ε) and (7.1. *h*) respectively on the other hand, we have,

$$\mu(H^+a) = Fh, \quad \mu(H_2^+a) = F(h-l), \quad \mu(H,a) = -Fl, \quad (9.3)$$

or substituting the latter into (3.4. ε), with due regards to (3.3),

$$w(H^+) = \varepsilon(H^+)_0 + FE_P - Fh, \quad (9.4. H^+)$$

$$w(H_2^+) = \varepsilon(H_2^+)_0 + FE_P - Fh + Fl, \quad (9.4. H_2^+)$$

$$w(H) = \varepsilon(H)_0 + Fl. \quad (9.4. H)$$

The s in (9.2) is now, at constant λ , h and l , the function only of E_P according to (3.6), (3.7) and (9.4), whereas $\left(\frac{dE}{dx} \right)_a$ varies with E_P as well as with ρ . We have now by differentiation of (9.2) with respect to ρ ,

$$\frac{1}{x_P} \frac{dE_P}{d\rho} - \frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x} \right)_a \frac{dE_P}{d\rho} - \frac{\partial}{\partial \rho} \left(\frac{\partial E_P}{\partial x} \right)_a = \frac{4\pi}{D_P} \frac{\partial s}{\partial E_P} \frac{dE_P}{d\rho}, \quad (9.5. \alpha)$$

or

$$\frac{dE_P}{d\rho} = \frac{D_P}{4\pi} \frac{\partial}{\partial \rho} \left(\frac{\partial E_P}{\partial x} \right)_a, \quad (9.5.b)$$

$$\left(\frac{\partial s}{\partial E_P} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.}$$

where $\left(\frac{\partial s}{\partial E_P} \right)_{Pois.}$ or $\left(\frac{\partial s}{\partial E_P} \right)_{Ads.}$ writes respectively $\frac{D_P}{4\pi x_P} - \frac{D_P}{4\pi} \frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x} \right)_a$ or $\frac{\partial s}{\partial E_P}$ in (9.5.a) in accordance with in the graphical presentation, the differential of ρ meaning that due to the increment of the parameter, for instance N in (2.2), which causes homogeneous increase of ρ at every E .

The denominator of (9.5.b) is thus positive, whereas the numerator is of opposite sign to E_P , since the same is the case with $\left(\frac{\partial E_P}{\partial x} \right)_a$ and the latter increases its absolute value with ρ according to § 4. The $\frac{\partial E_P}{\partial \rho}$ is in consequence also of opposite sign to E_P or E_P tends to zero as ρ increases, if it be either positive or negative as shown graphically in § 5.

The effect of varying dielectric constant outside P may be similarly derived.

Now is derived the dependence of E_P on λ at constant h , and l with definite $\rho = \rho(E)$ and $D = D(x)$ by differentiating (9.2) with respect to λ , remembering $\left(\frac{\partial E}{\partial x} \right)_a$ as well as s is the function of E_P alone, λ being not explicitly included in the expression (9.4) of $w(\delta_i)$'s, and hence not in s , as,

$$\frac{dE_P}{d\lambda} = -D_P / \left\{ 4\pi x \left(\left(\frac{\partial s}{\partial E_P} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.} \right) \right\}.$$

The above equation is in full accordance with (6.2) arrived at graphically.

The h being explicitly included in (9.4), s is the function of E_P as well as of h at constant λ and l with definite ρ and D . We have hence for the dependence of E_P on h from (9.2),

$$\frac{1}{x_P} \left(\frac{dE_P}{dh} - 1 \right) - \frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x} \right)_a \frac{dE_P}{dh} = \frac{4\pi}{D_P} \left(\frac{\partial s}{\partial E_P} \frac{dE_P}{dh} + \frac{\partial s}{\partial h} \right),$$

or

$$\frac{dE_P}{dh} = \frac{D_P/4\pi x_P + \frac{\partial s}{\partial h}}{\left(\frac{\partial s}{\partial E_P}\right)_{Pois.} - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.}} \quad (9.6)$$

The above expression of $\frac{dE_P}{dh}$ is in accordance with (7.4) inasmuch as,

$$\frac{\partial s}{\partial h} = - \left(\frac{\partial s}{\partial E_P}\right)_{Ads.},$$

as seen from (9.4) which includes E_P and $-h$ symmetrically. The latter transformation corresponds to the rightward shift of "Adsorption" in Fig. 4.

Similarly is derived analytically the dependence of E_P on l .

The variation of $w(\delta_i)$'s with one of factors ρ etc. is readily obtained from that of E_P derived above according to (9.4).

§ 10 Effect of Non-dissociative Base or Acid*

We have so far allowed for the effect of acid and base only in terms of the chemical potential of hydrogen ion expressed by h as well as, perhaps, of the space charge function.

The conclusion thus arrived at is accessible to experiments provided that $\mu(H^+b)$ is practically measurable, whereas not in the case of such medium of the surroundings as gas or aprotic liquid which is incapable of giving rise to the electrolytic dissociation of measurable extent of electrolytes inclusive of Brönsted's base or acid of whatever strength.

In the following several sections will be studied the effect on $w(\delta_i)$'s of the base or the acid at such a non-dissociative condition. It would be reasonable to assume, in so far as we admit the existence of proton and its compound with neutral hydrogen atom, i. e. hydrogen-molecule-ion at the boundary surface in equilibrium (1.2), that base or acid be capable, if not dissociative in the bulk of the surroundings, of fulfilling its part of accepting or donating proton respectively there. It then follows that their effect whatever must be closely connected

*) The result of the present discussion is, although indispensable for the development in later Part of this series not directly necessary for the application in Chapter 2 of this Part. It has nevertheless been given here because of the expedience of presentation in extension of the foregoing part of the theory.

with the occupation of the boundary surface. Modifying the model of our assembly specified in § 2 in this respect, we might study first the effect of the base in such a condition as detailed in the next section and, after having investigated in its connection, the effect of such molecules inclusive of the base of interest as depressing $\varepsilon(\delta_i)_0$ of charged δ_i by their nucleophilic nature in the subsequent sections, go over to that of the acid in the similar condition.

§ 11 Non-dissociative Base.

Here will be studied the effect of varying the chemical potential $\mu(B)$,

$$\mu(B) \equiv -Fh \tag{11.1}$$

of base B of $w(\delta_i)$'s, detailing the model of our assembly as below: the B will be attached to charged δ_i^* concurrently with some nucleophilic molecule R in the surroundings, for instance water or acetone, both to depress the appropriate $\varepsilon(\delta_i)_0$: the probability of B in the absence of charged δ_i in σ appearing in such a position as attached to charged δ_i in σ is negligible whereas that of R not necessarily: B or R in that position either with or without charged δ_i in it, is in equilibrium with the respective molecule in the bulk of the surroundings, the chemical potential $\mu(R)$ of R there being kept constant throughout the variation of $\mu(B)$.

The B and R will be called together the associate, when attached to the charged δ_i in what follows. The charge of $H^+(a)$ and $H_2^+(a)$ will rest on P, as specified in § 2, (B), irrespective of the presence or absence of the associate.

The total charge density s' on P is given in this case by,

$$s' = s + s_B, \tag{11.2. s'}$$

where s_B or s is that due to the charged δ_i with or without the associate of B respectively, expressed as,

$$s = \frac{GF}{N_A} (\theta(H^+) + \theta(H_2^+)), \tag{11.2. s}$$

*) Cf. the foot-note on page 54.

$$s_B = \frac{GF}{N_A} (\theta(H^+B) + \theta(H_2^+B)) \quad (11.2. s_B)$$

where,

$$\theta(H^+) = \theta(H^+0) + \theta(H^+R), \quad (11.2. H^+)$$

$$\theta(H_2^+) = \theta(H_2^+0) + \theta(H_2^+R), \quad (11.2. H_2^+)$$

$\theta(H^+0)$ is the probability that a σ is occupied by H^+ without any associate, $\theta(H^+R)$ or $\theta(H^+B)$ that with the associate of R or B respectively and $\theta(H_2^+0)$, $\theta(H_2^+R)$ or $\theta(H_2^+B)$ the corresponding ones of H_2^+ .

The $\theta(H^+0)$ etc. may be expressed in extension of (3.6)* as,

$$\theta(\delta_i, D_j) = \exp(-w(\delta_i, D_j)/RT) / \sum_{i,j} \exp(-w(\delta_i, D_j)/RT), \quad (11.3)$$

where δ_i denotes the absence of occupant or the presence of one of $H^+(a)$, $H_2^+(a)$ and $H(a)$ according respectively as $i=0, 1, 2, 3$ as in § 3 and D_j similarly the absence of the associate or the presence of R or B according respectively as $j=0, 1, 2$, the complex of δ_i and D_j as a whole being taken here the occupant of σ .

The $w(\delta_i, D_j)$ in (11.3) is expressed according to the premised equilibrium of D_j as,

$$w(\delta_i, D_j) = \varepsilon(\delta_i, D_j) - \mu(\delta_i) - \mu(D_j), \quad (11.4. w)$$

where,

$$\varepsilon(\delta_i, D_j) = \varepsilon(\delta_i, D_j)_0 + c_i F E_P, \quad (11.4. \varepsilon)$$

$$\mu(\delta_i) = 0, \quad F(\lambda + E_C - l), \quad F(\lambda + E_C - 2l) \text{ or } -Fl \quad (11.4. \delta)$$

for $i=0, 1, 2$ or 3 respectively,

$$\mu(D_j) = 0, \quad \mu(R) \text{ or } -Fh \quad (11.4. D)$$

for $j=0, 1$ or 2 respectively and c_i the number of elementary charge on the intermediate δ_i i. e. zero for $i=0$ and 3 or 1 for $i=1$ and 2 , as seen from (3.2), (5.1), (8.1. b) and (11.1). Eqs. (11.2), (11.3) and (11.4) show that s' is the function of E_D ,

$$E_D \equiv E_P - E_C \quad (11.5)$$

and of h at constant λ and l .

*) The equation of the form of (3.6) is valid for any number of kinds of occupant molecules in σ . Cf. § 19 of Ref. 13.

Eq. (4.3. *i*) assumes the form, because of the vanishing of $\left(\frac{\partial E}{\partial x}\right)_a$ due to (4.6) and the premised absence of ion in the surroundings,

$$E_D = \frac{4\pi x_P}{D_P} (s') \quad (11.6)$$

s in (4.3. *i*) being replaced here by s' of (11.2. s'), the total charge on P. The above equation gives by differentiation,

$$\frac{dE_D}{dh} = \frac{4\pi x_P}{D_P} \left(\frac{\partial s'}{\partial h} + \frac{\partial s'}{\partial E_D} \frac{dE_D}{dh} \right)$$

or

$$\frac{dE_D}{dh} = \frac{\partial s'}{\partial h} / \left(\frac{D_P}{4\pi x_P} - \frac{\partial s'}{\partial E_D} \right). \quad (11.7)$$

The $\frac{\partial s'}{\partial h}$ in the expression may be developed according to (11.2), (11.3) and (11.4) as,

$$\begin{aligned} \frac{\partial s'}{\partial h} = -\frac{GF^2}{N_A RT} \left\{ (\theta(0) + \theta(H)) (\theta(H^+ B) + \theta(H_2^+ B)) \right. \\ \left. - (\theta(0, B) + \theta(H, B)) (\theta(H^+) + \theta(H_2^+)) \right\}, \end{aligned}$$

where,

$$\theta(0) = \theta(0, 0) + \theta(0, R) \quad (11.8.0)$$

or

$$\theta(H) = \theta(H, 0) + \theta(H, R) \quad (11.8.H)$$

is, similarly as $\theta(H^+)$ or $\theta(H_2^+)$ of (11.2), the probability that σ is occupied by none of δ_i 's or by $H(a)$ respectively, either with or without the associate except B . Neglecting $\theta(0, B)$ and $\theta(H, B)$, i. e. the probability of appearance of B in the position of the associate without charged δ_i according to the premiss, we have,

$$\frac{\partial s'}{\partial h} = -\frac{GF^2}{N_A RT} (\theta(0) + \theta(H)) (\theta(H^+ B) + \theta(H_2^+ B)). \quad (11.8.h)$$

