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Author(s)	HORIUTI, Juro; KEII, Tominaga; HIROTA, Kozo
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MECHANISM OF HYDROGEN ELECTRODE OF MERCURY. "ELECTROCHEMICAL MECHANISM"

By

Juro HORIUTI, Tominaga KEII and Kozo HIROTA

INTRODUCTION

The elmentary reaction underlying to the hydrogen electrode process such as the electrolytic evolution of hydrogen gas at a cathode, the consumption of hydrogen at an anode, the phenomenon of reversible hydrogen electrode and finally the catalysed interchange reaction of hydrogen with water in the presence of metall catalyst may be formulated as that

$$2H^+B + 2\ominus \rightleftarrows H_2 + 2B$$

where B is the base of generalised sense due to Brönsted and $\ominus$ the metal electron. The reaction may be considered as consisting of three acts among two protons and two electrons, i. e. of twice the neutralizations of protons (or the ionization of hydrogen atom) and of once the combination (dissociation) of two hydrogen nuclei, which may take place in three different possible sequences any one of each sequence possibly governing the rate.[1)*)] On the basis of several experiments and theoretical considerations, OKAMOTO and one of the present authors[1)] have previously raised two of them as the possible mechanisms, i. e. the catalytic mechanism, in which the recombination of two chemisorbed hydrogen atoms on the electrode (or the reversed process) governed the rate, and the electrochemical mechanism, in which the neutralization of hydrogen molecule ions, H_2^+, situated at the electrode-solution interface to form a hydrogen molecule, H_2, (or the reversed process) i. e., the

*) It is however not altogether claimed that these cover all possible ones; any one consisting in the repetition of a set involving more than two electrons and two protons or even any chain mechanism may a priori possible.

1) HORIUTI and OKAMOTO, Sci. Pap. I.P.C.R. Tokio, 28 (1936), 231.

process, $H_2 \rightleftharpoons H_2^+$ was the rate determining step*). The catalytic mechanism was attributed to the hydrogen electrode process on Ni, Au, Cu, Fe, and Pb (in alkaline solution) and the electrochemical mechanism to that on Hg, Sn and Pb (in acidic solution).

After the preliminary account several experimental and theoretical investigations have been carried out in this laboratory[2] in confirmation of the catalytic mechanism. The rate of the governing reaction of the catalytic mechanism, i. e. of the recombination of chemisorbed atoms (or the reversed process) was thus statistical mechanically formulated to draw semi-quantitative conclusions on the behavior of the electrode process which were successfully confirmed by experiments.

It is the object of the present paper to establish the electrochemical mechanism with special reference to mercury electrode.

The general procedure was to derived several conclusions from the claim that it is the neutralization of adsorbed hydrogen molecule ion which governs the rate of evolution of hydrogen gas on a cathodically polarised mercury electrode in an aqueous solution of hydrogen ions and to confirm latters by experimental data.

The rate of the claimed governing reaction was thus expressed in accordance with our general theory of the absolute reaction rate[3),4)] in terms of statistical mechanical functions introduced by one of present authers[5].

By substituting the hydrogen electrode with a simplified model the formula for the reaction rate and the populations of hydrogen ions, hydrogen atoms, hydrogen molecule ions and hydrogen molecules, which will hereafter be called elementary systems, in the electrode-solution interface are expressed in Chapter I in terms of these statistical mech-

*) According to the original statement of the mechanism, it was the act of formation of hydrogen molecule from a chemisorbed hydrogen atom and a proton at the same time of neutralization, which governed the rate of the electrode process. The different representation was advanced here, since as seen later it turned out by an actual calculation of interatomic potentials, that the stable coordination of H and H^+ prior to the neutralization was adequately covered by the word "hydrogen molecule ion adsorbed on the electrode".

2) a. Okamoto, Horiuti and Hirota, Sci. Pap. I.P.C.R. Tokio, **29** (1936), 223.
b. Hirota and Horiuti, ibid., **30** (1936), 151.
c. Okamoto and Iijima, Bull. Inst. P.C.R. Tokio. **16** (1947), 1426. ((in Japanes).
d. Horiuti and Okamoto, Bull. Chem. Soc. Japan, **13** (1938), 216.
e. Okamoto, J. Faculty Sci. Hokkaido Imp. Univ. Ser. IV, **2** (1938), 116.

3) Horiuti, Bull. Chem. Soc. Japan. **13** (1938), 210.

4) Hirota and Horiuti, Sci. Pap. I.P.C.R. Tokio, **34** (1938), 1174.

5) Horiuti, Journal of The Research Institute for Catalysis, Hokkaido University, Vol. I, No. 1 (1948), 8.

anical functions.

The next step was the evaluation of these functions in Chapter II by developing the dynamics of the elementary systems.

The absolute reaction rate or the electrolytic current densty is now evaluated, several associate quantiative conclusions being drawn with regard to the relation between the current density and the electrode potential and the isotopic separation factor or the ratio of the specific rates of the electrolytic evolution of protium to that of deuterium from the solution were derived with the satisfactory concordance with available experimental data. (Chapter III).

CHAPTER I. THE EXPRESSION FOR THE ABSOLUTE REACTION RATE.

§ 1. Specification of the Assembly.

Our assembly with which the rates of the elementary reaction

$$H_2^+ + \ominus \longrightarrow H_2 \qquad (1.1)$$

and its reversed reaction are to be calculated consists of mercury, the solution containing hydrogen ions and the gaseous mixture of vapour and hydrogen gas. The assembly is kept at a constant temperature and the mercury phase cathodically polarised against the solution by an external electromotive force. Following simplifying assumptions, besides later numerical ones, will be introduced with regard to the configurations and to the behaviors of the assembly;

1°. The mercury and the solution have a plane interface, where the elementary reaction of interest takes place, mercury atoms there being arranged on a hexagonal pattern with the shortest distance 3.26 Å[6]. The mercury surface will mean the plane through centres of these mercury atoms in what follows.

2°. Each mercury atom on the mercury surface forms a cage, as called in what follows, being accompanied by a water molecule on the boundary layer of the solution, whose centre is allowed to move along the normal to the mercury surface through the mercury atom over a certain range leaving a gap between the spherical models of mercury atom and of the water molecule, of radii 1.48 Å and 1.38 Å, respectively, of length amounting from zero to a few molecular diameters.

3°. When the cage is empty, the dipole of the water molecule is directed with equal probability over the whole range of solid angle Ω,

6) O. Kratzky, Phys. Zeit., **34** (1933), 482.

while that to find its centre per unit length of the axis within the specified range is that expected from the concentration in the bulk of the solution.

4°. The configuration of the cage will be specified by Σ which stands for a definite Ω, and the distance L between the centres of the Hg atom and the water molecule. Beyond the boundary layer we have the aqueous acid solution after WEBB's model[7].

5°. The elementary system remains at its lowest electronic state throughout its all possible nuclear configurations.

6°. The elementary reaction proceeds only when the elementary system involved is situated inside the cage.

7°. The resonance energy between two different electronic states, $H_2^+ + \ominus$ and H_2 at the indentical or nearly identical nuclear configuration is taken to be big enough to assure a free transition from one to the other but small enough to be neglected for calculating the reaction rate by order of magnitude.

§ 2. Introduction of Statistial Mechanical Functions.

Before starting with our deduction on the basis of the model specified in the foregoing section, we will quote here a set of four functions, p^δ, q^δ, $\Theta_{\sigma(\delta)}$ and $\Theta_{\sigma(0)}$, for the sake of simplifying the statistical mechanical treatment[5].

By C and $\mathfrak{Q}C$ we will denote a macroscopic assembly composed of our systems free from any microscopic constraints and its partition function respectively.

The function p^δ is defined by

$$p^\delta = \frac{\mathfrak{Q}C^\delta}{\mathfrak{Q}C}, \tag{2.1}$$

where $\mathfrak{Q}C^\delta$ is partition function of C augmented by an elementary system δ. The p^δ is thus related to the chemical potential μ^δ, as that,

$$\mu^\delta = -RT \log p^\delta. \tag{2.2}$$

The function q_σ^δ is defined by

$$q_\sigma^\delta = \frac{\mathfrak{Q}C_{\sigma(\delta)}^\delta}{\mathfrak{Q}C_{\sigma(0)}} \tag{2.3}$$

where $\mathfrak{Q}C_{\sigma(\delta)}^\delta$ or $\mathfrak{Q}C_{\sigma(0)}$ is partition function of C^δ or C, respectively, subject to the microscopic constraint that a cavity σ of molecular di-

7) WEBB, J. Am. Chem. Soc., 48 (1926), 2589.

mension inside the assembly is occupied by δ or vacant. Thus q_σ^δ has the physical meaning that $-RT\log q_\sigma^\delta$ is the reversible work required to bring up one mol of δ from its standard state into σ.

We define further the functions $\theta_{\sigma(\delta)}$ and $\theta_{\sigma(0)}$, which has the physical meaning of the respective probability that σ is occupied and evacuated by δ, in terms of the partition functions appeared in (2.1) and (2.3) as that

$$\theta_{\sigma(\delta)} = \frac{\mathfrak{Q}C^{\delta}_{\sigma(\delta)}}{\mathfrak{Q}C^{\delta}} \tag{2.4}$$

and that

$$\theta_{\sigma(0)} = \frac{\mathfrak{Q}C_{\sigma(0)}}{\mathfrak{Q}C} \ . \tag{2.5}$$

It follows immediately from (2.1), (2.3), (2.4), and (2.5) that

$$p^{\delta} = \frac{\theta_{\sigma(0)}}{\theta_{\sigma(\delta)}} q_\sigma^\delta \ . \tag{2.6}$$

By the set of these functions including that for the critical complex δ^*, for the elementary reaction the general form of absolute reaction rate $\vec{v}$ is represented as that

$$\vec{v} = \frac{kT}{h} \frac{p^{\delta^{*\,\delta)}}}{p^{\delta I}} \tag{2.7}$$

where δ^I is the initial complex.

§ 3. Special Form of Statistical Mechanical Functions.

We will now specialize the functions introduced in the foregoing section to our present case and derive relations useful for later developements.

(i) Denoting the partition function of C with the constraint that one of cage K is empty by $\mathfrak{Q}C_{K(0)}$ and the latter with K at a particular confuguration Σ by $\mathfrak{Q}C_{K(0),\Sigma}$, we have the relation that

$$\mathfrak{Q}C_{K(0)} = \int \mathfrak{Q}C_{K(0),\Sigma}\, d\Sigma \tag{3.1}$$

where $\mathfrak{Q}C_{K(0),\Sigma}$ is reckoned per unit extension of Σ.

Defining further $\mathfrak{Q}C^{\delta}_{K(\delta)}$ that of $C^{\delta}_{K(\delta)}$ derived from $C_{K(0)}$ by putting additional δ in K and $\mathfrak{Q}C^{\delta}_{K(\delta),\Sigma}$ that of the latter with K at a particular confuguration Σ we have that

$$\mathfrak{Q}C^{\delta}_{K(\delta)} = \int \mathfrak{Q}C^{\delta}_{K(\delta),\Sigma}\, d\Sigma \ . \tag{3.2}$$

It is now according to the difinition of q_σ^δ that

$$q^{\delta}_{K,\Sigma} = \frac{\mathfrak{Q}C^{\delta}_{K(\delta),\Sigma}}{\mathfrak{Q}C_{K(0),\Sigma}} \tag{3.3}$$

or that

$$q^{\delta}_{K} = \frac{\mathfrak{Q}C^{\delta}_{K(\delta)}}{\mathfrak{Q}C_{K(0)}} . \tag{3.4}$$

From the above four relations we have further that

$$q^{\delta}_{K} = \int q^{\delta}_{K,\Sigma}\, \rho_{\Sigma}\, d\Sigma \tag{3.5}$$

where

$$\rho_{\Sigma} = \frac{\mathfrak{Q}C_{K(0),\Sigma}}{\int \mathfrak{Q}C_{K(0),\Sigma}\, d\Sigma} \tag{3.6}$$

is the probability for the unoccupied cage to assume unit extension of Σ, according to 2° in §1 or $0.233/4\pi$ per Å per unit solid angle taking molecuar density of water molecules in the bulk of the solution 3.37×10^{-2} Å^{-3} and the area of the mercury plane shared by one mercury atom 9.1 Å^2.

(ii) For our assembly of definite composition in which interconversion between elementary systems, $H_2^+ + \ominus$ and H_2, is forbidden but those

$$\begin{aligned} &(H_2)_K \rightleftharpoons (H_2)_g , \\ &(H^+)_K \rightleftharpoons (H^+)_l , \\ &(H)_K \rightleftharpoons (H^+)_l + \ominus \end{aligned} \tag{3.7}$$

and $(H_2^+)_K \rightleftharpoons 2(H^+)_l + \ominus$,

are allowed, we have, according to the relation[5],

$$p^{\delta_A} = p^{\delta_B} \tag{3.8}$$

for mutually interconverting elementary systems δ_A and δ_B, or that

$$p^{H_2}_{K} = p^{H_2}_{g} , \tag{3.9}$$

$$p^{H^+}_{K} = p^{H^+}_{l} , \tag{3.10}$$

$$p^{H}_{K} = p^{H^+}_{l} p^{\ominus}_{m} , \tag{3.11}$$

and

$$p^{H_2^+}_{K} = (p^{H^+}_{l})^2 p^{\ominus}_{m} \tag{3.12}$$

where the suffix l, g and m denote the δ in the solution, gas and metal respectively.

(iii) According to (2.2), we have

$$p^{\ominus}_{m} = e^{eV/kT} \tag{3.13}$$

for the metal electron, where e is the elementary charge and V the electrode potential.

§ 4. Special Relations between Functions.

The general relation (2.6) between p^{δ} and q_{δ}^{δ} may be written for our particular case, as that

$$q_K^{H^+} = \frac{\theta_{H^+}}{\theta_0} p_K^{H^+}, \tag{4.1}$$

$$q_K^{H_2^+} = \frac{\theta_{H_2^+}}{\theta_0} p_K^{H_2^+}, \tag{4.2}$$

$$q_K^{H} = \frac{\theta_{H}}{\theta_0} p_K^{H} \tag{4.3}$$

and

$$q_K^{H_2} = \frac{\theta_{H_2}}{\theta_0} p_K^{H_2}. \tag{4.4}$$

We have, now by virtue of (3.9), (3.10), (3.11) and (3.12), that

$$\frac{\theta_{H^+}}{q_K^{H^+} p_m^{\ominus} p^{H}} = \frac{\theta_{H_2^+}}{q_K^{H_2^+} p_m^{\ominus}} = \frac{\theta_{H}}{q_K^{H} p^{H}} = \frac{\theta_{H_2} p_g^{H_2}}{q_K^{H_2} (p^{H})^2} = \frac{\theta_0}{(p^{H})^2} \tag{4.5}$$

where abbreviations,

$$\theta_{K(\delta)} = \theta_{\delta}, \qquad \theta_{K(0)} = \theta_0 \tag{4.6}$$

and

$$p_l^{H^+} p_m^{\ominus} = p^{H} \tag{4.7}$$

will be used in what follows throughout.

Since $\theta_{H^+} + \theta_{H_2^+} + \theta_{H} + \theta_{H_2} + \theta_0 = 1$ so far as these elementary systems are all possible inhabitants in the cage, we have by summing up the numerators and denominators of (4.5) respectively that

$$\theta_0 = (p^{H})^2 / S \tag{4.8}$$

or substituting θ_0 back into (4.5) from (4.8), that

$$\theta_{H^+} = q_K^{H^+} p_m^{\ominus} p^{H} / S, \tag{4.9}$$

$$\theta_{H_2^+} = q_K^{H_2^+} p_m^{\ominus} / S, \tag{4.10}$$

$$\theta_{H} = q_K^{H} p^{H} / S \tag{4.11}$$

and

$$\theta_{H_2} = q_K^{H_2} (p^{H})^2 / S \tag{4.12}$$

where

$$S = q_K^{H^+} p_m^{\ominus} p^{H} + q_K^{H_2^+} p_m^{\ominus} + q_K^{H} p^{H} + q_K^{H_2} (p^{H}) / p_g^{H_2} + (p^{H})^2. \tag{4.13}$$

§ 5. Evaluation of p^{H}.