The $\frac{\partial s'}{\partial E_D}$ in (11.7) is given similarly as,

$$\frac{\partial s'}{\partial E_D} = -\frac{GF^2}{N_A RT} (\theta(0) + \theta(H)) (\theta(H^+ B) + \theta(H_2^+ B) + \theta(H^+) + \theta(H_2^+)). \quad (11.8.E)$$

Eq. (11.8) shows with due regards to (11.2) that both $\frac{\partial s'}{\partial h}$ and $\frac{\partial s'}{\partial E_D}$ are negative and the former is less than the latter in absolute value. It follows now according to (11.7) that $\frac{dE_D}{dh}$ is a negative proper fraction and hence from (11.4) because of the premised constancy of $\mu(R)$,

$$\frac{dw(H^+, D_j)}{dh} = \frac{dw(H_2^+, D_j)}{dh} = -F(1 - \alpha_h), \quad j = 0, 1, \quad (11.9.D)$$

$$\frac{dw(H^+, B)}{dh} = \frac{dw(H_2^+, B)}{dh} = F\alpha_h, \quad (11.9.B)$$

$$\frac{dw(H, D_j)}{dh} = 0, \quad j = 0, 1, \quad (11.9.H)$$

where,

$$\alpha_h = \left(\frac{D_F}{4\pi x_P} + \frac{\partial s'}{\partial h} - \frac{\partial s'}{\partial E_D} \right) / \left(\frac{D_F}{4\pi x_P} - \frac{\partial s'}{\partial E_D} \right), \quad (11.9.E)$$

and

$$0 < \alpha_h < 1.$$

We might develop the above results further in §13, after having coordinated in the next section the $\varepsilon(\delta_i, D_j)$ here introduced with $\varepsilon(\delta_i)_0$ hitherto used.

§ 12 $\varepsilon(\delta_i)_0$ and Associates.

We have so far assumed $\varepsilon(H)_0$ in § 2 dependent on the properties of the catalyst alone but $\varepsilon(\delta_i)_0$ of charged δ_i on those both of the catalyst and the surroundings except the space charge function ρ , the work function λ , the chemical potential $\mu(H^+ \delta)$ of hydrogen ion, that $\mu(H_2)$ of hydrogen and to electrode potential η of the catalyst thus deducing the effect of latters on $w(\delta_i)$'s. The picture of our assembly was now detailed in the foregoing section with special reference to the associate D_j of δ_i discriminating between $\varepsilon(\delta_i, D_j)_0$'s.

We might now investigate the correlation among the former and the latter detailed treatment.

Eq. (3.1) may be written along with its extension in the foregoing section of treating the complex of δ_i and D_j as a whole the occupant of σ , as,

$$\theta(\delta_i, D_j) = \theta(0, 0) \cdot \exp\left(-\frac{w(\delta_i, D_j)}{RT}\right), \quad i = 1, 2, 3, \quad (12.1. \delta)$$

or as,

$$\theta(0, D_j) = \theta(0, 0) \cdot \exp\left(-\frac{w(0, D_j)}{RT}\right), \quad (12.1. \sigma)$$

where,

$$w(\delta_i, D_j) = \varepsilon(\delta_i, D_j) - \mu(\delta_i) - \mu(D_j), \quad (12.1. w\delta)$$

$$w(0, D_j) = \varepsilon(0, D_j) - \mu(D_j). \quad (12.1. w\sigma)$$

Hence we have,

$$\theta(\delta_i, D_j) = \theta(0, D_j) \exp\left(-\frac{\varepsilon(\delta_i, D_j) - \varepsilon(0, D_j) - \mu(\delta_i)}{RT}\right), \quad (12.2. D)$$

or further,

$$\theta(\delta_i) = \theta(0) \exp\left(\frac{\mu(\delta_i)}{RT}\right) \frac{\sum_j \theta(0, D_j) \exp\left(-\frac{\varepsilon(\delta_i, D_j) - \varepsilon(0, D_j)}{RT}\right)}{\sum_j \theta(0, D_j)}, \quad (12.2. \Sigma)$$

where,

$$\theta(\delta_i) = \sum_j \theta(\delta_i, D_j), \quad i = 1, 2, 3, \quad (12.2. \delta_i)$$

$$\text{or} \quad \theta(0) = \sum_j \theta(0, D_j), \quad (12.2. 0)$$

which gives the probability that σ is occupied by any one of the hydrogen intermediates or none of them respectively irrespective of absence or presence of associates.

The latter probabilities should however satisfy the relation in accordance with (3.1. θ),

$$\theta(\delta_i) = \theta(0) \exp\left(-\frac{\varepsilon(\delta_i) - \mu(\delta_i)}{RT}\right), \quad (12.3)$$

valid*) whatever be the associate, where $\varepsilon(\delta_i)$ is the reversible work required to build up δ_i in a specified, empty σ , δ_i itself or its material being brought from the reference state.

*) Cf. Ref. 13, §2 & §5.

The comparison of (12.2. Σ) and (12.3) gives with due regards to (11.4. ϵ),

$$\exp\left(-\frac{\epsilon(\delta_i)_0}{RT}\right) = \frac{\sum_j \theta(0, D_j) \cdot \exp\left(-\frac{\epsilon(\delta_i, D_j)_0 - \epsilon(0, D_j)_0}{RT}\right)}{\sum_j \theta(0, D_j)}, \quad (12.4)$$

where $\epsilon(\delta_i)_0$ is the above mentioned work minus $c_i F E_p$. The $\epsilon(\delta_i, D_j)_0 - \epsilon(0, D_j)_0$ on the right of the above expression is the reversible work required to bring up δ_i from its reference state onto σ not occupied by δ_i but with the associate D_j less the electrostatical part $c_i F E_p$.

The Boltzmann factor of $\epsilon(\delta_i)_0$ is hence the "weighted mean" of Boltzmann factors of $\epsilon(\delta_i, D_j)_0 - \epsilon(0, D_j)_0$ with respect to the probabilities of each D_j assuming the position of the associate without any δ_i occupying the relevant σ . The $\epsilon(\delta_i)_0$ is in consequence depressed by increasing the chemical potential $\mu(D_j)$ of such D_j as providing low $\epsilon(\delta_i, D_j)_0$ and hence large $\exp\left(-\frac{\epsilon(\delta_i, D_j)_0 - \epsilon(0, D_j)_0}{RT}\right)$, inasmuch as its "weight" $\theta(0, D_j)$ increases with $\mu(D_j)$ according to (12.1.0) and (12.1. $w0$).

The present argument is of course applicable to any number of D_j 's present in the surroundings or even to the case when any D_j is composed of several molecules in the surroundings. The use of single constant $\epsilon(\delta_i)_0$ before is in consequence of the general validity with surroundings of respectively constant $\mu(D_j)$'s, provided that the $\epsilon(\delta_i)_0$ is identified with the above "weighted mean".

§ 13 Non-dissociative Base and Hydrogen Ion.

The conclusion arrived at in §11 is now developed on the basis of the foregoing section to compare the result with the effect of the chemical potential of hydrogen ion developed in §7.

We define $\epsilon(H^+)_0$ the mean in the sence of (12.4) with respect to $D_j=0, R$ exclusive of B as,

$$\begin{aligned} \exp\left(-\frac{\epsilon(H^+)_0}{RT}\right) \\ = \frac{\theta(0, 0) \exp\left(-\frac{\epsilon(H^+, 0)_0}{RT}\right) + \theta(0, R) \exp\left(-\frac{\epsilon(H^+, R)_0 - \epsilon(0, R)_0}{RT}\right)}{\theta(0, 0) + \theta(0, R)}, \end{aligned}$$

which gives in accordance with (11.4. w), (11.4. ϵ) and (3.3),

$$\begin{aligned} & \exp\left(-\frac{w(H^+)}{RT}\right) \\ &= \frac{\theta(0,0) \exp\left(-\frac{w(H^+,0)}{RT}\right) + \theta(0,R) \exp\left(-\frac{w(H^+,R) - w(0,R)}{RT}\right)}{\theta(0,0) + \theta(0,R)} \end{aligned} \quad (13.1)$$

noting the vanish of $\mu(0)$, $\epsilon(0,0)$ or $w(0,0)$, i. e. the respective reversible work for none of δ_i or $D_j^{*})$. The $w(H^+)$ here is thus the average of $w(H^+, D_j) - w(0, D_j)^{*)}$ over D_j except B or the reversible work according to the foregoing section required to fill up a particular σ occupied by none of intermediates with or without the associate except B , with proton brought from somewhere in the assembly^{*)}

We have now from (11.9. D) and (13.1),

$$\frac{dw(H^+)}{dh} = -F(1 - \alpha_h). \quad (13.2. H^+)$$

noting that $w(0, R)$ is constant and that $\theta(0,0)$ and $\theta(0, R)$ may vary individually with h but $\theta(0,0)/\theta(0, R)$ given in accordance with (12.1.0) by

$$\exp\left(\frac{w(0, R)}{RT}\right),$$

and hence $\theta(0,0)/(\theta(0,0) + \theta(0, R))$ or $\theta(0, R)/(\theta(0,0) + \theta(0, R))$ remains constant independent of h because of the premised constancy of $\mu(R)$.

It is concluded from (11.9) similarly,

$$\frac{dw(H_2^+)}{dh} = -F(1 - \alpha_h) \quad (13.2. H_2^+)$$

and,

$$\frac{dw(H)}{dh} = 0, \quad (13.2. H)$$

where $w(H_2^+)$ or $w(H)$ is respectively the "weighted mean" with respect to D_j except B similar to $w(H^+)$ of (13.1).

Eq. (13.2) is valid as readily be shown for any number of kinds of R .

Eq. (13.2) is formally in full accordance with (7.6) on the effect of

*) Cf. §11 and §3.

the chemical potential of hydrogen ion, h in the equations being defined either by (11.1) or by (7.1.h) in the respective cases. The h of these alternative definitions are congruent with each other in their increment Δh , provided that the chemical potential $\mu(BH^+)$ of the conjugate acid BH^+ of B is kept constant, so that the increase of $\mu(H^+b)$ equals the decrease of $\mu(B)$ by virtue of the equilibrium relation,

$$\mu(H^+B) = \mu(H^+b) + \mu(B),$$

as in the case of hydroxyl ion of B in aqueous solution.

We will now investigate α_h which modulates the effect on $w(\delta_i)$'s according to (13.2), in comparison with α_h of the hydrogen ion effect.

We have from (11.9.E) remembering (11.2.s'),

$$\alpha_h = \frac{\frac{D_P}{4\pi x_P} - \frac{\partial s}{\partial E_D} - \frac{\partial s_B}{\partial E_D} + \frac{\partial s'}{\partial h}}{\frac{D_P}{4\pi x_P} - \frac{\partial s_B}{\partial E_D} - \frac{\partial s}{\partial E_D}} = \frac{\frac{D_P}{4\pi x_P} - \frac{\partial s}{\partial E_D}}{\frac{D_P}{4\pi x_P} - \frac{\partial s_B}{\partial E_D} - \frac{\partial s}{\partial E_D}}, \quad (13.3)$$

$\frac{\partial s'}{\partial h}$ given by (11.8.h) being identical with $\frac{\partial s_B}{\partial E_D}$ of the expression,

$$\frac{\partial s_B}{\partial E_D} = -\frac{GF^2}{N_A RT} (\theta(0) + \theta(H)) (\theta(H^+B) + \theta(H_2^+B)), \quad (13.4)$$

derived similarly as (11.8.E) of $\left(\frac{\partial s'}{\partial E_D}\right)$. Eq. (13.3) is analogous to

(7.4.a) with $\left(\frac{\partial s}{\partial E_P}\right)_{Pots.}$ there substituted from (4.5.e), s_B or E_D in the former corresponding to $\frac{D_P}{4\pi} \left(\frac{\partial E}{\partial x}\right)_a$ or E_P in the latter respectively.

The analogy may be brought closer by transforming (7.4.a) as below; we see from (4.1.o) and (4.2) that,

$$-\vartheta_a = \int_{x_P}^{\infty} \rho dx = \frac{D_P}{4\pi} \left(\frac{\partial E}{\partial x}\right)_a = [\rho] \quad (13.5)$$

is the charge accumulated outside P per unit area of the catalysts surface due to the distribution of ions in the surroundings, which is the function solely of E_P at a given $\rho = \rho(E)$ and $D = D(x)$ as mentioned in §5. Substituting $\left(\frac{\partial E}{\partial x}\right)_a$ from (13.5) into (4.5.e) and transforming it from the set of independent variables E_P and E_C into that of $E_D \equiv E_P - E_C$ and E_C , we have,

$$\left(\frac{\partial s}{\partial E_P}\right)_{Pois.} = \frac{D_P}{4\pi x_P} - \frac{\partial[\rho]}{\partial E_D},$$

whereas for $\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ similarly,

$$\left(\frac{\partial s}{\partial E_P}\right)_{Ads.} = \frac{\partial s}{\partial E_D}.$$

Eq. (7.4.a) is now,

$$\alpha_h = \frac{\frac{D_P}{4\pi x_P} - \frac{\partial s}{\partial E_D}}{\frac{D_P}{4\pi x_P} - \frac{\partial[\rho]}{\partial E_D} - \frac{\partial s}{\partial E_D}}, \quad (13.6)$$

which is formally in close analogy with (13.3), the part of extra charge brought about by B on P in the latter being played by $[\rho]$ in the former, the space charge outside P ; as s_B or $[\rho]$ vanishes, so does $\frac{\partial s_B}{\partial E_D}$ or $\frac{\partial[\rho]}{\partial E_D}$ according respectively to (13.4) and (11.2. s_B) or to (13.5) and (4.6), drawing α_h close to 1 or the h -variation effect to nil: either through s_B or $[\rho]$ is $w(\delta_i)$ of charged δ_i affected by the variation h in the respective case.

The analogy breaks down however at greater s_B or $[\rho]$: whereas the increase of $[\rho]$ or ρ to infinity brings α_h close to zero in the latter case, the α_h in the former case increases again up to 1, as s_B increases to the upper extremity corresponding to $\theta(H^+B) + \theta(H_2^+B) = 1$ in (11.2. s_B) to squeeze $\theta(0) + \theta(H)$ in (13.4) or $\frac{\partial s_B}{\partial E_D}$ in (13.3) to zero in accordance with the relation,

$$\theta(0) + \theta(H^+) + \theta(H_2^+) + \theta(H) + \theta(H^+B) + \theta(H_2^+B) = 1,$$

which follows from the premiss and the definitions.

This discrepancy is expected from the impenetrability allowed for explicitly in the present case in terms of exclusive occupation of σ by δ_i inclusive of extra one due to B but not with the ρ -effect where the electrostatic interaction between δ_i 's and ions only is taken into account.

§ 14 Non-dissociative Acid.

Here will be discussed the effect of the project at constant λ and l in the practical absence of the space charge.

The acid AH will give off proton, as mentioned in §10, the resulting negatively charged acid rest A^- adhering to the boundary surface as an additional occupant of σ as illustrated in Fig. 5.

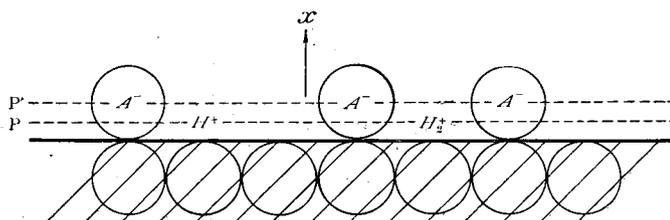


Fig. 5.
Non-dissociative Acid at Boundary

The plane through the centre of A^- will be taken outside P in accordance with the magnitude of radii of anions definitely greater than the calculated x_p of $H^+(a)$ and $H_2^+(a)^*$ and the variation of dielectric constant neglected.

The electrostatic potential varies then with distance x from C as illustrated by the bold broken line in Fig. 6, being constantly E_P^- outside P according to (4.6), the charge existing only on C, P and P^- but nowhere else.

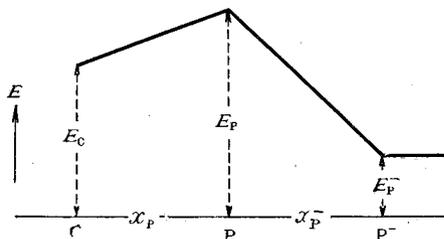


Fig. 6.
Electrostatic Potential at Boundary

The effect of increasing the chemical potential $\mu(AH)$,

$$\mu(AH) \equiv Fh \quad (14.1)$$

*) The proton of $H^+(a)$ or the centre of charge of $H_2^+(a)$ was found by the detailed calculation of Ref. 7, 2.7 Å or 2.5 Å respectively apart from the centre of mercury atom on the surface, the mean 2.6 Å of them or the sum 3.4 Å of 1.6 Å radius of mercury atom and 1.8 Å of chlorine ion being taken there the distance of the respective plane on which the appropriate positive or negative charge was homogeneously distributed.

of acid AH on $w(\delta)$'s is thus deduced below.

We have in accordance with (4.3. i),

$$\frac{E_P - E_C}{x_P} + \frac{E_P - E_P^-}{x_P^-} = \frac{4\pi s}{D} \quad (14.2. s)$$

and, in place of (4.3. P), for the charge density s^- on P^- ,

$$-\frac{E_P - E_P^-}{x_P^-} = \frac{4\pi s^-}{D}, \quad (14.2. s^-)$$

where x_P^- is the distance between P^- and P . The s is given by (3.7) and (3.4) as the function of $w(\delta_i)$'s of δ_i 's inclusive of A^- according to the premiss and s^- as,

$$s^- = -\frac{GF}{N_A} \theta(A^-). \quad (14.3)$$

The $w(H^+)$, $w(H_2^+)$ and $w(H)$ are expressed according to (3.3), (3.4. ϵ), (3.2), (5.1), (8.1. b) and (11.5) as,

$$w(H^+) = \epsilon(H^+)_0 + FE_D + Fl - F\lambda, \quad (14.4. H^+)$$

$$w(H_2^+) = \epsilon(H_2^+)_0 + FE_D + 2Fl - F\lambda, \quad (14.4. H_2^+)$$

$$w(H) = \epsilon(H)_0 + Fl, \quad (14.4. H)$$

whereas $w(A^-)$ similarly in the form,

$$w(A^-) = \epsilon(A^-)_0 - FE_P^- - \mu(A^-) = \epsilon(A^-)_0 - FE_D^- - Fh - Fl + F\lambda, \quad (14.4. A)$$

according to (5.1), (8.1. b), (14.1) and to the equilibrium relation,

$$\mu(AH) = \mu(A^-) + \mu(H^+ b),$$

where,

$$E_D^- \equiv E_P^- - E_C. \quad (14.5)$$

Eqs. (3.7), (14.3), (3.6) and (14.4) show now that s or s^- is the function of E_D , E_D^- and h at constant $\epsilon(\delta_i)_0$, l and λ .

Writing (14.2) according to (11.5) and (14.5) in the form,

$$\frac{E_D}{x_P} + \frac{E_D - E_D^-}{x_P^-} = \frac{4\pi s}{D} \quad (14.6. P)$$

$$\frac{E_D^- - E_D}{x_P^-} = \frac{4\pi s^-}{D} \quad (14.6. n)$$

we have by differentiation,

$$\left(\frac{1}{x_p} + \frac{1}{x_p^-}\right) \frac{dE_D}{dh} - \frac{1}{x_p^-} \frac{dE_D^-}{dh} = \frac{4\pi}{D} \left(\frac{\partial s}{\partial E_D} \frac{dE_D}{dh} + \frac{\partial s}{\partial E_D^-} \frac{dE_D^-}{dh} + \frac{\partial s}{\partial h} \right),$$

$$\frac{1}{x_p^-} \left(\frac{dE_D^-}{dh} - \frac{dE_D}{dh} \right) = \frac{4\pi}{D} \left(\frac{\partial s^-}{\partial E_D} \frac{dE_D}{dh} + \frac{\partial s^-}{\partial E_D^-} \frac{dE_D^-}{dh} + \frac{\partial s^-}{\partial h} \right),$$

or solving for $\frac{dE_D}{dh}$,

$$\frac{dE_D}{dh} = \frac{\frac{D(s, s^-)}{D(E_D^-, h)} + \frac{D}{4\pi x_p^-} \frac{\partial(s+s^-)}{\partial h}}{\frac{D(s, s^-)}{D(E_D, E_D^-)} - \frac{D}{4\pi x_p^-} \left\{ \frac{\partial(s+s^-)}{\partial E_D} + \frac{\partial(s+s^-)}{\partial E_D^-} \right\} - \frac{D}{4\pi x_p} \frac{\partial s^-}{\partial E_D^-} + \left(\frac{D}{4\pi}\right)^2 \frac{1}{x_p x_p^-}}, \quad (14.7)$$

where $D(s, s^-)/D(E_D^-, h)$ and $D(s, s^-)/D(E_D, E_D^-)$ are Jacobians.

The variation of $w(\delta)$ at constant $\varepsilon(\delta_i)_0$, l and λ is given by the left of the above equation according to (14.4) as,

$$\frac{dw(H^+)}{dh} = \frac{dw(H_2^+)}{dh} = F \frac{dE_D}{dh}, \quad \frac{dw(H)}{dh} = 0, \quad (14.8)$$

whereas terms on the right of (14.7), when expanded according to (3.7), (14.3), (14.4) and the relation,

$$\theta(0) + \theta(H^+) + \theta(H_2^+) + \theta(H) + \theta(A^-) = 1, \quad (14.9)$$

valid in this case, are,

$$\frac{D(s, s^-)}{D(E_D^-, h)} = -2 \left(\frac{GF^2}{N_A RT} \right)^2 \theta(A^-)^2 \{ \theta(H^+) + \theta(H_2^+) \}^2, \quad (14.10.a)$$

$$\frac{\partial(s+s^-)}{\partial h} = - \frac{GF^2}{N_A RT} \theta(A^-) \{ \theta(0) + 2\theta(H^+) + 2\theta(H_2^+) + \theta(H) \}, \quad (14.10.b)$$

$$\frac{D(s, s^-)}{D(E_D, E_D^-)} = 4 \left(\frac{GF^2}{N_A RT} \right)^2 \theta(A^-)^2 \{ \theta(H^+) + \theta(H_2^+) \}^2$$

$$+ \left(\frac{GF^2}{N_A RT} \right)^2 \theta(A^-) \{ \theta(H^+) + \theta(H_2^+) \} \{ 1 + 2\theta(H^+) + 2\theta(H_2^+) \} \{ \theta(0) + \theta(H) \}, \quad (14.10.c)$$

$$- \frac{\partial(s+s^-)}{\partial E_D} - \frac{\partial(s+s^-)}{\partial E_D^-} = \frac{GF^2}{N_A RT} \theta(A^-) \{ \theta(0) + 4\theta(H^+) + 4\theta(H_2^+) + \theta(H) \}$$

$$+ \frac{GF^2}{N_A RT} \{ \theta(0) + \theta(H) \} \{ \theta(H^+) + \theta(H_2^+) \}, \quad (14.10.d)$$

$$-\frac{\partial s^-}{\partial E_D^-} = \frac{GF^2}{N_A RT} \theta(A^-) \{ \theta(H^+) + \theta(H_2^+) \}. \quad (14.10. e)$$

We see now from the above expressions that both the terms in the numerator of (14.7) are negative, whereas those in the denominator exclusively positive and particularly from the comparison of (14.10.a) with (14.10.c) on one hand and of (14.10.b) with (14.10.d) on the other hand that the absolute value of the numerator is less than that of the denominator. The $\frac{dE_D}{dh}$ is thus a negative proper fraction i. e.,

$$\frac{dE_D}{dh} = \alpha_h - 1, \quad (14.11. E)$$

where,

$$0 < \alpha_h < 1 \quad (14.11. a)$$

and in consequence we have according to (14.8),

$$\frac{dw(H^+)}{dh} = \frac{dw(H_2^+)}{dh} = -F(1 - \alpha_h), \quad \frac{dw(H)}{dh} = 0 \quad (14.12)$$

in close analogy to (7.6) or to (13.2).