It will be shown by the analogous deduction that p^{H} can be expressed in terms of electrode potential η referred to a reversible hydrogen electrode and of $p^{H_2}_{g,0}$ of the relevant hydrogen gas, leading to the evaluation of p^{H} from given experimental conditions.

According to (3.13) the ratio of the function of metal electron of the electrode is given by

$$p^{\ominus}_{m}/p^{\ominus}_{m,0} = e^{\epsilon\eta/kT} \tag{5.1}$$

where

$$\eta = V - V_0 \tag{5.2}$$

is the electrode potential referred to that of the reversible bydrogen electrode.

Since however the reaction,

$$H_2 \rightleftharpoons 2H^+ + 2\ominus,$$

is in equilibrium at the reversible hydrogen electrode, we have according to (3.8) and (4.7) that

$$p^{H_2}_{g,0} = (p^{H}_{0})^2 \tag{5.3}$$

where the sufix 0 designates the quantities appropriate to the reversible hydrogen electrode.

Eliminating now $p^{\ominus}_{m}$ and $p^{\ominus}_{m,0}$ form (5.1) and (5.3) remembering (3.8), we have that

$$p^{H} = \sqrt{p^{H_2}_{g,0}}\, e^{\epsilon\eta/kT} \tag{5.4}$$

or according to the relation, $p^{\delta}_{g} = Q^{\delta}/N^{\delta}_{g}$[5] that

$$p^{H} = \sqrt{Q^{H_2}_{g}/N^{H_2}_{g,0}}\, e^{\epsilon\eta/kT} \tag{5.5}$$

where $Q^{H_2}_{g}$ is the partition function of a hydrogen molecule in unit volume and $N^{H_2}_{g,0}$ the number of hydrogen molecules per unit volume in the hydrogen gas of the reversible hydrogen electrode.

For an electrode polarised by η_C against a normal calomel electrode at 19°C in N/10. HCl solution, for example, p^{H} may be thus evaluated by (5.5) as shown in Table I below, taking into consideration that the potential of the normal calomel electrode referred to the reversible hydrogen electrode at one atomsphere in the same solution amounts to 0.34 volt or that

$$\eta - \eta_C = 0.34 \text{ volt}. \tag{5.6}$$

TABLE I

$-\eta_C\ (=-\eta+0.34)$ volt	0.38	0.41	0.44	1.23	1.26	1.29
p^{H}	1.85×10^{274}	5.62×10^{273}	1.17×10^{273}	4.04×10^{259}	1.22×10^{259}	3.71×10^{258}

§ 6. Rate Expression for the Governing Step.

By the set of these functions described above, absolute reaction rate, $\vec{v}$, of the governing step, $H_2^+ + \ominus \rightarrow H_2$ and $\overleftarrow{v}$ of its reverse one, $H_2 \rightarrow H_2^+ + \ominus$, are expressed*) as that

$$\vec{v} = \frac{kT}{h} G\Theta_{K(0)} \frac{q_K^*}{p_{K^2}^{H_2^+} p_m^{\ominus}}, \tag{6.1 $\vec{v}$}$$

$$\overleftarrow{v} = \frac{kT}{h} G\Theta_{K(0)} \frac{q_K^*}{p_{g,0}^{H_2}}. \tag{6.1 $\overleftarrow{v}$}$$

The $p_{K^2}^{H_2^+} p_m^{\ominus}$ in (6.1 $\vec{v}$) may be replaced by $(Q_g^{H_2}/N_{g,0}^{H_2})\, e^{2\mathfrak{e}\eta/kT}$ according to (3.12), (4.7) and (5.5) as that

$$\vec{v} = \frac{kT}{h} G\Theta_{K(0)} q_K^* \frac{N_{g,0}^{H_2}}{Q_g^{H_2}} e^{-2\mathfrak{e}\eta/kT} \tag{6.2 $\vec{v}$}$$

and $p_{g,0}^{H_2}$ in (6.1 $\overleftarrow{v}$) by $(Q_g^{H_2}/N_{g,0}^{H_2})$ according to (5.3) as that

$$\overleftarrow{v} = \frac{kT}{h} G\Theta_{K(0)} q_K^* \frac{N_g^{H_2}}{Q_g^{H_2}} \tag{6.2 $\overleftarrow{v}$}$$

rembering that $p_{g,0}^{H_2}$ is the particular value of $p_g^{H_2}$ at $\eta = 0$, where q_K^* is $q_K^{\ddagger}$ appropriate to the critical complex and G the total number of cages.

The current $\vec{I}$ and $\overleftarrow{I}$ accompanied by the rate-determining step and its reverse process respectively are now expressed as that

$$\vec{I} = 2\mathfrak{e} \frac{kT}{h} G\Theta_{K(0)} q_K^* \frac{N_{g,0}^{H_2}}{Q_g^{H_2}} e^{-2\mathfrak{e}\eta/kT} \tag{6.3}$$

and

$$\overleftarrow{I} = 2\mathfrak{e} \frac{kT}{h} G\Theta_{K(0)} q_K^* \frac{N_g^{H_2}}{Q_g^{H_2}}. \tag{6.4}$$

The $\vec{I}$ and $\overleftarrow{I}$ will respectively be called negative and positive currents in what follows.

*) Eq. (24. 9, $\vec{v}$) in the reference (5), κ being assumed here unity.

CHAPTER II. EVALUATION OF q_K^δ FOR Hg-ELECTRODE.

§ 7. General Procedure.

The q_K^δ may be evaluated according to the relations (3.5)

$$q_K^\delta = \int q_{K\Sigma}^\delta \rho_\Sigma d\Sigma ,$$

and (3.6)

$$\rho_\Sigma = \frac{\mathfrak{Q}C_{K(0),\Sigma}}{\int \mathfrak{Q}C_{K(0),\Sigma}\, d\Sigma}$$

by calculating $q_{K,\Sigma}^\delta$ as the function of Σ and integrating over the region where ρ_Σ is still significant. This will be done with the following approximations: (1°) that the distribution and the individual mean configurations of the elementary systems H^+, H, H_2, and H_2^+ in the cages around the one in question are affected neither by the configuration of the latter cage nor by absence or presence of elementary system in it. (2°) that the potential of the elementary system due to particles outside the cage can be replaced by the mean over its possible configurations: and (3°) that the motion of the elementary system is quick enough that the configuration of the cage may be considered quasi-statical with regard to the former.

It follows then that partition function of the assembly at any instantaneous configuration Σ of the cage $\mathfrak{Q}C_{K(\delta),\Sigma}^\delta$, may be factorized in two parts; i.e.

$$\mathfrak{Q}C_{K(\delta),\Sigma}^\delta = \Big(\sum_i e^{-\varepsilon_i/kT}\Big)_{K,\Sigma}\, \mathfrak{Q}'C_{K(\delta),\Sigma}^\delta \qquad (7.1)$$

where ε_i denotes the i-th energy state of the elementary system moving in the quasi-statical potential field of the cage of the configuration Σ, referred to that at rest at its equilibrium configuration and $\mathfrak{Q}'C_{K(\delta),\Sigma}^\delta$ the partition function of the assembly when the elementary system is at rest inside the cage K at configuration Σ.

The function $q_{K,\Sigma}^\delta$ of the elementary system as defined by (3.3) is now,

$$q_{K,\Sigma}^\delta = \frac{\mathfrak{Q}C_{K(\delta),\Sigma}^\delta}{\mathfrak{Q}C_{K(0),\Sigma}^\delta} = \Big(\sum_i e^{-\varepsilon_i/kT'}\Big)_{K,\Sigma} \frac{\mathfrak{Q}'C_{K(\delta),\Sigma}^\delta}{\mathfrak{Q}\,C_{K(0),\Sigma}} \qquad (7.2)$$

The logarithm of the second factor multiplied by $-RT$ which gives the reversible work required to bring up the elementary system from its state of reference to that of rest in K at configuration Σ will be

called the free energy of the elementary system at rest and denoted by $Y^{\delta}_{0\Sigma,}$.

The $q^{\delta}_{K,\Sigma}$ is now,

$$q^{\delta}_{K,\Sigma} = e^{-Y^{\delta}_{0,\Sigma}/kT}\left(\sum_{i} e^{-\varepsilon^{\delta}_{i,\Sigma}/kT}\right). \tag{7.3}$$

It is now necessary to evaluate $Y^{\delta}_{0,\Sigma}$ and $\varepsilon^{\delta}_{i,\Sigma}$ at every configuration Σ, which in turn requires the knowledge of the quasi-statical potential of the elementary system at every Σ. The latter potential is however given with respect to our model by

$$V^{\delta}_{\Sigma} = V^{\delta}_{K,\Sigma} + V^{\delta}_{M,\Sigma} + V^{\delta}_{W,\Sigma} + V^{\delta}_{E} \tag{7.4}$$

where $V^{\delta}_{K,\Sigma}$ is the sum of the mutual potential of the particles composing the elementary system and that due to the cage K, $V^{\delta}_{M,\Sigma}$ that due to the mercury electrode, $V^{\delta}_{W,\Sigma}$ that due to the WEBB's model of the aquous solution around the cage and V^{δ}_{E}, that due to other elementary systems inside the surrounding cages.

The former two potentials may be calculated as known functions of the coordinates of the elementary system from individual interatomic potentials. The $V^{\delta}_{W,\Sigma}$ depends on the other hand, besides on the coordinates of the elementary system, on the mean configuration of the WEBB's model, which is governed by the electronic state and the mean configuration of the elementary system just going to be determined, wheras V^{δ}_{E} on the population of the elementary system around the cage of interest, which, if not reciprocally affected by the elementary system in the cage according to (1°), is only determined according to (4.9), (4.10), (4.11), (4.12), and (4.13) by knowledge of q^{δ}_{K}'s in question.

To do with this situation, present authors proceed as will be described below seperately with the elementary systems at definite electronic configuration, i. e. H^{+}. H. H_2, and H_2^{+} which will be called the stable complexes in what follows and with the critical complex.

§ 8. The q^{δ}_{K} of Stable Complexes; I. Procedure of Calculation.

In the case of the stable complexes, we proceed to determine the quasi-statical potential field for the elementary systems in cages with an approximation of ignoring the gradient of the potential due to particles outside the cage, i. e. of $V^{\delta}_{M,\Sigma} + V^{\delta}_{W,\Sigma} + V^{\delta}_{E}$, in the neighbourhood of the mean configuration. Evaluating $V^{\delta}_{K,\Sigma}$ from various sources of interatomic potentials the dynamics of the elementary systems could thus be dealt with for any fixed configuration Σ of the cage. The

actual calculation of $\sum_i e^{-\varepsilon_{i,K,\Sigma}/kT'}$ is however carried through only at a configuration Σ_0, where another factor, $Y^{\delta}_{0,\Sigma}$ in (7.3) determined as below is found minimum, the resulting factor $\sum_i e^{-\varepsilon_{i,K,\Sigma_0}/kT'}$ being used as a constant at any other configurations.

The calculation of $Y^{\delta}_{0,\Sigma}$ to complete $q^{\delta}_{K,\Sigma}$ and hence q^{δ}_{K} according to (3.5) is carried out in two stages. In the first stage $Y^{\delta}_{0,\Sigma}$ is expressed as the sum of the work done against the force due to different part of the assembly, when the elementary system is reversibly brought up to the specified position in the cage, i.e.

$$Y^{\delta}_{0,\Sigma} = Y^{\delta}_{0,K,\Sigma} + Y^{\delta}_{I,\Sigma} + Y^{\delta}_{E} \tag{8.1}$$

where $Y^{\delta}_{0,K,\Sigma}$ is the part due to the interaction of particles with each other and with the cage, $Y^{\delta}_{I,\Sigma}$ that due to the electrode and WEBB's model around the cage and Y^{δ}_{E} that due to the surrounding elementary systems.

The $Y^{\delta}_{0,K,\Sigma}$ may be identified with the corresponding potential $V^{\delta}_{0,K,\Sigma}$ since their configurations remain unchanged with the position of the elementary system inside and Y^{δ}_{E} similarly with V^{δ}_{E} according to § 7, (1°) whereas $Y^{\delta}_{I,\Sigma}$ which includes the work due to the WEBB's model not, since the configuration of the latter and in consequence the statistical mean of the force due to the latter depends on the momentary configurations of the elementary system during the course of bringing it up to the specified position in the cage. Evaluating them individually as described later the sum $Y^{\delta'}_{0,\Sigma}$ of the first two terms which only depend on L and Ω is now developed around the mininum value Y^{δ}_{0,Σ_0} as the quadratic function of Σ in the form,

$$Y^{\delta'}_{0,\Sigma} = Y^{\delta}_{0,\Sigma_0} + \Gamma^{\delta}_{L}(L-L_0)^2 + \Gamma^{\delta}_{\Omega}(\Omega-\Omega_0)^2, \tag{8.2}$$

q^{δ}_{K} is obtained according to (7.3), (7.4) and (8.1) as a known function of V^{δ}_{E}, i.e.

$$q^{\delta}_{K} = q^{\delta}_{K} e^{-V^{\delta}_{E}/kT'}, \tag{8.3}$$

$$q^{\delta}_{K} = \left(\sum_i e^{-\varepsilon_i/kT}\right)_{K,\Sigma} \frac{\rho_{\Sigma}\pi kT'}{\sqrt{\Gamma^{\delta}_{L}\Gamma^{\delta}_{\Omega}}} e^{-Y^{\delta}_{0,\Sigma_0}/kT'}. \tag{8.4}$$

The calculations so far outlined are carried out as shown in the subsequent sections with individual elementary systems in the following steps;

(a) Evaluation of $V^{\delta}_{K,\Sigma}$; the determination of the mean position and the corresponding value $V^{\delta}_{0,K,\Sigma}$ or $Y^{\delta}_{0,K,\Sigma}$ therefrom.

(b) Determination of $Y^{\delta}_{I,\Sigma}$.

(c) Determination of $\sum_0$ corresponding to the minimnm value of $Y^{\delta'}_{0,\Sigma}$.

(d) Determination of ε^{δ}_{i},s at $\sum_0$ by developing $V^{\delta}_{K,\Sigma}$ into the quadratic function of small displacements of the configuration of the elementary system from the equilibrium position and solving the appropriate dynamical problem.

(e) Determination of $\int \rho_{\Sigma} e^{-Y^{\delta'}_{0,\Sigma}/kT'} d\Sigma$ by developing $Y^{\delta'}_{0,\Sigma}$ into the quadratic function of L and Ω around Y^{δ}_{0,Σ_0}.

(f) Determination of q^{δ}_{K} according to (8.4) with the special example of a mercury electrode polarised in N/10 HCl solution at 19°C at several different potentials.

In the next stage §13 the potential V^{δ}_{E} in (7.4) is expressed as a function of populations Θ_{δ}'s and of the electrostatical potential ζ_0 there, where δ is situated, by evaluating mutual interaction potentials among elementary systems on the basis of their mean configuration worked out above.