Eqs. (14.7), (14.10) and (14.11.E) show that the proper fraction α_h approximates unity when $\theta(A^-)$ or s^- of (14.3), which corresponds to $[\rho]$ or s_B in § 13, tends either to zero or the upper extremity 1 of $\theta(A^-)$ nullifying other $\theta(\delta_i)$'s similarly as in the case of the nondissociative base but in deviation from that of the space charge. This deviation is to be attributed to the impenetrability of B or A^- allowed for in the first two cases as mentioned before.

§ 15 Summary of Effects.

In the foregoing sections we have deduced first from the model of our assembly specified in § 2 the effect of varying the space charge function, the work function λ , the chemical potential $\mu(H^+b)$ of hydrogen ion, that $\mu(H_2)$ of hydrogen and the hydrogen overvoltage γ_0 on $w(\delta_i)$'s, which determine the abundance of intermediates on the catalyst.

In the next place the model has been modified to include the effect of BRÖNSTED'S base or acid in the surroundings incapable of causing any electrolytic dissociation whatever, the result being formally coincident with that of hydrogen ion, the chemical potential of the acid

or base playing the part of $\mu(H^+b)$ or $-\mu(H^+b)$ respectively.

The conclusion thus arrived at is summarized in Table 1.

TABLE 1 Effect on $w(\delta_i)$'s of Varying
Different Factors.

Factors Varied	Increment of			Bounds of $\alpha_\lambda, \alpha_h,$ and α_l
	$w(H^+)$	$w(H_2^+)$	$w(H)$	
λ	$-F\alpha_\lambda \Delta\lambda$	$-F\alpha_\lambda \Delta\lambda$	0	$1 > \alpha_\lambda > 0$
$h = \mu(H^+, b)/F,$ or $-\mu(B)/F,$ or $\mu(AH)/F$	$-F(1-\alpha_h)\Delta h$	$-F(1-\alpha_h)\Delta h$	0	$1 > \alpha_h > 0$
$l = \eta - \mu(H_2)/2F$	$F\alpha_l \Delta l$	$F(1+\alpha_l)\Delta l$	$F\Delta l$	$1 > \alpha_l > -1$

The variation of α_λ, α_h and α_l within the respective bounds indicated in the Table may be summarized as below. In the case of the model specified in § 2, when there exist ions in the surroundings and they interact with each other and with δ_i 's solely electrostatically without such impenetrability for instance as imposed upon by the exclusive occupation of σ , α_λ, α_h and α_l tend all to zero with increasing ρ ; as ρ decreases, α_h approaches unity and α_λ also, if $\theta(0) + \theta(H)$ or $\theta(H_2^+) + \theta(H^+)$ simultaneously tends to zero; α_l particularly increases up to 1 or decreases possibly down to a negative proper fraction with decreasing ρ according as both $\theta(H_2^+)$ and $\theta(0)$ simultaneously approach zero or $\theta(H_2^+)$ $\theta(0)$ becomes sufficiently large.

In the case of the modified model, when no ion exists in the surroundings but BRÖNSTED base or acid occupies σ concurrently with the intermediates, as an associate to-charged δ_i or an additional occupant A^- respectively, the appropriate proper fraction α_h approximates unity either at its vanishing or full occupation.

In the above treatment we have allowed for the variation of $\epsilon(\delta_i)_0$ of charged δ_i due to the interaction with the associate but not for that due to the mutual interaction among the intermediates. The latter sort of interaction will be taken into account in the later part of this series of paper.

CHAPTER 2 VARIETY OF INTERMEDIATES,

§ 16 Outlines.

The leading part in the reaction is transferred from one to the other intermediate from case to case as raised in the introduction. The abundance of each δ_i depends now, as shown in the foregoing chapter, on a set of $w(\delta_i)$'s of (3.6), which in turn on different factors defining the condition of our assembly.

An intermediate responsible for a prevailing mechanism may not necessarily be a most abundant one: nevertheless it must be sufficiently abundant to keep up the relevant reaction prevailing; as it decreases along with the variation of a certain factor, it would eventually hand its leading part over to the other one of some rival mechanism. The leading part and the abundance of an intermediate should hence change side by side, if not simultaneously, over a sufficient range of variation of factors.

Attributing now the variation of the factor properly to that of the *case*, we might proceed to explain the complex features raised in the introduction in subsequent sections in the light of the theory developed in the foregoing chapter.

§ 17 $w(\delta_i)$ on Nickel in Gas.

We consider first nickel catalyst in gaseous surroundings of hydrogen alone or of the latter mixed with some substrate of hydrogenation at ordinary temperature and pressure. The $w(H)$ may be nearly equal to zero or even slightly negative in accordance with (3.4. θ), since hydrogen is considerably adsorbed on nickel at the condition. The $w(\delta_i)$'s of other δ_i 's might be taken higher than $w(H)$ in conformity with the conclusion of them being not leading in the hydrogenation and the electrode process throughout. As to the relative magnitude of $w(H_2^+)$ and $w(H^+)$ we might infer as below.

It is known that original hydrogen-molecule-ion in vacuum liberates energy as much as 2.7 e-volt when formed from H and H^+ . The energy liberation of the same magnitude is expected for the formation of $H_2^+(a)$ from $H(a)$ and $H^+(a)$ by resonance^{*)} provided that respective

) Cf. Foot-note () on p. 54.

equilibrium position of protons of $H_2^+(a)$ referred to the appropriate σ and to the associate molecule, if any, happens to coincide respectively with those of $H(a)$ and $H^+(a)$. The resonance energy of $H_2^+(a)$ is however the greatest as well known, when the two component states of resonance i. e. HH^+ and H^+H are of the same energy, as realized by the symmetric position of the two protons involved^{*)}: it being not in general coincident with that at the state of $H(a)$ or $H^+(a)$, the latter must be brought to the former at the cost at least partially of the liberated energy. The energy liberation in vacuum exceeding however even the spectroscopic dissociation energy 2.6 e-volt of NiH^* , its negative being here approximately identified^{**)} with $\epsilon(H)_0$ referred to the state of free hydrogen atom at rest at infinity, we might safely assume that the former outweighs the cost, i. e.

$$\epsilon(H_2^+)_0 < \epsilon(H)_0 + \epsilon(H^+)_0,$$

or according to (3.4. ϵ), (3.3) and (3.2),

$$w(H_2^+) < w(H) + w(H^+) \tag{17.1}$$

Assuming,

$$w(H) \leq 0 \tag{17.2}$$

as above, we have,

$$w(H_2^+) < w(H^+) \tag{17.3}$$

Fig. 7 shows $w(\delta_i)$'s thus estimated qualitatively by the height of dot at the tip of the vertical lines with appropriate symbols.

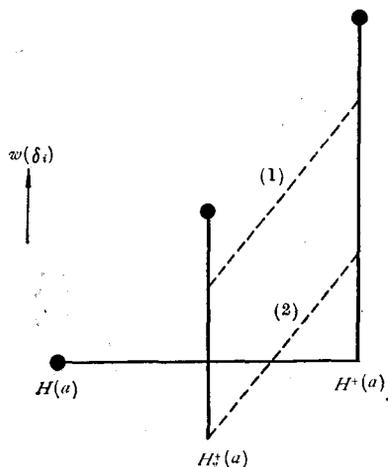


Fig. 7.

$w(\delta_i)$ on Nickel and Platinum

*) Landolt: "Tabellen", 1, 2 Teil, 32 (1951).

***) The $\epsilon(H)_0$ of the description must be exactly the negative dissociation energy plus a small quantity $-RT \log q_0$, where q_0 is the partition function of $H(a)$. Cf. Ref. 5 and 7.

§ 18 Passing over from Nickel to Platinum in Gas.

We will assume by passing from nickel to platinum in the same surroundings of the foregoing section, that $\varepsilon(H)_0$ as well as $\varepsilon(H^+)_0$ is not appreciably affected in accordance with the observed data of $H(a)^{*)}$ and the result of theoretical calculation on $H^+(a)^{**})$ respectively, only effective difference being that of the work function 4.6 volt¹⁴⁾ of nickel and 5.3 volt¹⁴⁾ of platinum. The α_λ in (6.3) should be nearly unity according (4.5, e), (4.6) and (3.9), because of the practical absence of the space charge in the surroundings and of charged δ_i in accordance with § 17.

The $w(H_2^+)$ ($< w(H^+)$) decreases hence rapidly with increasing λ until $\theta(H_2^+)$ ($> \theta(H^+)$) in (3.9) attains according to (6.3) and (3.6) to such a value as $\left(\frac{\partial s}{\partial E_p}\right)_{Ads.}$ in (6.2. λ) is no more negligible, when the further decrease of $w(H_2^+)$ is more or less retarded by the decrease of α_λ . The result is hence either the appreciable decrease of $w(H_2^+)$ as much as $F\Delta\lambda$ or else the appearance of $H_2^+(a)$ to an appreciable amount.

The conclusion is not altered, if the catalyst is in contact with some aprotic liquid, which hardly affects $\varepsilon(H_2^+)_0$ or $\varepsilon(H^+)_0$.

The $\theta(H_2^+)$ is thus more or less increased by the increase of λ from nickel to platinum but possibly not so much as to lead the reaction.

Horiuti and Polanyi¹⁾ concluded the associative mechanism assuming $H(a)$ the unique hydrogen intermediate both on the platinum and on the nickel catalyst. It is however not altogether conclusive that $H(a)$

*) Platinum black or reduced nickel adsorbs at 300°C, 0.57×10^{-3} cc NTP or 0.54 cc NTP hydrogen respectively at 1 mmHg pressure per unit BET area as calculated from KWAN's observation ["Catalyst" 4, 44 (1948)]. The $\theta(H)$ is calculated from the data at $0.57 \times 10^{-6} \times 6.0 \times 10^{23} \times 2/22400 \times 10^{15} = 3.1 \times 10^{-2}$ for platinum or 2.9×10^{-2} for nickel.

Assuming $H(a)$ practically the only δ_i in both the cases in accordance with § 17, it follows from (3.3) and (3.4) that $w(H)$ or $\varepsilon(H)_0$ is approximately the same.

**) The $\varepsilon(H^+)_0$ is identical with $-kT \log q_K^{H^+}$ of Ref. 7 which is according to the detailed theoretical calculation there -10.76 e-volt as referred to proton at rest in vacuum: the interaction with the mercury atom contributes to it only -1.18 e-volt, the remaining major part being due to the electrostatic interaction of proton with the conductor of the electrode around the mercury atom and with the dielectrics of the aqueous electrolyte. The former rather small contribution, which is electric polarization in nature and only part possibly specific to the atom involved, would presumably not make very much difference in $\varepsilon(H^+)_0$ from one catalyst material to the other in the common surroundings.

is actually the leading intermediate on platinum, if the associative mechanism stated in terms of $H(a)$ fitted in with experiments, inasmuch as any alternative intermediate does at least formally as well*.)

§ 19 Platinum in Nucleophilic Reagent.

The $\epsilon(H^+)_0$ as well as $\epsilon(H_2^+)_0$ ** is lowered by nucleophilic reagents as acetone, water or ammonia in the surroundings in accordance with the conclusion in § 12. The $w(H^+)$ and $w(H_2^+)$ thus lowers from dotted line (1) to (2) in Fig 7 rendering $H_2^+(a)$ more and more abundant.

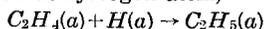
The part of keeping up the prevailing reaction may possibly be passed over from $H(a)$ to $H_2^+(a)$, if the increase of the work function alone, dealt with in the foregoing section, were not effective enough.

This accounts for the mechanism of the hydrogenation of acetone¹¹⁾ and that¹⁰⁾ of the hydrogen exchange between water and hydrogen both proceeding through the intermediary of $H_2^+(a)$ in the presence of platinum catalyst. It is concluded on the other hand from the contrasting persistence of $H(a)$ leading the reaction on nickel at the very condition where $H_2^+(a)$ assumes the part on platinum, that $H(a)$ on nickel is so much stable. This conclusion is amplified as discussed later by the further survival of $H(a)$ on nickel in much severer condition.