The q^{δ}_{K} thus obtained as the function of Θ_{δ} and ζ_0 gives, when combined with (4.9), (4.10), (4.11) and (4.12) in § 4, populations of respective elementary systems and hence the total charge due to elementary systems in the cage as the function of ζ_0. The total charge and ζ_0 have on the other hand to satisfy POISSON's equation. Solving the two simultaneous equations in §14, Θ_{δ}'s, ζ_0 and in consequence q^{δ}_{K}'s are finally determined.

§ 9. The q^{δ}_{K} of Stable Complexes; II. $q^{H^+}_{K}$.

a) Evaluation of $V^{\delta}_{K,\Sigma}$.

The potential of the proton $V^{H^+}_{K,\Sigma}$ due to the cage at the configuration Σ is expressed as the sum of that due to the mercury atom $V^{H^+}_{Hg,\Sigma}$ and that due to the water molecule $V^{H^+}_{0H_2,\Sigma}$, i.e.

$$V^{H^+}_{K,\Sigma} = V^{H^+}_{Hg,\Sigma} + V^{H^+}_{0H_2,\Sigma} \tag{9.1}$$

The $V^{H^+}_{Hg,\Sigma}$ is calculated by the usual method of variation with the variation function,

$$\Psi = \Psi_0(1 + \gamma r_1 \cos\theta_1)(1 + \gamma r_2 \cos\theta_2) \tag{9.2}$$

and with the Hamiltonian operator,

$$\boldsymbol{H} = \boldsymbol{H}_0 - \frac{e^2}{r_{H,1}} - \frac{e^2}{r_{H,2}} + \frac{2e^2}{r_{0,H}}, \tag{9.3}$$

where

$$\boldsymbol{H}_0\Psi_0 = W_{Hg}\Psi_0, \tag{9.4}$$

and

$$\Psi_0 = \varphi \cdot R(r_1)R(r_2) \tag{9.5}$$

assuming that only eigenfunctions $R(r_1)$ and $R(r_2)$ of the two 6*s* electrons siginified by suffixes 1 and 2 were distorted by the field of proton. The θ_1 or θ_2 is the angle extended between the radius vactor from the nucleus of mercury atom toward the electron 1 or 2 $Hg - H^+$ axis, $r_{H,1}$, $r_{H,2}$ and $r_{0,H}$ three distances from the proton respectively to the 6*s* electrons 1 and 2 and to the atom core and γ the variation parameter common to both the electrons, W_{Hg} and Ψ_0 the appropriate unperturbed eigenwert and eigenfunction, the latter being expressed by the product of the unperturbed eigenfunctions of the atom core, φ, $R(r_1)$ and $R(r_2)$.

The energy W corresponding to $\frac{\int \Psi^* \boldsymbol{H}\Psi d\tau}{\int |\Psi|^2 d\tau} = \min.$ is given by the following expression,

$$W = W_{Hg} + \frac{Ze^2}{r_{0,H}} + \frac{P + \int\left(\frac{e^2}{r_{H,1}} - \frac{e^2}{r_{H,2}}\right) R^2(r_1)R^2(r_2)(1+\gamma r_1\cos\theta_1)^2(1+\gamma r_2\cos\theta_2)^2 d\tau}{\int R^2(r_1)R^2(r_2)(1+\gamma r_1\cos\theta_1)^2(1+\gamma r_2\cos\theta_2)^2 d\tau}, \tag{9.6}$$

where

$$P = \frac{h^2\gamma}{2\pi^2 m} \times \int R^2(r_1)\, R^2(r_2)\, \frac{dR(r_1)}{dr_1}(\cos\theta_1 + r_1 r_2 \gamma \cos\theta_1\cos\theta_2)(1+\gamma r_1\cos\theta_1)(1+\gamma r_2\cos\theta_2)d\tau \tag{9.7}$$

and γ is calculated as follows.

Internuclear Distance (Å)	3.20	4.49	6.41	9.62	12.82
r (Å^{-1})	0.266	0.231	0.225	0.196	0.174

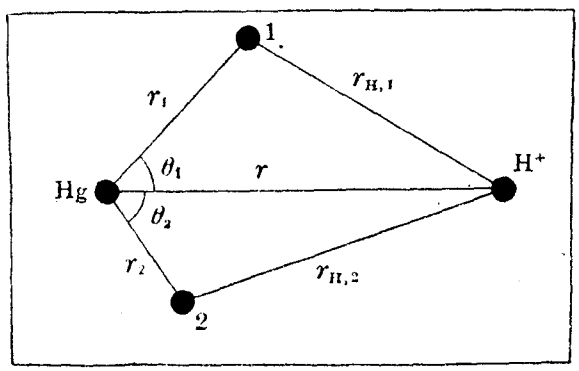

Fig. 1

Expressing $R(r)$ by the following analytical expression adapted to the numerical result[8] of HARTREE's self-consistent field method,

$$R(r) = (10{\cdot}4\,r - 2.7)\,e^{-1.475\,r}\ ,$$

the potential between mercury atom and proton, $V_{Hg}^{H^+} = W - W_{Hg}$, is worked out, the numerical result being recasted into the following Morse function,

$$V_{Hg}^{H^+} = 1.25\left\{ e^{-2\times 0.93\,(r-2.70)} - 2e^{-0.93\,(r-2.70)}\right\} \text{ e.V.} \quad (9.8)$$

where r is reckoned in Å unit.

The $V_{OH_2}^{H^+}$ is expressed on the other hand as follows,

$$V_{OH_2}^{H^+} = D\left\{ e^{-2a\,(r-r_0)} - 2e^{-a\,(r-r_0)}\right\} + N_A\frac{e\bar{\mu}(1-\cos 2\alpha)}{r^2} \quad (9.9)$$

where the Morse function in the first term is the potential energy of proton situated on the negative side of the dipole axis, the dissociation energy $D = 7.10$ e.V. being taken as the difference of the total heat of hydration of proton, 12.00 e.V.[9] and that of the hydronium ion as a

8) HARTREE, Proc. Roy. Soc., A **149** (1935), 210.
9) BERNAL and FOWLER, J. Chem. Phys., **1** (1933), 515.

whole, 4.9 e.V.*) The equilibrium distance r_0 is taken as the radius of the water molecule, 1.38 Å[9], and the anharmonic constant $a = 1.48\,\text{Å}^{-1}$ is calculated from the dissociation energy D and from the fundamental frequency of OH molecule, $\nu = 3660\,\text{cm}^{-1}$ [10] according to the expresion,

$$a = \sqrt{\frac{2\pi^2\mu c\nu_0^2}{hD}}\ [11] \quad (\mu = \text{reduced mass}).$$

The second term on the right of (9.9) allows for the excess of the potential energy due to departure of the position of proton from on the axis, where e is the elementary charge, $\bar{\mu}$ the dipole moment (1.80×10^{-18} e.s.u.), α the angle between the radius vector from the center of the water molecule to the proton and the direction of the dipole and N_A AVOGADRO's number.

b) Evaluation of $Y^{H^+}_{I,\Sigma}$.

The part of the reversible work $Y^{H^+}_{I,\Sigma}$, due to the electrode and the WEBB's model around the cage is estimated identifying the latter to the reversible work of bringing a proton into the one in qnestion from the corresponding position inside a cage of the same configuration but situated in vacuum and by replacing the cage with an ellipsoid of rotation circumscribed around it with an excentricity 0.80, filled with a homo-

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*) Attributing a spherical size of 1.38 Å radius to the hydronium ion, the latter's free energy of hydration as a whole can be calculated by the expression according to WEBB,

$$F = \frac{e^2}{2r_0} - e^{\frac{3}{2}}\int_0^{K_0} \frac{1+2\frac{\partial A}{\partial K}}{K+2A}\left\{K^2\left(\frac{1}{4}-\pi n\alpha\right) + AK - \frac{A^2}{2} - 2\pi mkT\ln\frac{\sinh\frac{\bar{\mu}K}{kT}}{\frac{\bar{\mu}K}{kT}}\right\} dK$$

$$- 2\pi e^{\frac{3}{2}}\int_0^{K_0} \omega_r \frac{1+2\frac{\partial A}{\partial K}}{(K+2A)^{5/2}}\, dK$$

where a: polarisability of water,
$\bar{\mu}$: dipolmoment of water,
r_0: radius of the ion,
K: internal field strength,
K_0: internal field strength at the surface of the ion,
A: $\frac{4\pi}{3}\times$ polarisation per unit volume,
ω_r: compression work per unit volume,
from which the energy of hydration is derived by HELMHOLTZ equation,

$$V = F - T\frac{\partial F}{\partial T}.$$

10) SPONER, Molekürspektren I. (Tabellen), (1936).
11) ibid. II. (1936), S. 103.

genous dielectrics of the optical dielectric constant $D_i = 1.7$*) except inside a small vacuum spherelt described around the charge, wich is taken to be situated on the major axis, and the surrounding medium, i. e. the electrode and the WEBB's aqueous solution, respectively, with homogeneous dielectrics of the dielectric constant infinite and 20**) respectively bounded from each other by a sharp plane surface.

The calculation was further simplified, taking the situation that the circumscribed eilipsoid is nealy halved by the boundary into account, by assuming $Y^{H^+}_{I,\Sigma}$ the mean of $Y^{H^+}_{W,\Sigma}$ and $Y^{H^+}_{M,\Sigma}$ or the reversible work calculated as though the ellipsoid are completely immersed either in the homogenous dielectrics of the WEBB's aquous solution or in that of the electrode respectively.

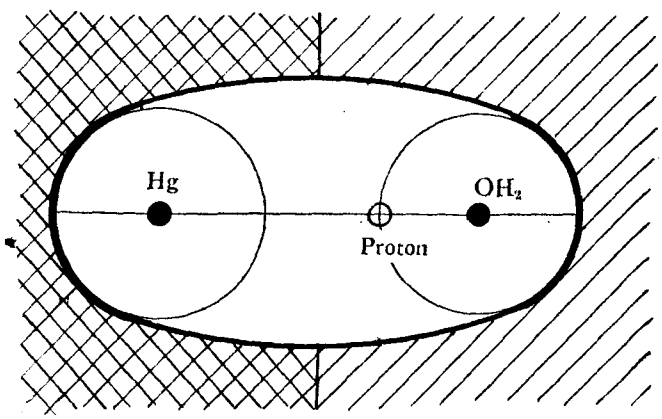

Fig. 2

Expressing now $Y^{H^+}_{W,\Sigma}$ or $Y^{H^+}_{M,\Sigma}$ by the difference of the electrostatical energies Y_D's of the ellipsoid in the respective medium of the dielectric constant D before and after the movement, as that,

$$Y^{H^+}_{W,\Sigma} = Y_{20} - Y_1, \tag{9.10}$$

$$Y^{H^+}_{M,\Sigma} = Y_\infty - Y_1, \tag{9.11}$$

we have

*) This value is the square of the refractive-index 1.30 of water which is extrapolated from experimental data for visible and ultraviolet lines (Landolt), using dispersion-formula of Ketteler-Helmholtz.

**) Dielectric constant of the WEBB's solution outside the ellipsoid 20 is evaluated according to WEBB, identifying the ellipsoid with a spherical ion of radius equal to the mean of its major and minor axes.

$$Y_{I,\Sigma}^{H^+} = \frac{1}{2}(Y_{W,\Sigma}^{H^+} + Y_{M,\Sigma}^{H^+}) = \frac{1}{2}(Y_{20} + Y_{\infty}) - Y_1 . \qquad (9.12)$$

The Y_D is obtained by summing up interaction potentials properly for individual part of the model. The charge density induced over the surface of the spherelet of radius ρ due to the point charge e at the centre is now given by $\frac{1}{4\pi}\left(\frac{1}{D_i}-1\right)\frac{e}{\rho}$. The mutual interaction potential of the latter is $\frac{1}{2}\left(\frac{1}{D_i}-1\right)^2\frac{e^2}{\rho}$ and its potential due to the charge at the centre is $\left(\frac{1}{D_i}-1\right)\frac{e^2}{\rho}$. Besides, the charge is accumulated only at the boundary surface of the ellipsoid due to the difference of the dielectric constant inside and outside. Denoting the surface density of the charge at the surface element df by ω_f' and the potential of the surface charge at df or at the centre of the spherelet by φ_f' or by φ_0' respectively, we have $\frac{1}{2}\int\omega_f'\varphi_f' df$ for the mutual interaction potential, $e\varphi_0'$ or $e\varphi_0'(1/D_i-1)$ for that between the latter and the charge at the centre of the spherelet or the charge induced over the surface of the spherelet by the charge at the centre, provided that ρ is taken sufficiently small. The interaction potential between the charge induced by the surface charge of the ellipsoid at the surface of the spherelet with other charge vanishes in total as easily be proved.

The Y_D is now expressed by summing up terms given above, as that

$$Y_D = \frac{1}{2}\left(\frac{1}{D_i}-1\right)^2\frac{e^2}{\rho} + \left(\frac{1}{D_i}-1\right)\frac{e^2}{\rho} + \frac{e\varphi_0'}{D_i} + \frac{1}{2}\int\omega_f'\varphi_f' df . \quad (9.13)^{*)}$$

The φ's and ω_f' may be evaluated as follows. From the continuity of the electric displacement at the boundary surface, we have

$$D_a\left\{\frac{\partial\left(\frac{e}{D_i r_0}+\varphi'\right)}{\partial n}\right\}_a = D_i\left\{\frac{\partial\left(\frac{e}{D_i r_0}+\varphi'\right)}{\partial n}\right\}_i , \qquad (9.14)$$

where φ' is the potential of the surface charge of the ellipsoid, r_0 the distance of the point on the surface from the point charge and a or i respectively signify the direction of the differentiation along the normal $\partial/\partial n$ outside or inside at the boundary surface of the ellipsoid.

*) The mathematical formulation of (9.13) and its related ones owes to Prof. M. KOTANI.