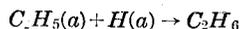
§ 20 Platinum in Electrolyte.

We consider now platinum in nucleophilic liquid as water added with electrolyte, in comparison with the nickel at the same condition. The theory developed in § 5 and § 6 tells us that electrolyte more or less diminishes the advantage of platinum over nickel in lowering $w(H_2^+)$ due to larger λ and nullifies it altogether at infinite concentration or infinite space charge function.

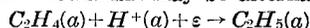
*) The association of hydrogen atom,



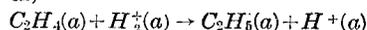
or



involved in the mechanism may be alternatively effected by $H^+(a)$ as,



or by $H_2^+(a)$ as,



for $C_2H_4(a)$ and similarly for $C_2H_5(a)$, $H^+(a)$ resulting from the reactant $H_2^+(a)$ being convertible to the latter as implied in (1.2).

) Cf. the Foot-note () on page 56.

The situation will be investigated below with reference to a fictitious electrode T, whose work function is supposed to increase from that of nickel to that of platinum, with other factors remaining the same, on the basis of the reasonable coincidence of $w(H)$ mentioned in § 18.

As T is at the state of nickel, $\theta(H^+)$ and $\theta(H_2^+)$ and hence $\left(\frac{\partial s}{\partial E_P}\right)_{Ads}$ in (6.2) may be taken practically zero according to § 17 and to (3.9). The value $\alpha_{\lambda,0}$ then of α_λ is expressed according to (4.5. e) and (6.2. λ) as,

$$\alpha_{\lambda,0} = \frac{D_P/4\pi x_P}{\left(\frac{\partial s}{\partial E_P}\right)_{Pois.}} = \left\{1 - x_P \frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x}\right)_a\right\}^{-1} \quad (20.1. \alpha)$$

from which $\alpha_{\lambda,0}$ is calculated at,

$$\alpha_{\lambda,0} = 0.53 \text{ at } 300^\circ K \quad (20.1. N)$$

for 1N uni-uni-valent neutral electrolyte as below.

The $\frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x}\right)_a$ in (20.1. α) is given by (4.3. P) as,

$$\frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x}\right)_a = \pm \sqrt{\frac{2\pi}{D}} \frac{\rho_P}{\sqrt{-\int_0^{E_P} \rho dE}} \quad (20.2. E)$$

where,

$$\bar{D} = \int_0^{E_P} \rho D dE / \int_0^{E_P} \rho dE \quad (20.2. D)$$

is the average dielectric constant outside P, ρ_P the ρ in the direct neighbourhood of P-plane,*) + or - sign being respectively relevant to positive or negative E_P in accordance with § 4.

Substituting now ρ for the uni-uni-valent electrolyte from (2.2) into (20.2. E), we have,

$$\frac{\partial}{\partial E_P} \left(\frac{\partial E}{\partial x}\right)_a = -F \sqrt{\frac{2\pi N}{D N_A R T}} \left(e^{-\frac{FE_P}{2RT}} + e^{\frac{FE_P}{2RT}} \right), \quad (20.3. a)$$

It is now required to determine E_P and \bar{D} for working out $\alpha_{\lambda,0}$. The same substitution of ρ from (2.2) into (4.3. P) gives,

$$\left(\frac{\partial E}{\partial x}\right)_a = \frac{\sqrt{\bar{D}}}{D_P} \sqrt{\frac{8\pi N R T}{N_A}} \left(e^{-\frac{FE_P}{2RT}} - e^{\frac{FE_P}{2RT}} \right), \quad (20.3. b)$$

which, further substituted into (4.3. v), in turn,

$$\frac{E_P - E_C}{x_P} - \frac{\sqrt{\bar{D}}}{D_P} \sqrt{\frac{8\pi N R T}{N_A}} \left(e^{-\frac{FE_P}{2RT}} - e^{\frac{FE_P}{2RT}} \right) = \frac{4\pi s}{D_P}. \quad (20.3. c)$$

*) The ρ_P does not of course include the charge due to δ_i 's on P-plane, ρ in the integral being the charge density outside P as implied in (4.1).

Hydrogen Intermediates on Catalysts and Electrodes

This equation allows us to determine E_p for a given set of values of E_C , x_p , \bar{D} , D_p , and s . The E_C was estimated at -0.14 volt for hydrogen electrode of nickel in neutral solution from the usual value $+0.56$ volt of E_C or the "absolute potential" of normal calomel electrode against the solution, by subtracting from it 0.28 volt to obtain that of reversible hydrogen electrode of mercury in $1 N$ acid solution and then further $\frac{RT}{F} \log_e 10^7 = 0.42$ volt to reduce it to that of the reversible hydrogen electrode in neutral solution. From this value of E_C of mercury that of nickel was calculated at -0.22 volt on the basis of 4.61 volt λ of nickel quoted in § 18 and 4.53 volt λ of mercury*) according to (5.1), $\mu(\epsilon)$ there being the same for any reversible hydrogen electrode in the same surroundings. The x_p was taken 10^{-8} cm as before, D_p at 10 intermediate between the optical dielectric constant 1.7 in σ^7 and the effective one 20 around σ^7 , \bar{D} at 40 , half-way between D_p , above and $D_\infty=80$, and s finally at zero in accordance with the practical absence of charged δ_i concluded in § 17.

The E_p was thus worked out from (20.3.c) at -0.065 volt which gives according to (20.3.a),

$$\frac{\partial}{\partial E_p} \left(\frac{\partial E}{\partial x} \right)_a = -3.8 \times 10^7 \text{ cm}^{-1}$$

and henceforth $\alpha_{\lambda,0}$ of (20.1.N).

The above estimation, although not very accurate, would show at least qualitatively that α_λ is a proper fraction remote from zero or that $1N$ concentration of electrolyte is far from being practically infinite in the sense of § 5. The lowering of λ should hence be amply effective in stabilizing $H^+(a)$ and $H_2^+(a)$ at the nickel state of T.

It follows now that the conclusion arrived at in § 18 on the effect of λ -increase i. e. either the appreciable decrease of $w(H^+)$ and $w(H_2^+)$ or else considerable increase of $H^+(a)$ and $H_2^+(a)$ remains valid at least qualitatively even in the surroundings of an aqueous electrolyte. This accounts for the contrast of the leading intermediates $H(a)$ on nickel and $H_2^+(a)$ on platinum persisting at the condition of hydrogen electrode.

§ 21 Effect of Hydrogen Ion.

We might now investigate the effect of varying the chemical potential of hydrogen ion in the surroundings of the hydrogen electrode of platinum or of nickel.

Eq. (7.6) shows that $w(H^+)$ and $w(H_2^+)$ effectively decrease, if α_h is sufficiently less than unity. The expression (7.4.a) may be written according to (20.1.a) and (3.9) as,

$$\alpha_h = \frac{1 + \kappa}{1/\alpha_{\lambda,0} + \kappa}, \quad (21.1.a)$$

where,

*) D'ANS & LAX: "Taschenbuch", Berlin 1949, p. 192.

$$\kappa = - \left(\frac{\partial s}{\partial E_P} \right)_{Ads.} / \frac{D_P}{4\pi x_P} = \frac{4\pi x_P G F^2}{N_A D_P R T} (\theta(H^+) + \theta(H_2^+)) (\theta(H) + \theta(0)) \quad (21.1. \kappa)$$

is an essentially positive number.

We see from (21.1. α) that α_h lies between $\alpha_{\lambda,0}$ and 1 and that it increases with $\alpha_{\lambda,0}$ as well as with κ , remembering $\alpha_{\lambda,0}$ a positive proper fraction. The maximum $\alpha_{h,max}$ of α_h thus corresponds to the maxima $\alpha_{\lambda,0,max}$ and κ_{max} of $\alpha_{\lambda,0}$ and κ respectively. The $\alpha_{\lambda,0}$ is now maximum at $E_P=0$, as seen from (20.1. α) and (20.3. α), i.e. at,

$$\alpha_{\lambda,0,max} = \left(1 - x_P F \sqrt{\frac{2\pi N}{D N_A R T}} \right)^{-1} = 0.69, \quad (21.2. \lambda)$$

whereas κ_{max} is,

$$\kappa_{max} = 17, \quad (21.2. \kappa)$$

according to (21.1. κ) and (3.5) at $(\theta(H^+) + \theta(H_2^+))(\theta(H) + \theta(0)) = 1/4$ on the basis of data given in § 20. We have hence according to (21.1. α),

$$\alpha_{h,max} = 0.97, \quad (21.2. h)$$

At given $|E_P|$, $\alpha_{\lambda,0}$ is definite according to (20.1. α) and (20.3. α) and hence to (21.1. α), α_h lies between,

$$\alpha_h(L) = \alpha_{\lambda,0} \text{ and } \alpha_h(U) = \frac{1 + \kappa_{max}}{1/\alpha_{\lambda,0} + \kappa_{max}} \quad (21.3. L), (21.3. U)$$

The $|E_P|$ depends on E_C and s according to (20.3. c), and E_C in turn according to (5.1) and (8.1. b) on λ at fixed l and $\mu(H^+, b)$, whereas s lies between 0 and GF/N_A according to (3.7).

Fixing now l and $\mu(H^+, b)$ at those of the reversible hydrogen electrode dealt with in the foregoing section, there were calculated

TABLE 2 Bounds $\alpha_h(L)$
and $\alpha_h(U)$ of α_h .

s	Bounds	Electrode	
		Ni	Pt
0	$\alpha_h(L)$	0.53 (-0.06)	0.21 (-0.145)
	$\alpha_h(U)$	0.95 (-0.06)	0.82 (-0.145)
$\frac{FG}{N_A}$	$\alpha_h(L)$	0.13 (+0.176)	0.28 (+0.126)
	$\alpha_h(U)$	0.72 (+0.176)	0.87 (+0.126)

E_P of nickel alternatively for $s=FG/N_A$ and that of platinum for both the values of s at $E_C = -0.93$ volt, shifted from $E_C = -0.22$ volt of nickel by the decrease of λ from 4.61 volt of nickel¹⁴⁾ to 5.32 volt of platinum¹⁴⁾ according to (5.1), $\alpha_h(L)$ and $\alpha_h(U)$ appropriate to each E_P according to (20.3. α), (20.1. α), (21.3)

and (21.2. *c*) being shown in Table 2. Figures in the parentheses shows the relevant $|E_p|$.

The application of cathodic polarization or the decrease of l at constant $\mu(H^+, b)$ brings now about according to (8.1. *b*) and (5.1) the decrease of E_c , which gives rise in turn to that of E_p just as in the case of λ -effect developed in § 6.

We might see from the Table that α_h is appreciably less than the general upper limit given by (21.2) except in the case when E_p happens to fall near to zero.

The decrease of h accompanies now, if α_h is sufficiently below 1, an appreciable increase of $w(H_2^+)$ relative to $w(H)$; there corresponds to $\alpha=0.5$ according to (3.6) and (7.6) the increase of $\theta(H)/\theta(H_2^+)$ by the factor $10^{14 \times 0.5} = 10^7$ *) or the conversion of the coverage for instance of $\theta(H^+)=0$, $\theta(H_2^+)=0.98$, $\theta(H)=0.01$ and $\theta(0)=0.01$ into that of $\theta(H^+)=0$, $\theta(H_2^+)=5 \times 10^{-6}$, $\theta(H)=0.50$, $\theta(0)=0.50$ for the change of 1*N* acidic to 1*N* alkaline surroundings.

§ 22 Effect of l -decrease of Nickel Hydrogen Electrode.

We now consider the effect of decreasing l i. e., according to (8.1. *a*), of increasing the cathodic polarization $-\eta$ or hydrogen pressure, on $w(\delta_i)$ of the hydrogen electrode of nickel in electrolyte either acidic or basic, starting from the state of the electrode of practically absent $H^+(a)$ and $H_2^+(a)$ at moderate hydrogen pressure and $\eta=0$ in accordance with previous sections.

It will be assumed that (17.1) is valid even in this case, the argument arriving at the relation being not affected by the presence of the nucleophilic medium, and that (17.2) too in accordance with the assumed absence of interaction of the neutral hydrogen atom with the surroundings. It follows now that (17.3) is also valid in this case.

The α_i of (8.6. *a*) is positive at the start, when $\theta(H^+) = \theta(H_2^+) = 0$, equaling $\alpha_{\lambda,0}$ of (20.1. *a*) or 0.53 particularly for the surrounding of 1*N* uni-univalent electrolyte, because the second term in the numerator and $\left(\frac{\partial s}{\partial E_p}\right)_{Ads.}$ in the denominator of (8.6. *a*) vanishes according to (3.9). All $w(\delta_i)$'s decrease now with decreasing l at the start according to (8.8) and $w(H_2^+)$ among them most rapidly.

*) The $\mu(H^+, b)$ is taken as $\mu(H^+, b) = RT \log N(H^+) + \text{const}$, where $N(H^+)$ is the concentration of hydrogen ion in the bulk of surroundings.

Further variation of $w(\delta_i)$'s after the start depends now on the resulting change of α_i . We may write the factor $\theta(H^+)\theta(H) - \theta(H_2^+)\theta(0)$ of the second term in the numerator of (8.6. a), according to (3.4) in the form,

$$\theta(H^+)\theta(H) - \theta(H_2^+)\theta(0) = \theta(H_2^+)\theta(0) \left\{ \exp\left(\frac{w(H_2^+) - w(H^+) - w(H)}{RT}\right) - 1 \right\}. \quad (22.1)$$

We see that the argument of the exponential function is a constant since the increments of $w(\delta_i)$'s cancel each other according to (8.9). The constant factor in { } is now negative according to (17.1) and the second term in the numerator of (8.6. a) necessarily too.

Along with the initial decrease of $w(H_2^+)$, $\theta(H_2^+)\theta(0)$ may increase and it may happen that the second term in the numerator (8.6. a) outweighs the first in absolute value. If it does at all, α_i is negative and the decrease is led by $H(a)$ instead by $H_2^+(a)$.

Sooner or later however α_i becomes again positive so that $w(H_2^+)$ restores the lead in decreasing, since

$$\exp\left(-\frac{w(H_2^+)}{RT}\right) / \left\{ \exp\left(-\frac{w(H_2^+)}{RT}\right) \right\}^2 = \exp \frac{w(H_2^+)}{RT}$$

or

$$\exp\left(-\frac{w(H_2^+)}{RT}\right) / \left\{ \exp\left(-\frac{w(H)}{RT}\right) \right\}^2 = \exp \frac{2w(H) - w(H_2^+)}{RT},$$

which is the upper bound to $\theta(H_2^+)\theta(0)$ i. e.,

$$\begin{aligned} & \theta(H_2^+)\theta(0) \\ &= \exp\left(-\frac{w(H_2^+)}{RT}\right) / \left\{ 1 + \exp\left(-\frac{w(H^+)}{RT}\right) + \exp\left(-\frac{w(H_2^+)}{RT}\right) + \exp\left(-\frac{w(H)}{RT}\right) \right\}^2, \end{aligned} \quad (22.2)$$

developed according to (3.6), monotonously decreases with decreasing l until at last the second term of the numerator of (8.6. a) recedes the first according to (22.1) in absolute value.

Alternatively it may possibly be the case that α_i remains throughout positive the second term never exceeding the first in absolute value, until $\theta(H_2^+)\theta(0)$ to which the second term is proportional according to (22.1) begins to decrease.

In any case further decrease of l causes $w(H_2^+)$ to decrease most

rapidly until $H_2^+(a)$ predominates.

It follows from the lack of any sign of $H_2^+(a)$ leading the reaction over a considerable range of cathodic polarization with nickel (Ref. 5, 15, 16) that $w(H)$ is initially appreciably lower than $w(H_2^+)$ or $w(H^+)$ at $l=0$ even in the presence of nucleophilic substance as water, which should considerably lower $w(H_2^+)$ and $w(H^+)$. It is thus almost convincing that the presence of the intermediate other than $H(a)$ is practically excluded at least in the absence of nucleophilic reagent as tacitly assumed by Horiuti and Polanyi¹⁾

§ 23 Effect of l -Decrease of Platinum Hydrogen Electrode.

The effect of decreasing l is now discussed starting from such a state of platinum hydrogen electrode in aqueous electrolyte as covered moderately by $H(a)$ in accordance with § 16, as well as by $H_2^+(a)$ of an abundance, if not foremost, enough to keep up the appropriate reaction prevailing.

The excess of $w(H)$ over $w(H_2^+)$, if any, should hence be only slight at the start in contrast to the case of nickel, when the assumption of considerable excess reversely of $w(H_2^+)$ over $w(H)$ is consistent with experiment.

Either $w(H)$ or $w(H_2^+)$ is most rapid in decreasing at the start according as $\theta(H_2^+)\theta(0)$ is sufficiently large as to render α_l negative or not as shown in the foregoing section; if negative, $w(H)$ continues to decrease most rapidly, possibly to loose for some while its slight excess over $w(H_2^+)$, so that $H(a)$ makes the leading intermediate of the reaction; if positive, it may turn easily negative provided that $\theta(H_2^+)\theta(0)$ still increases, to pursue then the above course of variation.

This conclusion is in accordance with the fact referred to in the introduction that the hydrogen electrode of platinum shows the electrolytic separation factor 7 characteristic to the catalytic mechanism led by $H(a)$ at 0.3 volt cathodic polarization⁹⁾ in contrast to the electrochemical mechanism through the intermediate $H_2^+(a)$ concluded¹⁰⁾ of being operative at lower polarization 0.1 volt.

The $H_2^+(a)$ will however restore its lead after all as l continues to decrease as disussed in the foregoing section although the experimental verification might not be practicable because of extremely high a current density of platinum hydrogen electrode.

In connection to the conclusion in § 21 we might further expect

that the point of conversion from $H_2^+(a)$ to $H(a)$ is shifted toward higher l by changing the surroundings from acidic to alkaline and the second one at lower l in the reverse direction, although no experimental material exists to verify it.

§ 24 $w(\delta_i)$'s on Mercury.

The $w(H)$ is estimated as high as around 2 e-volt identifying again according to (3.4. ϵ) and (3.3) the excess of $\epsilon(H)_0$ or of $w(H)$ on mercury over that on nickel with the difference of the spectroscopic dissociation energy 2.6 e-volt^{*)} of NiH and 0.37 e-volt^{*)} of HgH in accordance with previous sections and assuming $w(H)$ on nickel approximately zero at moderate hydrogen pressure in accordance with § 17.

The $w(H^+)$ is calculated at 0.8 e-volt as below on the basis of the previous result⁷⁾ for the mercury hydrogen electrode in neutral 1N uni-uni-valent electrolyte, in 1 atm pressure hydrogen, at $\eta=0$ and at 300°K, dealt with in § 20.

The $w(H_2^+)$ is now $2.6 - 0.37 + w(H^+) - 2.7 + X$ according to § 17, where X is the energy expense due to the shift of protons: assuming again X the fraction of the dissociation energy of the hydride, it follows that $w(H_2^+)$ is more or less lower than $w(H^+)$.

The $w(H^+)$ is expressed according to (3.2. H^+), (3.3) and (3.4. ϵ) as,

$$w(H^+) = \epsilon(H^+)_0 + FE_p - \mu(H^+, b)$$

or according to (8.1) and (5.1) at $\eta=0$ as,

$$w(H^+) = \epsilon(H^+)_0 + F(E_p - E_0 - \lambda) - \frac{1}{2}\mu(H_2).$$

The $\epsilon(H^+)_0$ is -10.76 e-volt as mentioned in § 18^{**)}. The $\mu(H_2)$ is -31.90 e-volt at 1 atm and 300°K according to the expression^{***)},

$$\mu(H_2) = RT \log (N(H_2)/Q(H_2)),$$

where $N(H_2)$ is the concentration of hydrogen molecule in gas and $Q(H_2)$ the partition function of a single hydrogen molecule reckoned to unit volume. The E_p is -0.065 volt according to (20.3. c) for $E_0 = -0.14$ volt, $r_p = 10^{-8}$ cm, $D = 40$ and $s = 0$. The $w(H^+)$ is obtained as above from these data and $\lambda = 4.53$ volt.^{****)}

It was presupposed in the calculation that $s = 0$ or neither $H^+(a)$ nor $H_2^+(a)$ practically present on the electrode surface of mercury at the specified condition. The result $w(H^+) = 0.8$ volt conforms with the presupposition with regard to $H^+(a)$, since it leads to

*) Landolt: "Tabellen", I, 2 Teil, 30-32 (1951).

) Cf. Foot-note (*) on p. 88.

***) Cf. Ref. 7, § 5.

****) D'ANS and LAX: "Taschenbuch" Berlin 1949, p.192.

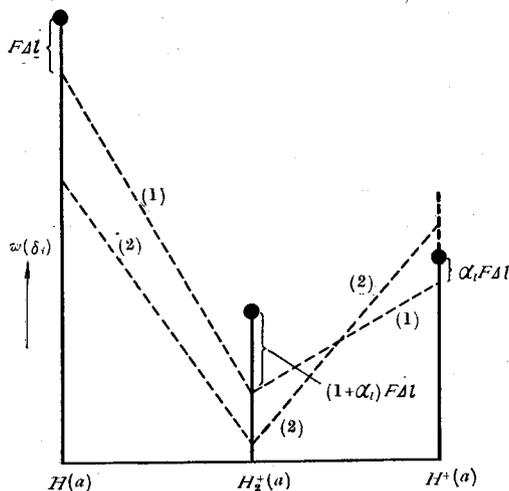


Fig. 8.
 $w(\delta_i)$ on Mercury and Lead

Fig. 8 illustrates the amount of $w(\delta_i)$'s estimated above by the height of dot appropriate to respective δ_i as indicated.

§ 25 Mercury Hydrogen Electrode.

We will follow the variation of $w(\delta_i)$'s and $\theta(\delta_i)$'s along with the decrease of l similarly as in the previous cases starting from the state specified in the foregoing section, remembering that the main difference from the previous cases consists in the outstanding height of $w(H)$ or the practically complete absence of $H(a)$.

It follows now from the height of $w(\delta_i)$'s given in Fig. 8, that $H^+(a)$ as well as $H(a)$ is practically absent, that $\theta(H_2^+) \ll \theta(0)^{**}$ and that $\theta(H)\theta(H^+)$ is negligible compared with $\theta(H_2^+)\theta(0)$, which is valid not only at the start of l -decrease but whole throughout, because of

*) We have by differentiation of (4.3.2) with respect to E_p , remembering $\left(\frac{\partial E}{\partial x}\right)_a$ is the function only of E_p ,

$$\left\{ \frac{1}{x_p} - \frac{\partial}{\partial E_p} \left(\frac{\partial E}{\partial x} \right)_a \right\} \Delta E_p = \frac{4\pi}{D_p} \Delta s$$

or according to (3.7) and (20.1.a) the expression in the text for the increase ΔE_p of E_p due to increase of $\theta(H^+)$ from zero. The upper bound to the appropriate ΔE_p is obtained as given in the text by substituting $\theta(H^+)$ in the latter expression by $\theta(H^+) = 4 \times 10^{-14}$ given there, inasmuch as $\theta(0) \leq 1$.

***) The lower limit 0.3 e-volt of $w(H_2^+)$ given in § 24 leads to the conclusion according to (3.4.θ).

$$\theta(H^+) = 4 \times 10^{-14} \cdot \theta(0)$$

according to (3.4.θ) or to the associated increase 4×10^{-14} volt ΔE_p of E_p at most as calculated by the expression,

$$\Delta E_p = \frac{GF}{N_A} \frac{4\pi x_p}{D_p} \lambda_{2,0} \cdot \theta(H^+)^{**}$$

We see from the above on the other hand $w(H_2^+)$ is at least $2.6 - 0.37 + w(H^+) - 2.7 = w(H^+) - 0.47$ or 0.3 volt at $X=0$, to which corresponds similarly $\theta(H_2^+) = 10^{-5} \cdot \theta(0)$ or 10^{-5} volt increase of E_p at most.