Denoting $$\varphi' = \mathrm{e}\varphi\,, \tag{9.15}$$
we have

$$D_a\left(\frac{\partial\varphi}{\partial n}\right)_a - D_i\left(\frac{\partial\varphi}{\partial n}\right)_i = \frac{D_i - D_a}{D_i}\frac{\partial}{\partial n}\left(\frac{1}{r_0}\right). \tag{9.16}$$

On the other hand ω_f' is expressed in the form,

$$4\pi\omega' = -\left\{\frac{\partial\left(\frac{\mathrm{e}}{D_i r_0} + \varphi'\right)}{\partial n}\right\}_a + \left\{\frac{\partial\left(\frac{\mathrm{e}}{D_i r_0} + \varphi'\right)}{\partial n}\right\}_i, \tag{9.17}$$

and hence, putting that

$$\omega' = \mathrm{e}\omega \tag{9.18}$$

we have $$4\pi\omega = -\left(\frac{\partial\varphi}{\partial n}\right)_a + \left(\frac{\partial\varphi}{\partial n}\right)_i\,. \tag{9.19}$$

In terms of φ and ω defined respectively by (9.15) and (9.18) the last term on the right of (9.13) is expressed as that

$$\frac{1}{2}\int \omega_f'\varphi_f'\,df = \frac{\mathrm{e}^2}{2}\int \omega_f\varphi_f\,df$$

or that

$$\frac{1}{2}\int \omega_f'\varphi_f'\,df = \frac{\mathrm{e}^2}{2}\int \omega_i\,df_i\int\frac{\omega_{fi}}{r_{ij}}df_j \tag{9.20}$$

where r_{ij} is the distance between two surface elements df_i and df_j. The integral on the right of (9.20) is now evaluated by introducing confocal elliptic coordinates ξ, η and ϕ, i. e.,

$$\left.\begin{aligned} x &= R\sqrt{\xi^2-1}\ \sqrt{1-\eta^2}\ \cos\phi \\ y &= R\sqrt{\xi^2-1}\ \sqrt{1-\eta^2}\ \sin\phi \\ z &= R\,\xi\eta \end{aligned}\right\} \tag{9.21}$$

ξ and η being expressed in terms of the distances r_{A} and r_{B} from foci as that

$$\xi = (r_{\mathrm{A}} + r_{\mathrm{B}})/2R\,, \qquad \eta = (r_{\mathrm{A}} - r_{\mathrm{B}})/2R\,. \tag{9.22}$$

The equation of our substituted ellipsoid is now

$$\xi = \xi_f\,, \tag{9.23}$$

the surface element

$$df = R^2\sqrt{(\xi_f^2-\eta^2)(1-\xi_f^2)}\;d\eta\,d\phi\,, \tag{9.24}$$

the differentiation along the normal

$$\frac{\partial}{\partial n} = \frac{1}{R}\sqrt{\frac{\xi_f^2-1}{\xi_f^2-\eta^2}}\,\frac{\partial}{\partial \xi}\,, \tag{9.25}$$

and henceforth (9.16) and (9.19) respectively assume the form,

$$D_a\left(\frac{\partial \varphi}{\partial \xi}\right)_a - D_i\left(\frac{\partial \varphi}{\partial \xi}\right)_i = \frac{D_i - D_a}{D_i}\,\frac{\partial}{\partial \xi}\left(\frac{1}{r_0}\right), \tag{9.26}$$

and

$$4\pi\omega = \frac{1}{R}\sqrt{\frac{\xi_f^2-1}{\xi_f^2-\eta^2}}\left\{-\left(\frac{\partial \varphi}{\partial \xi}\right)_a + \left(\frac{\partial \varphi}{\partial \xi}\right)_i\right\}. \tag{9.27}$$

We now expand φ in the spherical functions of the first and the second kind, as that

$$\varphi = \begin{cases} \sum\limits_n a_n \dfrac{P_n(\xi)}{P_n(\xi_f)}\,P_n(\eta) & \xi \leqq \xi_f \\ \sum\limits_n a_n \dfrac{Q_n(\xi)}{Q_n(\xi_f)}\,P_n(\eta) & \xi \geq \xi_f \end{cases} \tag{9.28}$$

and the reciprocal of the distance r_{ij} between any two points i and j in general as well according to NEUMANN[12] as that

$$\frac{1}{r_{ij}} = \frac{1}{R}\sum_{n=0}^{\infty}\sum_{\nu=0}^{n} D_{n\nu}\,P_n^\nu(\xi_i)Q_n^\nu(\xi_j)P_n^\nu(\eta_i)P_n^\nu(\eta_j)\cos\nu(\phi_j-\phi_i)\,, \tag{9.29}$$

where

$$D_{n0} = 2n+1\,, \qquad D_{n\nu} = (-)^\nu 2(2n+1)\left\{\frac{(n-\nu)!}{(n+\nu)!}\right\}^2 \quad (\nu \geq 1).$$

Because of the rotational symmetry of ω_f all the contribution to the integral with respect to f_j on the right of (9.20) vanishes except that of the term in (9.29) with $\nu = 0$. We may hence rewrite (9.29) in advance as that

$$\frac{1}{r_{ij}} = \frac{1}{R}\sum_n (2n+1)\,P_n(\xi_i)Q_n(\xi_j)P_n(\eta_i)P_n(\eta_j)\,. \tag{9.30}$$

On the other hand the reciprocal of the distance of any point (ξ_f, η) from that (ξ_0, η_0) on the major axis, or that for which $\xi_0 = 1$, is, expressed in particular, remembering that $P_n(\xi_0) = P_n(1) = 1$, according to (9.30) as that*)

*) In that case r_{ij}^{-1} should not depend on neither ϕ_j or ϕ_i, which is only possible when the terms with $\nu \neq 0$ vanish.

12) C. NEUMANN, Vorlesungen über die Theorie des Potentials, S. 341, (1887).

$$\frac{1}{r_0} = \frac{1}{R}\sum_n (2n+1)\, Q_n(\xi_f) P_n(\eta_0) P_n(\eta)\,, \tag{9.31}$$

whence we have,

$$\left\{ \partial\,(1/r_0)/\partial\xi \right\}_{\xi=\xi_f} = \sum_n \frac{(2n+1)}{R}\, Q_n'(\xi_f) P_n(\eta_0) P_n(\eta) \tag{9.32}$$

where

$$Q_n'(\xi_f) = \left\{ \partial Q_n(\xi)/\partial\xi \right\}_{\xi=\xi_f}.$$

We have thus from (9.16,), (9.28) and (9.32) that,

$$\sum_n a_n \left\{ D_a \frac{Q_n'(\xi_f)}{Q_n(\xi_f)} - D_i \frac{P_n'(\xi_f)}{P_n(\xi_f)} \right\} P_n(\eta)$$
$$= \left(\frac{D_i - D_a}{D_i}\right) \sum_n \frac{(2n+1)}{R} Q_n'(\xi_f) P_n(\eta_0) P_n(\eta)\,,$$

or

$$a_n = \frac{1}{R}\left(\frac{D_i - D_a}{D_i}\right) \frac{(2n+1)\, P_n(\xi_f) Q_n(\xi_f) Q_n'(\xi_f) P_n(\eta_0)}{D_a P_n(\xi_f) Q_n'(\xi_f) - D_i Q_n(\xi_f) P_n'(\xi_f)} \tag{9.33}$$

where

$$P_n'(\xi_f) = \left\{ \partial P_n(\xi)/\partial\xi \right\}_{\xi=\xi_f}.$$

According to (9.19) and (9.28) we have finaly,

$$\omega = \frac{(D_a - D_i)/D_i}{4\pi R^2 \sqrt{\xi_f^2 - \eta^2}\,\sqrt{\xi_f^2 - 1}} \sum_n \left[\frac{(2n+1)\, Q_n'(\xi_f) P_n(\eta_0)}{D_a P_n(\xi_f) Q_n'(\xi_f) - D_i Q_n(\xi_f) P_n'(\xi_f)} \right] P_n(\eta). \tag{9.34}$$

The φ_0 is expressed, according to the definition of ω and r_0, as that

$$\varphi_0 = \int \frac{\omega}{r_0}\, df \tag{9.35}$$

where the integration is taken over the region $-1 \leqq \eta \leqq 1$.
Substituting r_0^{-1}, df and ω respectively from (9.31), (9.24) and (9.34), we have, carrying through the integration, that

$$\varphi_0 = \frac{1}{R}\left(\frac{D_a}{D_i} - 1\right) \sum_n \left[\frac{(2n+1)\, Q_n(\xi_f) Q_n'(\xi_f) P_n^2(\eta_0)}{D_a P_n(\xi_f) Q_n'(\xi_f) - D_i Q_n(\xi_f) P_n'(\xi_f)} \right], \tag{9.36}$$

remembering the orthogonality of $P_n(\eta)$,

$$\int_{-1}^{1} P_n(\eta) P_m(\eta)\, d\eta = \begin{cases} 1 & n = m \\ 0 & n \neq m\,. \end{cases}$$

The integration $\int \omega_{fi}\, df_i \int (\omega_{fi}/r_{ij})\, df_j$ is now expressed by substitut-

ing ω and r_{ij}^{-1} from (9.34) and (9.30), and expressing df according to (9.24) and by carrying out the integration with respect to η_i, η_j, as that

$$\int\omega_{fi}df_i\int\frac{\omega_{fj}}{r_{ij}}df_j=\frac{1}{R}\left(\frac{D_a}{D_i}-1\right)^2\sum_n\left[\frac{(2n+1)\,Q_n(\xi_f)Q_n'(\xi_f)P_n(\xi_f)P_n^2(\eta_0)}{D_aP_n(\xi_f)Q_n'(\xi_f)-D_iQ_n(\xi_f)P_n'(\xi_f)}\right] \tag{9.37}$$

The value of R, ξ_f and η_0, which have to be substituted into these expressions for further evaluation of $Y_{I,\Sigma}^{H^+}$ with respective Σ, may be determined from a particular value of L. It will be seen that the length of the major axis C of our ellipsoid is given in Å as that

$$C=\frac{1}{2}(L+1.48+1.38),$$

where 1.48 and 1.38 Å are the radius of mercury atom and of water molecule respectively. (in Fig. 2).

According to the geometry of our ellisoid with excentricity of 0.80, R and ξ_f are determined as that

$$R=0.80\,C$$

and

$$\xi_f=C/R=1.250,$$

while the coordinate of H^+, η_0 may be represented, for instance ,in the case when H^+ is situated at x apart from an end of the major axis, as that

$$\eta_0=(C-x)/R=\xi_f(1-x/C).$$

Substituting Y_D thus expressed for different D_a's into (9.12), $Y_{I,\Sigma}^{H^+}$ is finally obtained as that

$$Y_{I,\Sigma}^{H^+}=\frac{e^2}{D_i}\left[\frac{\varphi_0(20)+\varphi_0(\infty)}{2}-\varphi_0(1)\right]+\frac{e^2}{2}\int\left[\frac{\varphi_f(20)\omega_f(20)+\varphi_f(\infty)\omega_f(\infty)}{2}-\varphi_f(1)\omega_f(1)\right]df. \tag{9.38}$$

c) Determination of Σ_0 and the corresponding $Y_{0,\Sigma_0}^{H^+}$.

Σ_0 and the corresponding $Y_{0,\Sigma_0}^{H^+}$ are now determined according to §8 by varying $Y_{0,\Sigma}^{\delta}$ as expressed by (8.1) with respect to L and Ω, the result being that,

$$V_{0,K,\Sigma_0}^{H^+}+Y_{I,\Sigma_0}^{H^+}=-11.38\text{ e.V.},$$

$$L_0=4.08\text{ Å}\quad\text{and}\quad\Omega_0=0.00.$$

where

$$V^{H^+}_{0,K,\Sigma_0} = (V^{H^+}_{Hg})_{0,\Sigma_0} + (V^{H^+}_{OH_2})_{0,\Sigma_0} = -8.28 \text{ e.V.}$$

$$(V^{H^+}_{Hg})_{0,\Sigma_0} = -1.18 \text{ e.V.} \quad \text{and} \quad (V^{H^+}_{OH_2})_{0,\Sigma_0} = -7.10 \text{ e.V.}$$

the proton being situated on the axis of the cage at 2.70 Å apart from the mucleus of the mercury atom.

d) Evalution of $\sum_i e^{-\varepsilon_i/kT'}$ at $\sum_0$.

The expansion of $V^{H^+}_{K,\Sigma}$ in small displacemets in rectangular coordinates around $V^{H^+}_{0,K,\Sigma_0}$ was

$$V^{H^+}_{K,\Sigma} = V^{H^+}_{0,K,\Sigma_0} + \alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2 , \tag{9.39}$$

where $\alpha_x = 15.1$ e.V./Å^2 and $\alpha_y = \alpha_z = 0.10$ e.V./Å^2, x being the axis perpendicular to the mercury plane.

The frequencies of three-fold modes of vibration are now easily found as that

$$\nu_x = 4040 \text{ cm}^{-1} \quad \text{and} \quad \nu_y = \nu_z = 1050 \text{ cm}^{-1} ,$$

from which $(\sum_i e^{-\varepsilon_i/kT'})_{\Sigma_0}$ is expressed as that

$$\left(\sum_i e^{-\varepsilon_i/kT'}\right)_{\Sigma_0} = \prod^{j=x,y,z} \left(2 \sinh \frac{h\nu_j}{2kT'}\right)^{-1} . \tag{9.40}$$

e) Evaluation of $\int \rho_\Sigma e^{-Y_L/kT'} dL \int e^{-Y_\Omega/kT'} d\Omega$.

The $Y^{H^+}_{0,\Sigma}$ is expanded around $Y^{H^+}_{0,\Sigma_0}$ in the quadratic function of the departure of L and Ω from L_0 and from Ω_0 respectively as that

$$Y^{H^+}_{0,\Sigma} = Y^{H^+}_{0,\Sigma} + \Gamma^{H^+}_L (L-L)^2 + \Gamma^{H^+}_\Omega (\Omega - \Omega)^2 , \tag{9.41}$$

where

$$\Gamma^{H^+}_L = 0.89 \text{ e.V/Å} \quad \text{and} \quad \Gamma^{H^+}_\Omega = 1.41 \text{ e.V.},$$

thus arriving at,

$$\int \rho_\Sigma e^{-Y_L/kT'} dL \int e^{-Y_\Omega/kT'} d\Omega = \rho_\Sigma \frac{\pi kT'}{\sqrt{\Gamma^{H^+}_L \Gamma^{H^+}_\Omega}} . \tag{9.42}$$

f) Calculation of $q^{H^+}_K$.

The $q^{H^+}_K$ is now according to (8.3), (8.4), (9.40) and (9.42) given by

$$q^{H^+}_K = q^{H^+}_K \, e^{-V^{H^+}_E/kT'}$$

where

$$q^{H^+}_K = \prod^{j=x,y,z} \left(2 \sinh \frac{h\nu_j}{2kT'}\right)^{-1} \frac{\rho_\Sigma \pi kT'}{\sqrt{\Gamma^{H^+}_L \Gamma^{H^+}_\Omega}} \, e^{-Y^{H^+}_{0,\Sigma_0}/kT'} . \tag{9.43}$$

The numerical value of the latter at 19°C is by the data given above, that

$$q_K^{H^+} = 6.11 \times 10^{185}. \tag{9.44}$$

§ 10. q_K^{δ} of Stable Complexes; III q_K^{H}.

a) Evaluation of $V_{K,\Sigma}^{H}$.

The $V_{K,\Sigma}^{H}$ is expressed by the sum of the negative ionization potential of hydrogen atom, the potential V_{Hg}^{H} due to Hg atom and that $V_{OH_2}^{H}$ due to the water molecule of the cage, i.e.,

$$V_{K,\Sigma}^{H} = V_{Hg,\Sigma}^{H} + V_{OH_2,\Sigma}^{H} + (-13.53)\ \text{e.V.} \tag{10.1}$$

V_{Hg}^{H} is expressed, in accordance with spectroscopic data[13] by the Morse function,

$$V_{Hg}^{H} = D\left\{ e^{-2a(r-r_0)} - 2\,e^{-a(r-r_0)} \right\} \tag{10.2}$$

where notations are

D: Dissociation energy, 0.46 e.V.[13]
a: Anharmonic constant, 2.55 Å^{-1} [13]
r_0: Equilibrium distance, 1.73 Å [13]
r: Nuclear distance.

The repulsive potential $V_{OH_2}^{H}$ is estimated in two alternative ways:

Identifying the water molecule with neon atom, we have according to BUTLER[14],

$$V_{OH_2}^{H} = 395.7 \times 10^{-1.6\,r}\ \text{e.V.} \qquad (r \text{ in Å})$$

Alternatively one can estimate it from the spectroscopic dissociation energy of OH molecule by adding to the latter $-3/2$ times of the exchange energy J as evaluated VAN VLECK and CROSS[15] to allow for the change from the paired state of bond electrons to the unpaired state, and twice the repulsive potential between hydrogen atoms*). The result is -1.4 e.V. at the equilibrium distance of OH molecule, which considerably recedes the corresponding value 11.1 e.V. of BUTLER's repulsive potential.

The serious discrepancy may be due to the ionic part of the interaction energy between hydrogen and oxgen atom which was not included

*) Negative value of 35% of the Morse function of hydrogen atoms is taken as this repulsive potential.

13) SPONER, Molekülspektren (1936).

14) BUTLER, Proc. Roy. Soc., A 157 (1936), 426.