The presupposition of the negligible s is thus consistent with the above conclusion. The alternative one of greater s leads to higher E_p and hence higher $w(H^+)$ and $w(H_2^+)$ as generally inferred from (4.3.2), (3.4.ε) and (3.3) in contradiction with the premiss. The above value of $w(H^+)$ thus follow necessarily from the basic data.

the constancy of their ratio $\frac{\theta(H)\theta(H^+)}{\theta(H_2^+)\theta(H)}$ independent of l as shown in § 22. The α_i is positive at the start, $\theta(H_2^+)\theta(0)$ being sufficiently small,^{*)} so that $w(H)$ decreases by $-F\Delta l$, $w(H^+)$ its positive fraction and $w(H_2^+)$ most rapidly by the sum of the latter two decreases according to (8.9) as illustrated in Fig. 8 by the descent from the tip of the bold vertical appropriate to the respective $w(\delta_i)$ to the respective intersection with the dotted line (1).

As l continues to decrease the α_i must turn sooner or later negative, since the ratio of terms in the numerator of (6.7. a) is,

$$-\frac{4\pi x_p G F^2}{N_A D_p R T} \theta(H_2^+)\theta(0) = -67\theta(H_2^+)\theta(0),$$

neglecting $\theta(H^+)\theta(H)$, which attains to -17 at maximum $1/4$ of $\theta(H_2^+)\theta(0)$ according to the estimation in § 21.

This argument inclusive of the maximum $\theta(H_2^+)\theta(0)$ value is valid in the practical absence of $H^+(a)$ and $H(a)$. The latter condition fulfilled at the start is however *a fortiori* assured at lower l so long as α_i is positive by the associated rapidest decrease of $w(H_2^+)$ among $w(\delta_i)$'s. The assumption of positive α_i throughout leads us hence to the contradiction since then $\theta(H_2^+)\theta(0)$ should fully increase to turn α_i necessarily negative. The α_i should hence sooner or later turn negative.

As α_i becomes negative, $w(H)$ decreases by $-F\Delta l$ as before, whereas $w(H^+)$ by its negative fraction and hence $w(H_2^+)$ by the algebraic sum of them or the positive fraction of $-F\Delta l$ as illustrated by the descent from the respective intersection with (1) to that with (2).

At any rate $w(H_2^+)$ continues to decrease with decreasing l until $\theta(H_2^+)\theta(0)$ is finally reduced to infinitesimal similarly as in the case of nickel or platinum, α_i turning then again positive in favour of the predominance of $H_2^+(a)$.

It is not however *a priori* excluded from data given above that $H(a)$ appears to some extent over the range of negative α_i on the course of l -decrease.

If it does not practically appear after all, $\theta(H_2^+)\theta(0)$ increases up to the maximum $1/4$ at $\theta(H_2^+)\theta(0) = 1/2$ and then decreases monotonously with decreasing l . If it does to an appreciable extent, the maximum $\theta(H_2^+)\theta(0)$ is less than that in practical absence, according to (3.5).

^{*)} Cf. Footnote **) on p. 97.

The negative of α_i there is thus not fully developed because of the above diminution of the factor $\theta(H_2^+) \theta(0)$ in the numerator of (8.6. α) and of the invariance of the term $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ in the denominator.*) The appearance of the intermediate other than $H_2^+(a)$ thus buffers more or less the effect of the negative α_i , which favours the abundance of $H(a)$ in the course of the l -decrease in accordance with (8.8).

The $H_2^+(a)$ is however strongly protected in this case of mercury hydrogen electrode against the momentary replacement by extremely high a value of initial $w(H)$ compared with that on platinum: if it were possible at all in the latter case, it would not be after all in the former. This conclusion is in accordance with the persistence of mercury to $H_2^+(a)$ in contrast with the versatility of platinum.

§ 26 Passing over from Mercury to Lead Hydrogen Electrode.

The $w(\delta_i)$'s on lead hydrogen electrode are worked out below with reference to those on mercury one given in the foregoing sections.

Identifying the excess of $\varepsilon(H)_0$ with the recess of the dissociation energy, $\varepsilon(H)_0$ on lead must be 1.4 e-volt lower than that on mercury but 0.8 e-volt higher than that on nickel on the basis of observed dissociation energies 0.37 e-volt of HgH ,***) 1.8 of PbH ***) and 2.6 of NiH ***) The $\varepsilon(H^+)_0$ might be taken much the same as that on mercury in the common surroundings of aqueous electrolyte on the ground mentioned before***)

The $\varepsilon(H_2^+)_0$ is now according to § 17 or § 24, $\varepsilon(H)_0 + \varepsilon(H^+)_0 - 2.7 + X$ e-volt, the energy X of compensation being assumed less than but increases with $-\varepsilon(H)_0$ referred to the free atom at rest in vacuum, so that decrease $-\Delta\varepsilon(H_2^+)_0$ of $\varepsilon(H_2^+)_0$ is the positive proper fraction α_X of that $-\Delta\varepsilon(H)_0$ of $\varepsilon(H)_0$ i. e.

*) By differentiating the factor $(\theta(H^+) + \theta(H_2^+)) (\theta(0) + \theta(H))$ of $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ partially by $w(H)$ according to (3.6), we have $\theta(H) (\theta(H^+) + \theta(H_2^+)) (\theta(0) + \theta(H) - \theta(H^+) - \theta(H_2^+)) / RT$ which shows that $-\left(\frac{\partial s}{\partial E_P}\right)_{Ads.}$ remains stationary at the point $\theta(0) = \theta(H_2^+) = \frac{1}{2}$, $\theta(H^+) = \theta(H) = 0$ with respect to the decrease of $w(H)$.

**) Landolt: "Tabellen", 1, 2 Teil, 30-33 (1951).

***) Cf. Foot-note (**) on page 88.

$$\Delta\varepsilon(H_2^+)_0 = \alpha_x \Delta\varepsilon(H)_0, \quad (26.1.s)$$

where

$$0 < \alpha_x < 1. \quad (26.1.a)$$

We might pass over from mercury to lead just as from nickel to platinum did previously, varying $\varepsilon(H)_0$ and $\varepsilon(H_2^+)_0$ in accordance with (26.1.s) gradually keeping other factors constant.

The decrease of $\varepsilon(H_2^+)_0$ and of $\varepsilon(H)_0$ at constant E_p causes now the increase Δs of (3.7) according to (3.6), (3.4. ε) and (3.3) as,

$$\Delta s = \frac{GF}{N_A RT} \left\{ -\theta(H_2^+) (\theta(H) + \theta(0)) \Delta\varepsilon(H_2^+)_0 + \theta(H) (\theta(H^+) + \theta(H_2^+)) \Delta\varepsilon(H)_0 \right\} \quad (26.2)$$

or so much an upward shift of "Adsorption" similarly as in the case of h - or l -increase.

The corresponding shift ΔE_p of the intersection is,

$$\Delta E_p = \Delta s / \left\{ \left(\frac{\partial s}{\partial E_p} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_p} \right)_{Ads.} \right\}$$

or substituting Δs from (26.2),

$$\Delta E_p = -\alpha_T \Delta\varepsilon(H)_0, \quad (26.3.E)$$

where,

$$\alpha_T = \frac{GF^2}{N_A RT} \frac{\alpha_x \theta(H_2^+) (\theta(H) + \theta(0)) - \theta(H) (\theta(H^+) + \theta(H_2^+))}{\left(\frac{\partial s}{\partial E_p} \right)_{Pois.} - \left(\frac{\partial s}{\partial E_p} \right)_{Ads.}} \quad (26.3.\theta)$$

It may be shown,

$$0 < \alpha_x - \alpha_T < 1 \quad (26.3.X)$$

or

$$\alpha_x - 1 < \alpha_T < \alpha_x \quad (26.3.T)$$

as below.

The $\alpha_x - \alpha_T$ is, according to (3.9) and (26.3. θ),

$$\alpha_x - \alpha_T = \frac{\alpha_x \frac{N_A RT}{GF^2} \left(\frac{\partial s}{\partial E_p} \right)_{Pois.} + \alpha_x \theta(H^+) (\theta(0) + \theta(H)) + \theta(H) (\theta(H^+) + \theta(H_2^+))}{\frac{N_A RT}{GF^2} \left(\frac{\partial s}{\partial E_p} \right)_{Pois.} + (\theta(0) + \theta(H)) (\theta(H^+) + \theta(H_2^+))} \quad (26.4)$$

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which is essentially positive according to (4.5. *u*).

The difference of the second term in the denominator and the sum of the second and third term in the numerator is,

$$\begin{aligned} & (\theta(0) + \theta(H)) (\theta(H^+) + \theta(H_2^+)) - \alpha_x \theta(H^+) (\theta(0) + \theta(H)) - \theta(H) (\theta(H^+) + \theta(H_2^+)) \\ & = (\theta(0) + \theta(H)) \theta(H^+) (1 - \alpha_x) + \theta(0) \theta(H_2^+) - \theta(H^+) \theta(H). \end{aligned}$$

The first term on the right of the above identity is obviously positive and the second term too, according to (17.1) and (22.1).

The $\alpha_x - \alpha_T$ is thus the positive proper fraction as stated by (26.3. *X*).

The associated total increase of $w(\delta_i)$'s are according to (3.4), (3.3), (26.1. *s*) and (26.3. *E*),

$$\Delta w(H^+) = -\alpha_T \Delta \varepsilon(H)_0, \quad (26.5. H^+)$$

$$\Delta w(H_2^+) = (\alpha_x - \alpha_T) \Delta \varepsilon(H)_0, \quad (26.5. H_2^+)$$

$$\Delta w(H) = \Delta \varepsilon(H)_0. \quad (26.5. H)$$

We have deduced (26.5) as if increments involved were infinitesimal but it may readily be shown that the relation is valid qualitatively for any finite increments with appropriate $\alpha_x - \alpha_T$ or α_T satisfying the relation (26.3. *X*) or (26.3. *T*), it being the average $\int_{\varepsilon}^{\varepsilon + \Delta \varepsilon} \alpha_T d\varepsilon / \Delta \varepsilon$ or $\int_{\varepsilon}^{\varepsilon + \Delta \varepsilon} (\alpha_x - \alpha_T) d\varepsilon / \Delta \varepsilon$ of that given by (26.3. θ) or by (26.4) respectively for the infinitesimal increment of $\varepsilon \equiv \varepsilon(H)_0$ over its finite range of variation from ε to $\varepsilon + \Delta \varepsilon$.

Eq. (26.5) shows that $w(H^+)$ increases by a positive or negative proper fraction of $\Delta \varepsilon(H)_0$, $w(H_2^+)$ its positive proper fraction and $w(H)_0$ just by its amount.

Assuming $w(H)$ on nickel approximately zero at moderate hydrogen pressure and $\eta=0$ in accordance with §17, that on mercury or lead is now according to (26.5. *H*) *ca.* $2.6 - 0.37 = 2.2$ e-volt or $2.6 - 1.8 = 0.8$ e-volt respectively. The $\theta(H)$ is in consequence extremely small compared with $\theta(0)$ throughout the range of variation of $\varepsilon(H)_0$ from that on mercury to that on lead according to (3.4. θ). The appropriate average α_T is in consequence either a positive proper fraction or practically zero according to (26.3. θ) and hence $w(H^+)$ generally increases as $\Delta \varepsilon(H)_0$ decreases.

The $\varepsilon(H)_0$ -decrease thus causes such a variation of $w(\delta_i)$'s as the dotted line drawn through the tips of $w(\delta_i)$'s vertical lines slants down with turn from (1) onto (2) in Fig. 8 similarly as in the case of

l-decrease with negative α_l .