15) VAN VLECK and CROSS, J. Chem. Phys., 1 (1933), 357.

in the BUTLER's estimation. Being combined with the two hydrogen atoms, the oxgen atom would loose more or less its electronegativity and in consequence the ionic part would be reduced but not so completely as that of the neon atom. If then we are to expect an extra attractive part in the potential and in consequence a potential hollow since such an attractive potential reaches further than the repulsive one.

In accordance with the above consideration, present authors proceed in rather crude approximation to put the potential in the form:

$$V^{\mathrm{H}}_{\mathrm{OH}_2} = \frac{30}{r^7} - \frac{16}{r^6}\ \mathrm{e.}V., \tag{10.3}$$

the distance, r, between centres of H and OH being reckoned in Å. The first term is adjusted over the range 1.5—2.2 Å to the BUTLER's repulisive potential, whereas the second term approximates the extra attractive potential by the inverse sixth power of the distance, its numerical coefficient being fixed from the assumption that $V^{\mathrm{H}}_{\mathrm{OH}_2}$ has its minimum at $r = 2.22$ Å, the average of OH distance in hydrogen bond, 1.80 Å,*) and of the sum 2.65 Å of van der WAALS radii 1.25[16] Å and 1.40 Å[16] respectively of O and H atom or the distance between the two, when combined by van der WAALS force.

b) Evaluation of $Y^{\mathrm{H}}_{I,\Sigma}$.

An actual calculation in accordance with (10.2) and (10.3) has shown that the potential of H due to Hg atoms and to OH_2 molecules outside the cage and hence the corresponding part of the free energy $Y^{\mathrm{H}}_{I,\Sigma}$ was negligible.

c) Determination of Σ_0 and the corresponding $Y^{\mathrm{H}}_{0,\Sigma_0}$.

The configuration Σ_0 at the minmum free energy $Y^{\mathrm{H}}_{0,K,\Sigma_0} + Y^{\mathrm{H}}_{I,\Sigma_0}$ is easily determined with the results;

$$L_0 = 3.95 \ \text{Å}, \qquad \Omega_0 = 0.00$$

where

$$\begin{aligned} &Y^{\mathrm{H}}_{0,\Sigma_0} = -13.53 + (V^{\mathrm{H}}_{\mathrm{Hg}})_{0,\Sigma_0} + (V^{\mathrm{H}}_{\mathrm{OH}_2})_{0,\Sigma_0} = -14.01\ \mathrm{e.V.}, \\ &(V^{\mathrm{H}}_{\mathrm{Hg}})_{0,\Sigma_0} = -0.46\ \mathrm{e.V.} \quad \text{and} \quad (V^{\mathrm{H}}_{\mathrm{OH}_2})_{0,\Sigma_0} = -0.02\ \mathrm{e.V.}, \end{aligned} \tag{10.4}$$

the hydrogen atom being situated 1.73 Å apart from the nucleus of the mercury atom.

*) (bond distance of hydrogen molecule 2.76 Å)[16] − (equilibium distance of OH molecule 0.96 Å)[16] = 1.80 Å.

16) L. PAULING; Nature of The Chemical Bond.

d) Evaluation of ε_i's and $\sum_i e^{-\varepsilon_i/kT'}$ at $\sum_0$.

The $V^{\mathrm{H}}_{K,\Sigma_0}$ in small displacements of the atom in rectangular coordinates around $V^{\mathrm{H}}_{0,K,\Sigma_0}$ is expanded as

$$V^{\mathrm{H}}_{K,\Sigma} = V^{\mathrm{H}}_{0,K,\Sigma_0} + \alpha_x x^2 + \alpha_y y^2 + \alpha_z z^2 , \qquad (10.5)$$

where

$$\alpha_x = 3.07 \ \text{e.V./Å}^2$$

and

$$\alpha_y = \alpha_z = 0.00 \ \text{e.V./Å}^2 ,$$

x being perpendicular to the mercury-plane. Only the mode of motion along x axis is vibrational with the frequency $\nu_x = 1285\ \mathrm{cm}^{-1}$ as calculated from α_x whereas those in other degree of freedom are translational so far as we remain with the approximation of retaining terms of displacements up to the second order ones.

$\left(\sum_i e^{-\varepsilon_i/kT'}\right)_{K,\Sigma_0}$ is hence expressed as that

$$\left(\sum_i e^{-\varepsilon_i/kT'}\right)_{K,\Sigma_0} = \left(2\sinh\frac{h\nu_x}{2kT'}\right)^{-1}\left(\frac{2\pi mkT'A}{h^2}\right) , \qquad (10.6)$$

where the first factor is quantum mechanical partition function for the vibration in x-direction and the second the cassical partition function for the translation in y–and z–directions, m being the mass of the hydrogen atom. The area $A = 9.1$ Å^2 over which the latter translation is allowed is taken that of the section of the ellipsoid perpendicular to the axis.

e) Evaluation of $\int \rho_\Sigma e^{-Y_L/kT'} dL \int e^{-Y_\Omega/kT'} d\Omega$.

The $Y^{\mathrm{H}}_{0,\mathrm{H}}$ is expanded around $Y^{\mathrm{H}}_{0,\Sigma_0}$ in the quaratic function of the departure of L and Ω from L_0 and from Ω_0 respectively; i. e.,

$$Y^{\mathrm{H}}_{0,\Sigma} = Y^{\mathrm{H}}_{0,\Sigma_0} + \Gamma^{\mathrm{H}}_L (L-L_0)^2 + \Gamma^{\mathrm{H}}_\Omega (\Omega-\Omega_0)^2 , \qquad (10.7)$$

where

$$\Gamma^{\mathrm{H}}_L = 0.0786 \ \text{e.V/Å}, \qquad \Gamma^{\mathrm{H}}_\Omega = 0.000 \ \text{e.V.}$$

we obtained similarly as in the previous case that

$$\int \rho_\Sigma e^{-Y_L/kT'} dL \int e^{-Y_\Omega/kT'} d\Omega = 4\rho_\Sigma \sqrt{\frac{\pi^3 kT'}{\Gamma^{\mathrm{H}}_L}} . \qquad (10.8)$$

f) Calculation of q^{H}_K.

The q^{H}_K is now according to (8.3), (8.4), (10.6) and (10.8) given by,

$$q_K^{\mathrm{II}} = q_K^{\mathrm{H}} e^{-V_E^{\mathrm{II}}/kT'},$$

where

$$q_K^{\mathrm{H}} = \left(2\sinh\frac{h\nu_x}{2kT'}\right)^{-1}\left(\frac{2\pi mkT'A}{h^2}\right)4\rho_\Sigma\sqrt{\frac{\pi^3 kT'}{I'^H_L}}\, e^{-Y^{\mathrm{H}}_{0,\Sigma_0}/kT'}. \quad (10.9)$$

The numerical value of the latter at 19°C is, by data given above,

$$q_K^{\mathrm{H}} = 1.38 \times 10^{251}. \quad (10.10)$$

§ 11. q_K^{S} of Stable Complexes; IV. $q_K^{\mathrm{H_2}}$,

No detailed calculation is carried out in this case, it having turned out by the following estimation $q_K^{\mathrm{H_2}}$ is insignificant with regard to the present calculation of the reaction rate.

With the simplifying assumption that the hydrogen molecule behaved in the cage of the fixed configuration, as if it were a free gas molecule under the constant potential, we have for $q_K^{\mathrm{H_2}}$ as that

$$q_K^{\mathrm{H_2}} = v_K Q_g^{\mathrm{H_2}} e^{-V_0/kT'}, \quad (11.1)$$

where $Q_g^{\mathrm{H_2}}$ is the partition function of a single hydrogen molecule per unit volume in vacuum, v_K the volume inside the cage and V_0 the assumed constant potential of the molecule inside the cage referred to that in vacuum.

The potential due to the mercury atom is the repulsive one as worked out §16 and that due to the water molecule has a hollow according to the preceeding paragraph whereas those due to outside the cage is negligible as inferred from the previous result. To estimate $q_K^{\mathrm{H_2}}$ preferably by its upper limit V_0 is identified to the minimum possible negative potential due to the water molecule of the cage, i.e.

$$V_0 = -0.04 \text{ e.V.},$$

neglecting the repulsive potential due to a mercury atom.

With $v_K = 10^{-24}\,\mathrm{cm}^3$ by order of magnitude it was obtained by (11.1) that

$$q_K^{\mathrm{H_2}} = q_K^{\mathrm{H_2}} e^{-V_E^{\mathrm{H_2}}/kT'} \quad (11.2)$$

where

$$q_K^{\mathrm{H_2}} = 1.47 \times 10^{545}, \quad (11.3)$$

which turned out, as will be seen later §14, in any way negligible with regard to the calculation of $\theta_{\mathrm{H_2}}$.

§ 12. q_K^{δ} of Stable Complexes; V. $q_K^{\Pi\cdot+}$.

The $V_{K,\Sigma}^{H_2^+}$ is expressed by the following quantum mechanical deduction in terms of known individual intraction potentials between H—H^+, H—Hg, H—OH_2, H^+—Hg, H^+—OH_2.

Let W_i and Ψ be the eigenwert and the eigenfunction of the system as consisting of the cage of the definite configuration Σ and the hydrogen molecule ion H_2^+, the two nuclei of the latter being situated at two definite positions a and b so that

$$\boldsymbol{H}\Psi = W_i\Psi . \tag{12.1}$$

For our present purpose Hamiltonian $\boldsymbol{H}$ is expressed in the form

$$\boldsymbol{H} = \boldsymbol{H}_0 - \sum_n \frac{e^2}{r_{a,n}} + R_a - \sum_n \frac{e^2}{r_{b,n}} + R_b + \frac{e^2}{r_{a,b}} , \tag{12.2}$$

and the eigenfunction Ψ approximated by the linear combination

$$\Psi = \alpha\psi_A + \beta\psi_B$$

where $\boldsymbol{H}_0$ is the Hamitionian of the whole system S except the potential due to proton situated at a and b; $\sum e^2/r_{a,n}$ ($\sum e^2/r_{b,n}$) is the potential of n-th electrons due to the proton situated at a (b), R_a (R_b) that of positive particles due to the proton at a (b) and $e^2/r_{a,b}$ the mutual potential of the two protons. ψ_A or ψ_B are eigenfunction of the system $S(a)$ or $S(b)$ consiting of the cage and an atom situated at a or b respectively, α and β being the variation parameters.

The Schrödinger equation for ψ_A and ψ_B may hence be written in the form,

$$\left\{\boldsymbol{H}_0 - \sum_n \frac{e^2}{r_{a,n}} + R_a\right\}\psi_A = W_A\psi_A , \tag{12.3}$$

$$\left\{\boldsymbol{H}_0 - \sum_n \frac{e^2}{r_{b,n}} + R_b\right\}\psi_B = W_B\psi_B . \tag{12.4}$$

Energy W_i is now given as usual by the secular equation,

$$\begin{vmatrix} W_A + H_{AA} - W_i & \Delta W_B + H_{AB} - \Delta W_i \\ \Delta W_A + H_{BA} - \Delta W_i & W_B + H_{BB} - W_i \end{vmatrix} = 0 , \tag{12.5}$$

where

$$H_{AA} = -\sum_n \int \psi_A^2 \frac{e^2}{r_{b,n}} d\tau + \frac{e^2}{r_{a,b}} + R_b ,$$

$$H_{BB} = -\sum_n \int \psi_B \frac{e^2}{r_{a,n}} d\tau + \frac{e^2}{r_{a,b}} + R_a ,$$

$$H_{AB} = -\sum_n \int \psi_A \psi_B \frac{e^2}{r_{a,n}} d\tau + \Delta \frac{e^2}{r_{a,b}} + \Delta R_a ,$$

$$H_{BA} = -\sum_n \int \psi_A \psi_B \frac{e^2}{r_{b,n}} d\tau + \Delta \frac{e^2}{r_{a,b}} + \Delta R_b ,$$

$$\Delta = \int \psi_A \psi_B \, d\tau .$$

These integrals are evaluated by approximating ψ with the normalised linear combination of the products of the atomic orbital of the hydrogen atom u and the eigenfunction of the cage ψ', i.e. that

$$\psi = \sum_m^{m=N} a_m \psi'_m u_m \qquad \text{with} \quad \sum_m^{m=N} a_m^2 = 1 ,$$

suffix m denoting the state with m-th electron on the orbital u and N the total number of electrons. Negleting orthogonal integrals between ψ' and u, H_{AA}, H_{BB}, H_{AB} and H_{BA} are now

$$H_{AA} = \omega_A + K + \frac{e^2}{r_{a,b}} ,$$

$$H_{BB} = \omega_B + K + \frac{e^2}{r_{a,b}} ,$$

$$H_{AB} = J + \Delta \frac{e^2}{r_{a,b}} + \Delta \omega_B ,$$

and

$$H_{BA} = J + \Delta \frac{e^2}{r_{a,b}} + \Delta \omega_A ,$$

where

$$K = -\int \frac{e^2}{r_a} u_b^2 \, d\tau , \tag{12.6}$$

$$J = -\int \frac{e^2}{r_a} u_a u_b d\tau , \tag{12.7}$$

$$\Delta = \int u_a u_b d\tau , \tag{12.8}$$

$$\omega_A = -\sum_{m=1}^{m=N} a_m^2 \sum_{n \neq m} \int \psi_n'^2 \frac{e^2}{r_{b,n}} d\tau + R_b , \tag{12.9}$$

and

$$\omega_B = -\sum_{m=1}^{m=N} a_m^2 \sum_{n \neq m} \int \psi_n'^2 \frac{e^2}{r_{a,n}} d\tau + R_a . \tag{12.10}$$

Secular equation (12.5) is now

$$\begin{vmatrix} W_A+\omega_A+K+\dfrac{e^2}{r_{a,b}}-W_i & \Delta W_B+\Delta\omega_B+J+\Delta\dfrac{e^2}{r_{a,b}}-\Delta W_i \\ \Delta W_A+\Delta\omega_A+J+\dfrac{e^2}{r_{a,b}}-\Delta W_i & W_B+\omega_B+K+\dfrac{e^2}{r_{a,b}}-W_i \end{vmatrix} = 0 . \tag{12.11}$$

As seen from (12.9) and from (12.10), ω's are simply the potential between the proton and the cage or the sum of potentials $V^{H^+}_{Hg,\Sigma}$ and $V^{H^+}_{OH_2,\Sigma}$ respectivly given by (9.8) and (9.9), whereas W's are by defnition the sum of potentials W_0, V^{H}_{Hg} and $V^{H}_{OH_2}$, or

$$W = W_0 + V^{H}_{Hg} + V^{H}_{OH_2} , \tag{12.12}$$

where W_0 is the energy of the system consisting of the cage and the hydrogen atom infinitely apart from each other. The $W+\omega$ in the secular equation is hence

$$W+\omega = W_0 + V^{H^+}_{Hg} + V^{H^+}_{OH_2} + V^{H}_{OH_2} + V^{H}_{Hg} .$$

The energy W_i is now calculable by solving the secular equation when we have evaluated Δ, K and J.

In the special case when $W_A+\omega_A = W_B+\omega_B$ we have

$$W_i - W_0 = V^{H^+}_{Hg} + V^{H^+}_{OH_2} + V^{H}_{Hg} + V^{H}_{OH_2} + \frac{e^2}{r_{a,b}} + \frac{K\pm J}{1\pm\Delta} . \tag{12.13}$$

The sum of the last two terms give the dissociation energy of hydrogen molecule ion H_2^+ according to PAULING[17]. The actual numerical calculation has been carried out, by replacing it with the accurate result of HYLLERAAS' calculation[18].

It is held in such a case when $W_A+\omega_A \fallingdotseq W_B+\omega_B$ or when the energy of the system differs according as either of orbitals u_a or u_b houses an electron that the seperation of the accurate dissociation energy into individual terms K, J and Δ is significant. This is done by "analyzing" the accurate dissociation energy after the manner of EYRING and POLANYI[19], i.e. by solving the equation, $\dfrac{e^2}{r_{a,b}} - \dfrac{K+J}{1+\Delta}$ = (HYLLERAAS' accurate dissociation energy), for K and J reserving PAULING's approximate results for Δ and for the ratio K/J. $W_i - W_0$ thus evaluated gives directly $V^{H_2^+}_{K,\Sigma}$ in question.

17) PAULING, Chem. Rev., **5** (1928), 173.
18) HYLLERAAS, Z. f. Phys., **71** (1931), 739.
19) EYRING and POLANYI, Z. f. phys. Chem., **B 12** (1931) 279.

b) Evaluation of $Y^{H_2^+}_{I,^2\Sigma}$.

From the results obtained in §10 that the potential of a hydrogen atom in the cage due to the surroundings practically vanished, it would follow, so far as we remain with the approximation of composing the potential of H_2^+ additively from those of constituent particles H and H^+, that the potential of H_2^+ due to the surroundings consists practically solely in electrostatical one. Assuming this and in addition that charge of H_2^+ is concentrated at its centre of gravity, $Y^{H_2^+}_{I,^2\Sigma}$ is calculated in the same way as that for H^+ described in b), §8.

c) Determination of $\sum_0$ and the corresponding $Y^{K_3^+}_{0,^2\Sigma_0}$.

This is just similarly carried out as in the previous cases with the result that

$$Y^{H_2^+}_{0,^2\Sigma} = Y^{H_2^+}_{0,^2K,\Sigma_0} + Y^{H_2^+}_{I,^2\Sigma_0} = -27.27 \text{ e.V.} \qquad (12.14)$$

$$L_0 = 3.94 \text{ Å}, \qquad \Omega_0 = 0.00$$

where

$$Y^{H_2^+}_{0,^2K,\Sigma_0} = V^{H_2^+}_{0,^2K,\Sigma_0} = -13.53 + (V^{H^+}_{Hg})_{0,\Sigma_0} + (V^{H^+}_{OH_2})_{0,\Sigma_0} + (V^{H}_{Hg})_{0,\Sigma_0} + (V^{H}_{OH_2})_{0,\Sigma_0} + (V^{H}_{H^+})_{0,\Sigma_0} = -24.09 \text{ e,V.}$$

$$Y^{H_2^+}_{I,^2\Sigma_0} = -3.18 \text{ e.V.}$$

$$(V^{H^+}_{Hg})_{0,\Sigma_0} = -1.15 \text{ e.V.}$$

$$(V^{H^+}_{OH_2})_{0,\Sigma_0} = -6.92 \text{ e.V.}$$

$$(V^{H}_{Hg})_{0,\Sigma_0} = -0.14 \text{ e.V.}$$

$$(V^{H}_{OH_2})_{0,\Sigma_0} = 0.42 \text{ e.V.}$$

and $$(V^{H}_{H^+})_{0,\Sigma_0} = -2.77 \text{ e.V.}$$

and that the two nuclei of H_2^+ are situated symmetrically around the axis of the cage, 1.04 Å apart from each other, with the centre of gravity 2.50 Å apart from the nucleus of the mercury atom.

d) Evaluation of ε_i's and $\sum_i e^{-\varepsilon_i/kT}$ at $\sum_0$.

The expansion of $V^{H_3^+}_{K,^2\Sigma_0}$ around $V^{H_3^+}_{0,^2K,\Sigma_0}$ as the quadratic function of small displacements of the elementary system from the equilibrium position is

$$V^{H_3^+}_{K,^2\Sigma_0} = V^{H_3^+}_{0,^2K,\Sigma_0} + \sum_{r}^{r,\bar{r},\xi,\bar{\xi},\theta,\bar{\theta}} \frac{k_{rr}}{2}(r-r_0)^2 + k_{\xi r}(\xi-\xi_0)(r-r_0) + k_{\bar{\xi}\bar{r}}(\bar{\xi}-\bar{\xi}_0)(\bar{r}-\bar{r}_0),$$

where r, $\bar{r}$, ξ, $\bar{\xi}$, θ and $\bar{\theta}$ are the linear combinations,

$$2r = r_{\mathrm{I}} + r_{\mathrm{II}}, \quad 2\xi = x_{\mathrm{I}} + x_{\mathrm{II}}, \quad \theta = (I_{\mathrm{I}}\theta_{\mathrm{I}} + I_{\mathrm{II}}\theta_{\mathrm{II}})/I_{\mathrm{I}} + I_{\mathrm{II}},$$
$$2\bar{r} = r_{\mathrm{I}} - r_{\mathrm{II}}, \quad 2\bar{\xi} = x_{\mathrm{I}} - x_{\mathrm{II}}, \quad \bar{\theta} = \theta_{\mathrm{I}} - \theta_{\mathrm{II}}, \tag{12.15}$$

of cylindrial coordinates r_{I}, r_{II}, x_{I}, x_{II}, θ_{I}, θ_{II} of individual particles I and II as illustrated in Fig. 3, and $I_{\mathrm{I}} = m_{\mathrm{I}} r_{\mathrm{I}}^2$ and $I_{\mathrm{II}} = m_{\mathrm{II}} r_{\mathrm{II}}^2$ the moments of inertia around Hg—OH_2 axis of H_{I}^+ and H_{II}^+ of masses m_{I} and m_{II} respectively. Cross terms other than ξr and $\bar{\xi}\bar{r}$ vanish from the symmetry of the figure*).

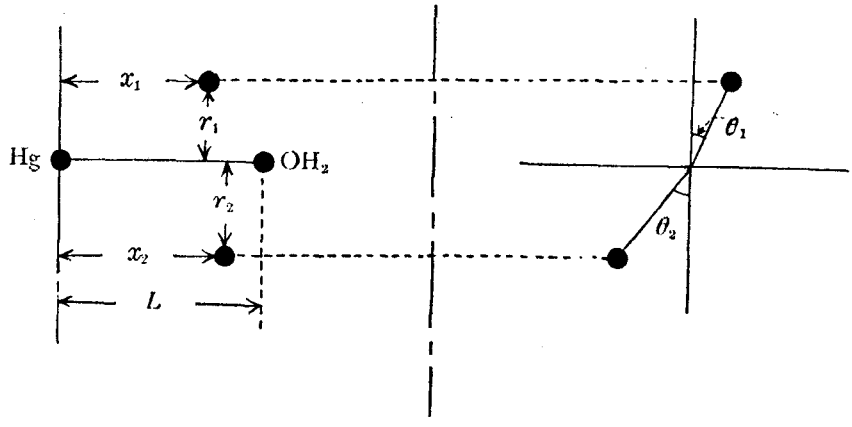

Fig. 3

Suffix 0 refers to the equilibrium position, their numerical values being,

r_0	$\bar{r}_0$	ξ_0	$\bar{\xi}_0$	$\bar{\theta}_0$
0.52 Å	0.00	2.50 Å	0.00	0.00

(12.16)

whereas θ has no distinguished stable value because of the assumed symmetry of the potential around Hg—OH_2 axis. Calculated values of force constants k's are,

k_{rr}	$k_{\bar{r}\bar{r}}$	$k_{\xi\xi}$	$k_{\bar{\xi}\bar{\xi}}$	$k_{r\xi}$	$k_{\bar{r}\bar{\xi}}$	$k_{\theta\theta}$
40.8	4.37	33.0	33.5	−11.0	−11.0	0.23 e.V.

(12.17)

Expressing the kinetic energy, T, in terms of the corresponding velocities, $\dot{r}$, $\dot{\bar{r}}$, $\dot{\xi}$, $\dot{\bar{\xi}}$, $\dot{\theta}$ and $\dot{\bar{\theta}}$, i.e.

$$T = \frac{m_{\mathrm{I}} + m_{\mathrm{II}}}{2}(\dot{r}^2 + \dot{\bar{r}}^2 + \dot{\xi}^2 + \dot{\bar{\xi}}^2) + (m_{\mathrm{I}} - m_{\mathrm{II}})(\dot{r}\dot{\bar{r}} + \dot{\xi}\dot{\bar{\xi}})$$
$$+ \frac{I_{\mathrm{I}} + I_{\mathrm{II}}}{2}\dot{\theta}^2 + \frac{I_{\mathrm{I}} I_{\mathrm{II}}}{2(I_{\mathrm{I}} + I_{\mathrm{II}})}\dot{\bar{\theta}}^2, \tag{12.18}$$

*) Since the potential energy must be invariant by interchange of H_{I}^+ and H_{II}^+ or by reflection of the figure at the symmetry axis or by rotation around the latter, cross terms other than ξr and $\bar{\xi}\bar{r}$, which change signe or vary by the symmetry operations, should vanish.

following equation of motion are obtained,

$$(I_{\mathrm{I}}+I_{\mathrm{II}})\,\ddot{\varphi}=0\,, \tag{12.19}$$

$$\frac{I_{\mathrm{I}}I_{\mathrm{II}}}{(I_{\mathrm{I}}+I_{\mathrm{II}})}\ddot{\theta}+k_{\theta\theta}(\theta-\theta_0)=0\,, \tag{12.20}$$

and

$$\left.\begin{aligned}
&(m_{\mathrm{I}}+m_{\mathrm{II}})\ddot{r}+(m_{\mathrm{I}}-m_{\mathrm{II}})\ddot{\bar{r}}+k_{rr}(r-r_0)+k_{r\xi}(\xi-\xi_0)=0\,,\\
&(m_{\mathrm{I}}-m_{\mathrm{II}})\ddot{r}+(m_{\mathrm{I}}+m_{\mathrm{II}})\ddot{\bar{r}}+k_{\bar{r}\bar{r}}(\bar{r}-\bar{r}_0)+k_{\bar{r}\bar{\xi}}(\bar{\xi}-\bar{\xi}_0)=0\,,\\
&(m_{\mathrm{I}}+m_{\mathrm{II}})\ddot{\xi}+(m_{\mathrm{I}}-m_{\mathrm{II}})\ddot{\bar{\xi}}+k_{\xi\xi}(\xi-\xi_0)+k_{r\xi}(r-r_0)=0\,,\\
&(m_{\mathrm{I}}-m_{\mathrm{II}})\ddot{\xi}+(m_{\mathrm{I}}+m_{\mathrm{II}})\ddot{\bar{\xi}}+k_{\bar{\xi}\bar{\xi}}(\xi-\xi_0)+k_{\bar{r}\bar{\xi}}(\bar{r}-r_0)=0\,.
\end{aligned}\right\} \tag{12.21}$$

(12.19) gives the free rotation, (12.20) the rotational-vibration and (12.21) four-fold modes of vibration.

By solving the appropriate secular equation, i.e.

$$\begin{vmatrix}
-(m_{\mathrm{I}}+m_{\mathrm{II}})\lambda+k_{rr} & (m_{\mathrm{I}}-m_{\mathrm{II}})\lambda & k_{r\xi} & 0\\
(m_{\mathrm{I}}-m_{\mathrm{II}})\lambda & -(m_{\mathrm{I}}+m_{\mathrm{II}}\lambda+k_{\bar{r}\bar{r}} & 0 & k_{\bar{r}\bar{\xi}}\\
k_{r\xi} & 0 & -(m_{\mathrm{I}}+m_{\mathrm{II}})\lambda+k_{\xi\xi} & (m_{\mathrm{I}}-m_{\mathrm{II}})\lambda\\
0 & k_{\bar{r}\bar{\xi}} & (m_{\mathrm{I}}-m_{\mathrm{II}})\lambda & -(m_{\mathrm{I}}+m_{\mathrm{II}})\lambda+k_{\bar{\xi}\bar{\xi}}
\end{vmatrix}=0$$

where $\lambda=4\pi^2\nu^2$,

their frequencies ν's are now calculated for H_2^+ as well as for HD^+ from the force constants (12.16) as follows,

	ν_1	ν_2	ν_3	ν_4	ν_5	cm^{-6}
H_2^+	1850	2570	305	2250	340 ,	
HD^+	1470	2370	249	1890	299 ,	

(12.22)

where ν_5 is that of rotational-vibration.

Eigenwerts ε_i of the Schrödinger equation corresponding to the above classical solution are

$$\varepsilon_i=\varepsilon_{j,l_1,l_2\cdots l_6}=\frac{h^2j^2}{8\pi^2(I_{\mathrm{I}}+I_{\mathrm{II}})}+\sum_k^{1,\cdots,5}(n_{l_k}+\frac{1}{2})h\nu_k\,,$$

where k enumerates ν's given above. $\sum_i e^{-\varepsilon_i/kT'}$ is now given by

$$\sum_i e^{-\varepsilon_i/kT'}=\frac{\sqrt{2\pi(I_{\mathrm{I}}+I_{\mathrm{II}})kT'}}{sh}\prod_k^{1,\cdots,5}\left(2\sinh\frac{\zeta\nu_k}{2kT'}\right)^{-1}, \tag{12.23}$$

the rotational partition function being classically computed.

e) Evaluation of $\int\rho_\Sigma e^{-Y_L/kT'}dL\int e^{-Y_\Omega/kT'}d\Omega$.

Expansion of $Y^{H_2^+}_{0,\Sigma}$ around $Y^{H_2^+}_{0,\Sigma}$ is similarly obtained as in the previous cases,as that

$$Y^{H_2^+}_{0,\Sigma} = Y^{H_2^+}_{0,\Sigma_0} + \Gamma^{H_2^+}_L (L-L_0)^2 + \Gamma^{H_2^+}_\Omega (\Omega-\Omega_0)^2 , \qquad (12.24)$$

where $\Gamma^{H_2^+}_L = 1.41$ eV/Å^2, $\Gamma^{H_2^+}_\Omega = 1.13$ eV.,

from which there is obtained

$$\int \rho_\Sigma e^{-Y_L/kT'} dL \int e^{-Y_\Omega/kT'} d\Omega = \frac{\rho_\Sigma \pi kT'}{\sqrt{\Gamma_L \Gamma_\Omega}} . \qquad (12.25)$$

f) Calculation of $q^{H_2^+}_K$.

In accordance with (8.3), (8.4), (12.24) and (12.25), we have that

$$q^{H_2^+}_K = q^{H_2^+}_K e^{-V^{H_2^+}_E/kT'} , \qquad (12.26)$$

where

$$q^{H_2^+}_K = \frac{\sqrt{2\pi (I_I + I_{II}) kT'}}{sh} \prod_k^{1,\ldots,5} \left(2 \sinh \frac{h\nu_k}{2kT'}\right)^{-1} \frac{\rho_\Sigma \pi kT'}{\sqrt{\Gamma_L \Gamma_\Omega}} e^{-Y^{H_2^+}_{0,\Sigma_0}/kT'} , \qquad (12.27)$$

the numerical value at 19°C being,

$$q^{H_2^+}_K = 7.14 \times 10^{105} \qquad (12.28)$$

§ 13. Calculation of V^δ_E.

In accordance with §7, V^δ_E is now reduced to a function of θ and η as follows taking in the sum of pure electrostatical part, due to the interaction of net chages e of elementary systems and the remaining part U^δ, so that

$$V^\delta_E = e\zeta_0 + U^\delta , \qquad (13.1)$$

where ζ_0 is the electrostatical potential at the position of the charge. The U^δ will be evaluated in what follows in accordance with the approximation (2°) in §7 on the basis of the configuration*) of stable complexes worked out in the preceeding paragraphs.