The work function decreases from 4.53 volt^{*)} of mercury to 4.15 volt^{*)} of lead in addition to the decrease of $\varepsilon(H)_0$ taken above into account. The former's effect may be superposed on the latter's by (6.3), α_l there being 0.53 at most at the ordinary condition of the hydrogen electrode according to § 20. The result is $(4.53-4.15) \times 0.53 = 0.2$ e-volt elevation at most of $w(\delta_i)$'s of charged δ_i but none of $w(H)$. This effect might be ignored in the present qualitative consideration with regard to the above rather large effect of $\varepsilon(H)_0$ -decrease.

§ 27 Change of Intermediate on Lead Cathode.

It is important that $w(H_2^+)$ lowers less than $w(H)$ does or the stability of $H_2^+(a)$ is decreased relative to that of $H(a)$ with decreasing $\varepsilon(H)_0$ according to (26.5) which is valid irrespective of the magnitude of $\theta(\delta_i)$'s during the "transition" from one to the other electrode. We might go with this decrease taking advantage of much the same amount of the work function as far as nickel, where $w(H)$ recedes $w(H_2^+)$ at last. The considerable increase of the work function from nickel to platinum narrowly restores the lowest $w(H_2^+)$ or the predominance of $H_2^+(a)$, which is however readily upset by lowering *l* as inferred in § 23.

The situation with lead is hence some half-way between platinum and mercury, $H_2^+(a)$ there being well protected against the momentary yield to $H(a)$ compared with on platinum but not so strongly as on mercury.

It would hence be possible for the momentary yield to take place on lead, whereas the *l*-decrease alone is sufficient to effect the same on platinum, by superposing the *h*-effect on it, if it be excluded on mercury. The $H_2^+(a)$ covering the electrode surface may be practically replaced by $H(a)$, so that the electrochemical mechanism prevailing converts into the catalytic mechanism by changing the surroundings from alkaline to acidic as shown in § 21, provided $\theta(H)/\theta(H_2^+)$ in alkaline surroundings lies above a certain bound or, according to (3.4. θ), the excess of $w(H_2^+)$ over $w(H)$ there is sufficiently small.

This conclusion is in accordance with the observation mentioned in the introduction that the lead cathode gives at -0.3 volt η in 1 atm hydrogen pressure the characteristic separation factor 7 of the catalytic mechanism, whereas in acid solution 3 of the electrochemical mechanism.

*) D'ANS & LAX: "Taschenbuch" Berlin 1949, p. 192.

§ 28 Cathodic Hydrogenation.

We have from (3.2. H_2^+) and (8.1. b),

$$\mu(H_2^+) = \mu(H^+, b) - Fl,$$

which shows that the chemical potential of $H_2^+(a)$ on the electrode surface may be chosen of any desired height by lowering l . Through the intermediary of $H_2^+(a)$ occurs now the hydrogenation of such an atom group as carbonyl, as mentioned in the introduction, which associates the intermediate on the electrode surface by virtue of its nucleophilic nature.*) An elementary reaction increases now its rate with the increase of the chemical potential of any participant which remains sufficiently abundant as detailed in the later Part of this series. The lowering of l should thus accelerate the hydrogenation of this kind, provided that $H_2^+(a)$ exists practically on the electrode surface at all or it does not yield to $H(a)$.

If it does at all, the rate of the hydrogenation of the above kind decreases, while the resulting $H(a)$ would cause such a hydrogenation as that of ethylenic linkage according to the scheme (i) in the introduction deteriorating the efficiency and selectivity of hydrogenation with respect to the atom group: $H(a)$ causes further the evolution of hydrogen gas which proceeds bimolecularly⁹⁾ with its coverage, further decreasing the current efficiency. The persistence of the cathode in $H_2^+(a)$ is thus favourable for both the efficiency and the selectivity of the cathodic hydrogenation.

This conclusion accounts for the well known competence of mercury and lead cathode for the cathodic hydrogenation of acetone and carbon dioxide.

Summary

Complex features of the following conclusions hitherto arrived at on hydrogen intermediates of the hydrogenation and the hydrogen electrode process were raised for explanation.

(1) Hydrogen intermediate on nickel is the adsorbed hydrogen atom $H(a)$ throughout the hydrogenation and the hydrogen electrode process, whereas that on the mercury hydrogen electrode is solely the adsorbed hydrogen-molecule-ion $H_2^+(a)$.

*) Cf. § 13.

(2) On platinum the hydrogen intermediate $H(a)$ fits in with the observation of hydrogenation in gas or in the presence of liquid benzene, whereas that of $H_2^+(a)$ exclusively in the presence of acetone or water throughout the hydrogenation and the hydrogen electrode process: the platinum cathode in aqueous electrolyte gave the electrolytic separation factor of deuterium 7 at 0.3 volt cathodic polarization in consistence with the hydrogen intermediate of $H(a)$, whereas experimental results below 0.1 volt led to the intermediate of $H_2^+(a)$.

(3) Lead gave the separation factor 7 or 3 at 0.3 volt cathodic polarization respectively in alkaline or in acidic electrolyte.

Referring to the model specified below was now discussed the effect of varying different factors determining the particular condition of the assembly consisting of the metallic catalyst, inclusive of the hydrogen electrode, and the surroundings, in which the reaction of interest was going on, in order to interpret the above features; any one of physically identical sites σ 's, which covered the catalyst's surface, was empty or occupied exclusively by one of $H(a)$ and $H_2^+(a)$ as well as by adsorbed hydrogen ion $H^+(a)$ concluded of existence under certain conditions elsewhere; the charge of $H^+(a)$ and $H_2^+(a)$ rested on a plane P parallel to that of the catalysts surface; on the opposite side of P to the catalyst the space charge of ions of density ρ in the surroundings was distributed one-dimensionally along the normal according to the law that $\rho \leq 0$ according as $E \geq 0$, where E is the electrostatic potential referred to that at infinite distance from P in the surroundings; the interaction among ions and charged intermediates in σ was the electrostatic one incorporated with that of impenetrability in terms of the above exclusive occupation of σ ; intermediates δ_i 's, which stood for $H^+(a)$, $H_2^+(a)$ or $H(a)$ according respectively as $i=1,2$ or 3, were individually in partial equilibrium prevailing by virtue of a certain rate-determining step with metal electron in the catalyst and hydrogen ion in the surroundings.

One-dimentional Poisson equation and the adsorption isotherm formulated in accordance with the above model were now solved simultaneously for the effect of the variation of the ion concentration in the surroundings, of the work function λ of the catalyst, of the chemical potential $\mu(H^+, b)$ of hydrogen ion, and of quantity l which included the chemical potential $\mu(H_2)$ of hydrogen gas and the electrode potential η of the catalyst referred to the reversible hydrogen electrode in the same surroundings, as

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$$l = \eta - \mu(H_2)/2F,$$

where F is Faraday.

The effect was expressed by that on $w(\delta_i)$, the work required to compose δ_i in a specified, empty σ keeping the whole assembly in statistical equilibrium throughout the appropriate process, which determined the probability $\theta(\delta_i)$ of occupation of σ by δ_i as,

$$\theta(\delta_i) = \exp\left(-\frac{w(\delta_i)}{RT}\right) / \sum_{i=0}^{i=3} \exp\left(-\frac{w(\delta_i)}{RT}\right),$$

where $i=0$ referred to none of occupant for which $w(\delta_i)=0$.

The conclusion was summarised in the Table, where $\Delta\lambda$ etc. showed respectively the increment of the factors λ etc. defined in the first column.

Factors Varied	$w(H^+)$	Increment of $w(H_2^+)$	$w(H)$	Range of α_λ, α_h & α_l
Work Function λ	$-F\alpha_\lambda \Delta\lambda$	$-F\alpha_\lambda \Delta\lambda$	0	$1 > \alpha_\lambda > 0$
Chem. Pot. $\mu(H^+, b)$ of Hydrogen Ion $h = \mu(H^+, b)/F$	$-F(1-\alpha_h) \Delta h$	$-F(1-\alpha_h) \Delta h$	0	$1 > \alpha_h > 0$
Electrode Pot. η and Chem. Pot. $\mu(H_2)$ of Hydrogen $l = \eta - \mu(H_2)/2F$	$F\alpha_l \Delta l$	$F(1+\alpha_l) \Delta l$	$F\Delta l$	$1 > \alpha_l > -1$

Further conclusion was that the increase or decrease of the ion concentration shifted α_λ , α_h and $|\alpha_l|$ toward zero or 1 respectively, E or $\frac{dE}{dx}$ at P vanishing at the respective extremities, where x is the distance from the catalyst's surface along its normal.

In extension of the above was discussed the effect of BRÖNSTED'S base B or acid AH in the surroundings, which were incapable of causing any electrolytic dissociation inclusive of that of B or AH in its bulk; the model was modified so that B attached to $H^+(a)$ or $H_2^+(a)$ by its proton affinity or the acid rest A^- resulting from AH made an additional occupant of σ . The conclusion was formally similar to that of h given in the Table, h being identified with $-\mu(B)/F$ or with $\mu(AH)/F$, where $\mu(B)$ or $\mu(AH)$ was the chemical potential of B or AH respectively; the appropriate α_h decreased from 1 as occupant B or A^-

of σ increased from zero just as in the case of the foregoing model, when the space charge outside P assumed the part of the charge of $H^+(a)$ to which B is attached or of A^- : α_h approached however 1 again as the probability of occupation by B or A^- tended to 1 in deviation from the case in the presence of ion, when α_h tended to 0 with their increasing concentration or with the increasing space charge: this difference was attributed to the impenetrability between δ_i 's and the additional occupant giving rise to the h -effect, particularly allowed for in this case.

The complex features raised above was now accounted for on the basis of the above theoretical conclusions.

The $w(\delta_i)$'s on nickel in gas was plausibly estimated as the starting point and shown that its transition to platinum with increasing work function favoured the relative increase of $H_2^+(a)$, if not enough to play the leading part in the observable reaction. The introduction of nucleophilic reagent as acetone or water was shown to amplify the decrease of $w(H_2^+)$ or the further increase of $\theta(H_2^+)$ thus accounting for the change of leading intermediate from $H(a)$ on nickel to $H_2^+(a)$ on platinum.

It was then concluded that the l -decrease of nickel or platinum electrode initially increased $H(a)$ relative to $H_2^+(a)$ but acted reversely later at sufficiently low l , thus accounting for the contrast of the hydrogen intermediate of $H_2^+(a)$ or of $H(a)$ respectively consistent with experiments at lower or higher cathodic polarization (higher or lower l). It was concluded on the other hand from the lack of any sign of $H_2^+(a)$ on nickel playing the leading part even in the severest condition of considerable l -decrease, that $w(H)$ there was originally appreciably low or $H(a)$ was of such a high stability.

The $w(\delta_i)$'s on mercury hydrogen electrode was determined as $w(H) \gg w(H^+) > w(H_2^+) > 0$ on the basis of the previous detailed calculation [HORUHI, KEII & HIROTA: This Journal 2, 1 (1951)]. The l -decrease preferred again the $H(a)$ -increase initially, but far from sufficient to cause any appropriate reaction owing to extremely high a value of $w(H)$ in distinction from the case of Pt.

The $w(\delta_i)$'s on lead hydrogen electrode was now derived from those on mercury arriving at the conclusion that the relative increase of $H(a)$ to $H_2^+(a)$ under the course of l -decrease was not so appreciable as in the case of platinum, but still not practically exclusive as in the case of mercury. On this l -effect was now superposed the h -effect,

which increased $H_2^+(a)$ relative to $H(a)$ according to the Table and to the above $\theta(\delta_i)$ expression; the transition of the separation factor from 7 to 3, appropriate respectively to the intermediate of $H(a)$ to $H_2^+(a)$, by changing the electrolyte from alkaline to acidic was thus explained.

It was finally shown that the chemical potential of $H_2^+(a)$ was raised by the decrease of l to accelerate the hydrogenation of nucleophilic reagent as acetone apt to attach to $H_2^+(a)$, if it remained sufficiently abundant or was protected from yielding to $H(a)$ by high a value of $w(H)$ as in the case of *Hg* and *Pb*; the known expedience of their electrodes for the cathodic hydrogenation of such reagent was thus accounted for.

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