We have from the approximation that

$$U^i = \sum_j \Theta_j U^j_i , \qquad (13.2)$$

$$U^j_i = \sum_k u^i_j(k) \qquad (13.3)$$

*) Such configurations of elementary systems are determined in the preceeding paragraph except for H^-, it being unnecessary for the crude estimation of the relevant function, $q^{H_2^+}_K$. To estimate V's formally for all elementary systems, H_2 is assumed to be situated symmetrically inside the cage, with its axis perpendicular to that of the latter, at the same distance, 2.7 Å as that of H^+_2 apart from the mercury-plane.

and

$$U_i^j = U_j^i \tag{13.4}$$

where U_i^j is the potential of an elementary system of i-th kind situated in a particular cage K_i due to those of j-th ones supposed fully occupying the cages around K_i and $u_j^i(k)$ the individual potential due to that of j-th kind situated inside k-th cage K_k, which depends simply on the distance between K_k and K_i.

Nine different kinds of u^i, i.e., $u_{H_2}^H$, u_H^H, $u_{H_2^+}^{H^+}$, $u_{H^+}^{H_2^+}$, $u_{H_2}^H$, $u_{H_2}^{H^+}$, $u_{H_2^+}^{H^+}$, $u_{H^+}^H$ and $u_{\delta_3^+}^{H^+}$*) are now to be evaluated in order to obtain U^i's.

In the case of u_H^H and $u_{H^+}^H$, when elementary systems involved, i.e. H and H^+, are respectively situated simply on the axis of the cage at the equilibrium position of the mininum free energy. The interaction potential κ_H^H between two neutral hydrogen atoms is taken as the mean of those of the singlet and the triplet states of the hydrogen molecule, as evaluated by JAMES, COOLIDGE, PRESENT,[20] and RYDBERG,[21] attributing weights 1 and 3 to them respectively. Thus the following results are obtained.

TABLE II

Distance between protons Å	0.793	1.059	1.321	1.585	1.850	2.112
κ_H^H e.V/mol	2.71	1.23	0.63	0.35	0.16	0.05

The interaction potential $\kappa_H^{H^+}$ between a proton and a neutral hydrogen atom is given by the Coulomb integral, i.e.

$$\kappa_H^{H^+} = -\int u^2 \frac{e^2}{r} d\tau + \frac{e^2}{R} \tag{13.5}$$

where u is the eigenfunction of the hydrogen atom at the ground state, r the distance from the perturbing proton of the electron and R that of the proton of the hydrogen atom. The u_H^H and $u_{H^+}^H$ are now simply the values of κ_H^H and $\kappa_H^{H^+}$ respectively at the particular distance between the appropriate cages.

Other ones, whice inuolve the elementary systems rotating freely

*) $u_{H^+}^{H^+}$ is excluded because it consists purely of the electrostatical interaction potential already included in the term $e\zeta_0$.

20) JAMES, COOLIDGE and PRESENT, J. Chem. Phys., 4 (1936), 187.

21) RYDBERG, Z. f. Physik, **73** (1931), 376.

around the axis of the cage are approximated in accordance with (ii), §7, by the sum of individual potentials of concequent particles averaged over the azimuthal angle around the axis. The H_2^+, in this case, was formally replaced by a neutral hydrogen atom and a proton, the distortion of the former's eigenfunction benig taken into account as described below only with its potential due to the proton but not with that due to the neutral atom. Ignoring a small difference in the nuclear distances of H_2 and H_2^+, u's are expressed as that

$$u_{H_2}^{H_2} = 4\bar{\kappa}_H^H, \tag{13.6}$$

$$u_{H_2^+}^{H_2^+} = 2\bar{\kappa}_H^H + 2\bar{\kappa}_H^{H^+}, \tag{13.7}$$

$$u_{H_2}^{H} = 2\bar{\kappa}_H^H, \tag{13.8}$$

$$u_{H_2}^{H^+} = 2\bar{\kappa}_H^{H^+}, \tag{13.9}$$

$$u_{H_2^+}^{H_2^+} = \bar{\kappa}_H^H + 2\bar{\kappa}_{H_p}^{H^+}, \tag{13.10}$$

$$u_{H^+}^{H^+} = \bar{\kappa}_H^H + \bar{\kappa}_H^{H^+}, \tag{13.11}$$

$$u_{H^+}^{H^+} = \bar{\kappa}_{H_p}^{H^+}, \tag{13.12}$$

where

$$\bar{\kappa}_j^i = \frac{1}{2\pi}\int_0^{2\pi} \kappa_j^i \, d\bar{\theta} \tag{13.13}$$

or

$$\bar{\bar{\kappa}}_j^i = \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi} \kappa_j^i d\theta_i d\theta_j \tag{13.14}$$

is the potential between particles i and j averaged over the azimuthal angle of either one, or of both the elementary systems respectively in the case when either or both are capable of free rotation; the distorted hydrogen atom in the hydrogen molecule ion being distinguished from the normal one by the notation H_p.

The κ_H^H and $\kappa_{H^+}^{H^+}$ are already given in Table II and by (13.5) respectively; the $\kappa_{H_p}^{H^+}$ is calculated as follows by describing the coordinates of the electron by a rather datailed eigenfunction,

$$\{u(H^+) + u(H)\}/\sqrt{2+2\Delta},$$

where $u(H^+)$ and $u(H)$ are atomic orbitals of hydrogen atom around protons denoted by H_1 and H_1^+ respectively (Fig. 4), and by identifying it with the difference of the total potential between the perturbing proton H_0^+ and the hydrogen molecule ion $H_1 - H_1^+$ and the electrostatical one between H_0^+ and the constituent proton H_1. The result is that,

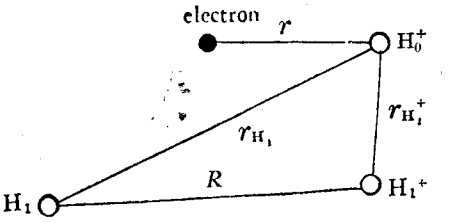

Fig. 4

$$\kappa_{H_p}^{H^+} = \frac{e}{r_{H_1}} - \frac{e^2}{2(1+\Delta)}\left[\int \frac{1}{r}u^2(H_1^+)\,d\tau + \int \frac{1}{r}u^2(H)\,d\tau + 2\int u(H_1)\,u(H_1^+)\,\frac{1}{r}\,d\tau\right] \quad (13.15)$$

where

$$\Delta = \int u(H_1)\,u(H_1^+)\,d\tau$$

and r_{H_1} or r is respectively the distances from H_0^+ to H_1 or to the electron. Integrals in the parenthesis are already evaluated by EYRING[22] and GORDASIE[23] as gollows;

$$\int \frac{1}{r}u^2(H_1)\,d\tau = \frac{1}{a_0}\left\{-\frac{a_0}{r_{H_1+}} + \left(1+\frac{a_0}{r_{H_1}}\right)e^{-2r_{H_1}/a_0}\right\} \quad (13.16)$$

and

$$\int \frac{1}{r}u(H_1)u(H_1^+)\,d\tau = K_0(R,\mathfrak{S}) + \mu^2 K_2(R,\mathfrak{S}) \quad (13.17)$$

where r_{H_1+} is the distance between H_0^+ and H_1^+, a_0 the first Bohr orbit,

$$\mathfrak{S} = (r_{H_1} + r_{H_1+})/2a_0\,, \quad (13.18)$$

$$K_0(R,\mathfrak{S}) = \frac{1}{4R}\left[3(\mathfrak{S}+1)D - 6\mathfrak{S}\Delta + (6\mathfrak{S} - 2R/a_0)\,e^{-R\mathfrak{S}/a_0}\right], \quad (13.19)$$

and

$$K_2(R,\mathfrak{S}) = \frac{3}{4R}\left[-(3\mathfrak{S}-1)D - 6\mathfrak{S}\Delta - (6\mathfrak{S}+2R)\,e^{-R\mathfrak{S}/a_0}\right]. \quad (13.20)$$

Further notations involved are

$$D = \Delta \ln\{(\mathfrak{S}+1)/(\mathfrak{S}-1)\} + E_i(-R\overline{\mathfrak{S}-1}) - \Delta' E_i(-R\overline{\mathfrak{S}-1})\,, \quad (13.21)$$

22) HIRSHFELDER, EYRING & ROSEN, J. Chem. Phys., 4 (1936), 121.
23) CORDASIE, Z. f. Phys. **96** (1935), 542.

$$\Delta = (R^2/3+R+1)\,e^{-R}, \qquad \Delta' = (R^2/3-R+1)\,e^{R}, \tag{13.22}$$

and $$E_i(-z) = -\int_z^\infty z^{-1}\,e^{-z}\,dz.$$

The $\bar{\kappa}$'s, $\bar{k}$'s and henceforth u's are now calculable, the numerical results being given in Table III for different cage distances.

TABLE III

Distances Å / Potentials e.V.	3.26 Å	5.65 Å	6.52 Å
$\bar{k}^{H}_{H}$	0.02_7	0.000	0.000
$\bar{k}^{H^+}_{H}$	0.01_5	0.000	0.000
$\bar{\kappa}^{H}_{H}$	0.03_1	0.000	0.000
$\bar{\kappa}^{H^+}_{H}$	0.02_4	0.000	0.000
$\bar{\kappa}^{H^+}_{H_2}$	0.01_5	0.00_3	0.00_1
$u^{H}_{H_2}$	0.12_4	0.000	0.000
$u^{H_3^+}_{H_2}$	0.06_1	0.00_6	0.00_2
$u^{H}_{H_3}$	0.05_4	0.000	0.000
$u^{H^+}_{H_2}$	0.03_0	0.000	0.000
$u^{H_2^+}_{H_2}$	0.10_4	0.000	0.000
$u^{H}_{H^+}$	0.04_2	0.000	0.000
$u^{H_2}_{H^+}$	0.01_5	0.000	0.000

The U^i_j's are finally obtained according to (13.3) as given in Table IV.

TABLE IV

$U^{H_2^+}_{H^+}$	$U^{H}_{H^+}$	$U^{H_2}_{H^+}$	$U^{H_2^+}_{H_2^+}$	$U^{H}_{H_2^+}$	$U^{H_3^+}_{H_3^+}$	U^{H}_{H}	$U^{H_2}_{H}$	$U^{H_2}_{H_3}$
0.09	0.09	0.18	0.41	0.25	0.62	0.16	0.32	0.74 e.V.

§ 14. $q^{\bar{\delta}}_K$'s as the function of ζ_0.

By virtue of the developments of the preceeding paragraphs $q^{H^+}_K p^{\ominus}_m$, q^{H}_K, $q^{H_2^+}_K p^{\ominus}_m$ and q^{H}_K in the expressions of Θ's given in (4.10), (4.11), (4.12) and (4.13) are now obtained as known functions of Θ and ζ_0 according to (3.13), (9.43), (11.2), (12.26), (12.27) and (12.28), i.e.,

$$q^{H^+}_K p^{\ominus}_m = q^{H^+}_K\, e^{-(e\zeta_0+\sum\Theta_i U^i_H)/kT'}, \tag{14.1}$$

$$q^{H}_K = q^{H}_K\, e^{-\sum\Theta_i U^i_H/kT'}, \tag{14.2}$$

$$q_K^{H_2} = q_K^{H_2} e^{-\sum \Theta_i U^i_{H_2}/kT'}, \tag{14.3}$$

and

$$q_K^{H_2^+} p_m^{\ominus} = q_K^{H_2^+} e^{-(e\zeta_0 + \sum \Theta_i U^i_{H_2^+})/kT'}, \tag{14.4}$$

where ζ_0 is refered to the potential at the surface of the electrode. By solving families of equations (4.9)–(4.12) and (14.1)–(14.4) simultaneously with constants hitherto obtained for q^H, $q_g^{H_2}$, q^δ's and U_j^i's we have now Θ_δ's of respective elementary systems as a known function of $\mathfrak{S}_0$.

Introducing following approximations (i) etc as to the electrostatical properties of our model, Θ_δ's and in consequence q_K^δ's for indvidual elementary systems are finally determined by virtue of POISSON's equation,

$$-\operatorname{div} \zeta = 4\pi\rho_e/D, \tag{14.5}$$

with a special example of the hydrogen electrode in N/10 HCl solution at 19°C polarised at several different potentials, where ζ is the electrostatical potential referred to that at the surface of the electrode, D being the dielectric constant and ρ_e the charge density.

(i). The electrode is replaced by an equivalent conductor with its geometrical plane surface situated $\epsilon 4\phi = 0.2$ Å inside the outermost end of mercury atom at which the potential of the mirror image force for an electron due to the equivalent conductor equals to the work function ϕ.

(ii). Centres of charges of H_2^+ and H^+ are treated as if situated on a plane 1.1 Å apart from the equivalent conductor, which corresponds to the mean positions of H^+ and H_2^+, worked out in the preceding paragraphs. The plane will be called the adsorpion layer.

(iii). Variation of the electrostatical potential is taken into account only in the direction x perpendicular to the plane surface of the equivalent conductor.

(iv). Distribution of ions, except those captured in cages, is governed only by the electrostatical potential ζ.

(v).[24] Hydrogen ions in the solution are allowed to wander about directly up to the adsorption layer, whereas chlorine ions are kept apart from the outermost end of the mercury atom by 1.8 Å, the radius of the chlorine ion.[25]

(vi). The effective dielectric constant is the optical one of water $D_i = 1.7$ between the surface of the equivalent conductor and adsorption layer and $D_s = 80$ outside the adsorption layer.

24) Cf. STERN, Z. Elecktrochem., **30** (1924), 508.

25) Smithsonian Table p. 49.

(vii). The absolute potential of the normal calomel electrode is 0.56 Volt as used to be assumed and hence the potential ζ_b in the bulk of the solution referred to that at the equivalent conductor of the mercury electrode polarised against the normal calomel electrode by η_c Volts or against the deci-normal hydrogen electrode by η Volts that

$$\zeta = -\eta_c - 0.56 = -\eta - 0.22 \text{ Volt.} \tag{14.6}$$

Denoting now the distance of the adsorption layer from the surface of the equivalent conductor by x_0 that of the nearest approach of the centre of the chlonine ion by x_1 and the corresponding electrostatical potentials there referred to that of the surface of the equivalent conductor by ζ_0 and by ζ_1 respectively, POISSON equation, assuming now by virtue of (iii) the form,

$$-\frac{D}{4\pi}\frac{d^2\zeta}{dx^2} = \rho_e \tag{14.7}$$

may be integrated for the individual regions of x as that

$$\left(\frac{d\zeta}{dx}\right)_i = \frac{\zeta_0}{x_0} = \text{constant} \quad \text{for} \quad 0 > x > x_0 \tag{14.8}$$

since there is no true charge there,

$$-\frac{D_i}{4\pi}\frac{\zeta_0}{x_0} + \frac{D_s}{4\pi}\left(\frac{d\zeta}{dx}\right)_a = \epsilon G(\theta_{H_3O^+} + \theta_{H^+}) \quad \text{for} \quad x = x_0 \tag{14.9}$$

since the charge is concentrated on the adsorption layer or at $x = x_0$ as much as given on the right hand side of the equation according to (ii), where G is the number of the cage per unit area, suffix i or a signifying the differential coefficient respectively inside or just outside $x = x_0$, and finally,

$$-\frac{D_s}{4\pi}\left(\frac{d\zeta}{dx}\right)^2 = 2\int \rho_e \left(\frac{d\zeta}{dx}\right) dx + \text{constant} \quad \text{for} \quad x > x_0 \tag{14.10}$$

The charge density ρ_e in the latter equation, which is given by the total sum of the product of the charge, ϵ, and the concentration of ions, N_i, in the solution, may be expressed as a function of ζ by virtue of (iv), postulates that the work required to bring up an ion from the state of referrence into a small volume σ of a definite size in the solution, $-kT\log q_\sigma^\delta$ depends only on the mean electrostatical potential ζ or that,

$$-kT\log q_\sigma^\delta = \epsilon\zeta + \text{constant}, \tag{14.11}$$

and hence that,

$$N_i \propto e^{-\epsilon\zeta/kT},$$

inasmuch as p_a^2 of any kind of ions remains the same everywhere in the solution. We have now that

$$\frac{D_s}{4\pi}\left(\frac{d\zeta}{dx}\right)^2 = 2\epsilon N_{i,b} kT\, e^{-\epsilon(\zeta-\zeta_b)/kT} + \text{const.}, \qquad (14.12)$$

for the region, $x_0 < x < x_1$, where only hydrogen ions are admitted according to (vi) and that

$$\frac{D_s}{4\pi}\left(\frac{d\zeta}{dx}\right)^2 = 2\epsilon N_{i,b} kT\left(e^{-\epsilon(\zeta-\zeta_b)/2kT} - e^{\epsilon(\zeta-\zeta_b)/kT}\right)^2, \qquad (14.13)$$

for the region $x > x_1$, where both the hydrogen and chlorine ions exist in accordance with the condition that $\frac{d\zeta}{dx} = 0$ at $x = \infty$ or at the bulk of the solution, where the concentration both of hydrogen and of chlorine ion is $N_{i,a}$ and the electrostatical potential referred to that of the equivalent conductor ζ_b.

Eq. (14.12) may be written in the form by determining the integration constant according to the condition of the continuity of $d\zeta/dx$ at $x = x_1$ or that $d\zeta/dx$ as given by (14.12) and (14.13) should coincide there, as that

$$\left(\frac{d\zeta}{dx}\right)^2 = \frac{8\pi kT\epsilon N_{i,b}}{D_s}\left(e^{-\epsilon(\zeta-\zeta_b)/kT} - 2 + e^{\epsilon(\zeta_1-\zeta_b)/kT}\right), \quad x_0 < x < x_1 \qquad (14.14)$$

or by integration that

$$\frac{\epsilon(\zeta_1-\zeta_0)}{kT} + 2\ln\left[\frac{\left(e^{-\epsilon(\zeta_1-\zeta_b)/kT} - 2 + e^{\epsilon(\zeta_1-\zeta_b)/kT}\right)^{\frac{1}{2}} - \left(e^{\epsilon(\zeta_1-\zeta_b)/kT} - 2\right)^{\frac{1}{2}}}{\left(e^{-\epsilon(\zeta_1-\zeta_b)/kT} - 2 + e^{\epsilon(\zeta-\zeta_b)/kT}\right)^{\frac{1}{2}} - \left(e^{\epsilon(\zeta_1-\zeta_b)/kT} - 2\right)^{\frac{1}{2}}}\right]$$
$$= \pm\epsilon(x_1-x_0)\left\{\frac{8\pi\epsilon N_{i,b}}{D_s kT}\left(e^{\epsilon(\zeta-\zeta_b)/kT} - 2\right)\right\}^{\frac{1}{2}}. \qquad (14.15)$$

On the other hand (14.14) gives for $(d\zeta/dx)$ $\zeta = \zeta_0$ in (14.9). The equation (14.16) thus obtained gives together with (14.9) and (14.15) give simultaneously, with due regard to (14.6), another independent relation between θ_s and ζ_0. Both the quantities θ_s's and ζ_0 may thus be determined solving (4.9), (4.10), (4.11), (4.12), (4.13), (4.9), (14.15) and (14.16) simultaneously with constants hitherto evaluated. For our example of the mercury electrode in N/10 HCl solution at 19°C, the results are given in Table V.

TABLE V

$-\eta_c$ volt.	0.38	0,41	0.44	1.23	1.26	1.29
$\theta_{H_2^+}$	4.00×10^{-3}	9.60×10^{-3}	1.88×10^{-2}	0.874	0.906	0.939
θ_{H^+}	8.24×10^{-9}	3.42×10^{-9}	1.21×10^{-9}	3.60×10^{-17}	2.11×10^{-17}	8.45×10^{-18}
θ_H	1.19×10^{-20}	3.88×10^{-20}	8.76×10^{-20}	4.31×10^{-10}	7.61×10^{-10}	1.41×10^{-9}
θ_{H_2}	9.22×10^{-5}	8.95×10^{-5}	8.41×10^{-5}	5.61×10^{-14}	1.90×10^{-14}	6.44×10^{-15}
θ_0	0.986	0.980	0.981	0.126	0.094	0.060
ζ_0 Volt.	−0.148	−0.111	−0.071	1.010	1.047	1.083
U^{H^+} e.v.	0.0004	0.0009	0.00169	0.0787	0.0815	0.0847
U^H	0.0010	0.0024	0.0047	0.2190	0.2270	0.2350
U^{H_2}	0.0025	0.0066	0.0117	0.5419	0.5617	0.5820
U^H	0.0016	0.0039	0.0077	0.3583	0.3715	0.3850

§ 15. $q_K^{\ddagger}$ of Critical Complexes or q_K^*; I Procedure of Calculation.

In the present paragraph q_K^* for the elementary reaction,

$$H_2^+ + \ominus \longrightarrow H_2$$

will be evaluated along the general line developed in §7. The calculation cannot be started as in the case of the stable complexes with the first facter $\sum_i e^{-\varepsilon_i^*/kT'}$ of q_K^* in (7.3) without regard to the configuration of surroundings of the cage in as much as the mean configuration and especially the effective charge of the critical complex is reciprocally conjugated to that of the surroundings as already mentioned in §7.

Our procedure to do with the present situation is based on the following consideration. Let $q_{K,\Sigma,\mu}^*$ be the $q_3^{\ddagger}$ of the critical complex under an external force specified by parameter μ's which confines the surroundings to a certain prescribed mean configuration. The $-kT'\ln q_{K,\Sigma,\mu}^*$ is now the reversible work required to bring up the elementary system from the reference state to the prescribed critical state and $-kT'(\partial \ln q_{K,\Sigma,\mu}^*/\partial\mu_i)$ the force conjugated to the i-th parameter.[5] The required quantity is now the particular value of $q_{K,\Sigma,\mu}^*$ which satisfies the condition, that

$$kT' \frac{\partial \ln q_{K,\Sigma,\mu_1,\mu_2}^*}{\partial\mu_i} = 0\,, \qquad (15.1)$$

or that all additional external forces conjugated respectively to μ_i's

vanishes, since there exists virtually no external force.

In accordance with the above consideration we will precede in calculation by introducing several simplifying assumptions; that (1°) the approximation 2° in §7 is justified even in the case of $q^*_{K,\Sigma,\mu}$ and, similarly as in the case of H_2^+ that (2°) the interaction potential between the critical complex and the surroundings, consists practically only in the electrostatical one, and that (3°) the effective charge is concentrated at the same point in the cage as that of H_2^+.

The effective charge e^* being now only parameter according to (2°) and (3°) for a particular Σ (15.1) assums the form,

$$\frac{\partial \ln q^*_{K,\Sigma,e^*}}{\partial e^*} = 0 . \tag{15.2}$$

The q^*_{K,Σ,e^*} may on the other hand be expressed according to (1°) and (7.3) as that,

$$q^*_{K,\Sigma,e^*} = \left(\sum_i e^{-\varepsilon_i^*/kT} \right)_{\Sigma,e^*} e^{-Y^*_{0,\Sigma,e^*}/kT} \tag{15.3}$$

where, as deduced from general definition, the first factor is due to the motion of the critical complex with the critical surface particular to Σ and to e^*, and Y^*_{0,Σ,e^*} the reversible work required first to produce such dipole orientation of the WEBB's model around the cage as would be induced by the prescribed point charge e^* in the cage and then to bring up the elementary sysuem from the state of reference to the mean configuration appropriate to the latter dipole orientation.

Our procedure is now first to work out the critical surface for each assigned value of Σ and e^*.

According to (iii) in §7 however, the WEBB'S model should keep its configuration at the critical state during a certain period of time immediately before and after the transition of the critical state. This allows us to construct as actually carried out in §16 the potential energy V^* at prescribed values of Σ and e^* or V^*_{Σ,e^*} which governs the motion of the elementary system at least in the neighbourhood of the critical state by combining according to 5° in §1 the potential energies, $V^{H_2}_{\Sigma,e^*}$ and $V^{H_2^+ + \ominus}_{\Sigma,e^*}$ respectively of the elementary systems, H_2 and $H_2^+ + \ominus$ or by taking the smaller one of the potential energies, $V^{H_2}_{\Sigma,e^*}$ and $V^{H_2^+ + \ominus}_{\Sigma,e^*}$ at every nuclear configuration of the elementary system, with some allowance for the depression due to quantum mechanical resonance in the neighbourhood of the configuration, where $V^{H_2}_{\Sigma,e^*} = V^{H_2^+ + \ominus}_{\Sigma,e^*}$. The potential energy thus derived as the function of the coordinates will

be called the potential surface of the critical state in what follows.

From the general feature of the latter thus obtained at different Σ and e^*, it will be concluded in §16 that the equation $V^{H_2}_{\Sigma,e^*} = V^{H_2^+ + \ominus}_{\Sigma,e^*}$ satisfies the conditions for being that of the critical surface.

Adopting the latter as the equation of the critical surface the dynamics of the critical surface will be developed with the critical surface as constraint arriving at the determination of the mean position of the factor $\left(\sum_i e^{-\varepsilon_i/kT}\right)_{\Sigma,e^*}$ in §18 and of Y^*_{0,Σ,e^*} in §19. The numerical calculation will however be simplified similarly as in the case of stable complexes by calculating the factor $\left(\sum_i e^{-\varepsilon_i/kT}\right)_{\Sigma,e^*}$ only at Σ_0 and e^*_0 where Y^*_{0,Σ,e^*} is found minimum or the factor $e^{-Y^*_{0,\Sigma,e^*}/kT}$ maximum, and by attributing the latter value to all other cases of Σ and e^*.

The final step of our procedure in §19 will be the determination of $q^*_{K,\Sigma}$ by locating the minimum of Y^*_{0,Σ,e^*} with respect to e^* at defferent Σ, and of q^*_K by integrating $q_{K,\Sigma}$ according to (3.5).

§16. q^*_K; II The Potential Surface of the Critical State at Prescribed Values of e^* and Σ.

The potential energies of the elementary system involved in the governing reaction, H_2 and $H_2^+ + \ominus$ are obtained by evaluating each term on the right of (7.4).

The potential energy of H_2 or $V^{H_2}_{\Sigma,e^*}$ is thus obtained by expressing as below $V^{H_2}_\Sigma$ in (7.4) by the sum of twice negative of the ionization potential 13.529 Volt of hydrogen atom, the mutual potential of hydrogen atoms at the ground state of the hydrogen molecule or V^H_H, that due to mercury atom or $V^{H_2}_{Hg,\Sigma}$, that due to the water molecule of the cage or $V^{H_2}_{OH_2,\Sigma}$ and that $\sum_i \theta_j U^j_{H_2}$ due to surrounding elementary systems δ_j's, as that

$$V^{H_2}_{\Sigma,e^*} = -2\times 13.529 + V^H_H + V^{H_2}_{Hg,\Sigma} + V^{H_2}_{OH_2,\Sigma} + \sum_j \theta_j U^j_{H^3}\,. \quad (16.1)$$

$Y^{H_2}_{M,\Sigma}$ and $Y^{H_2}_{W,\Sigma}$ in (7.4) not being included in accordance with §10 and §11. The V^H_H is given by the well-kown Morse function, i.e.,

$$V^H_H = 4.733 \times \left[e^{-2\times 1.989\,(r-0.74)} - 2e^{-1.989\,(r-0.74)}\right] \text{e.V.}$$

The $V^{H_2}_{OH,\Sigma}$ is evaluated as the sum of two individual potentials between hydrogen atom and water molecule which is given by (10.3) in §10. The $V^{H_2}_{Hg,\Sigma}$ is evaluated similarly as $V^{H_2}_{OH,\Sigma}$ as the sum of potentials

$V^{H}_{Hg,\Sigma}$ between Hg and individual H derived from the following data for the potential between respective pairs of atoms, i.e. H—He, He—He and Hg—Hg or that

$$V^{H}_{He} = 10^{6.50-1.40\,r_{H\text{-}He}}\ \text{e.V./mol},$$

$$V^{H}_{He} = 10^{7.05-1.98\,r_{He\text{-}He}}\ \text{e.V./mol},$$

$$V^{Hg}_{Hg} = 10^{14.00-4.8\,r_{Hg\text{-}Hg}}\ \text{e.V./mol},$$

where r is the distance between two atoms involved in Å unit, according to the rule[28] that the distance, at which the repulsive potential for atom pairs assumes a definite value, is additive with respect to consituent atoms, or in particular, that, denoting by r_1 and r_2 and r_3 respectively such distances of the three pairs of atoms i.e. H—He, He—He and Hg—Hg, as,

$$V^{H}_{He}(r_1) = V^{He}_{He}(r_2) = V^{Hg}_{Hg}(r_3),$$

the same value of the repulsive potential for the pair Hg—H corresponds to the distance $r_1 - \frac{r_2}{2} + \frac{r_3}{2}$ between Hg and H. The results is that

$$V^{H}_{Hg,\Sigma} = 2.44\times 10^{3-1.78\,r}\ \text{e.V./mol}. \qquad (16.2)$$

The potential $V^{H_2^+\ominus}_{\Sigma,e^*}$ of $H_2^+ + \ominus$ or of the elementary system consisting of a metal electron and a hydrogen molecule ion situated inside the cage with surrounding WEBB's aquaus solution outside orientated by the prescribed point charge e^* is given according to (7.4) by

$$V^{H_2^+\ominus}_{\Sigma,e^*} = -\ V + V^{H_2}_{K,\Sigma} + Y^{H_2^+}_{M,\Sigma} + Y^{H_2^+}_{W,\Sigma,e^*} + V^{H_2^+}_{E}, \qquad (16.3)$$

The $V^{H_2^+}_{K,\Sigma}$ is the expression already worked out in §12, whereas $V^{H_2^+}_{E}$ given by (13.1) or by (13.2) as that

$$V^{H_2^+}_{E} = e\zeta_0 + \sum_j \theta_j U^j_{H_2^+}. \qquad (16.4)$$

The remaining part of the potential, $Y^{H_2^+}_{M,\Sigma} + Y^{H_2^+}_{W,\Sigma,e^*}$ is taken similarly as for $Y^{H_2^+}_{I,\Sigma}$ in (b), §9 as the mean of the two electrostatical works $Y^{H_2^+}_{M,\Sigma}$ and $Y^{H_2^+}_{W,\Sigma}$, each being required to transfer the point charge e for

*) Calculated by the expression (Coulomb potential) $-\frac{1}{2}$ (Exchange potential), the value of the latter potentials being taken from the result of ROSEN and IKEHARA [Phys. Rev., **43** (1935), 5].

26) GENTILE, Zeit. f. Physik, **63** (1930), 795.

27) SLATER, Phys. Rev., **32** (1928), 349.

28) BORN and MAYER. Z. f. Physik, **75** (1932), 1.

H_2^+ from inside the electrostatical model of the cage in vacuum into that immersed in the dielectrics corresponding respectively to the electrode, or to the WEBB'r model arrested at the dipole orientation particular to the prescribed charge e^*. $Y_{M,\Sigma}^{H_2^+} + Y_{W,\Sigma,e^*}^{H_2^+}$ is now given by (9.12) in §9, by replacing Y_D there by Y_{e^*} or the work required to bring up the elementary charge from infinity up to the centre of the small sphere inside the ellipsoid which is immersed in the WEBB'S model of the particular orientation appropriate to e^*. The latter work Y_{e^*} is, along the similar line of reasoning as far (9.13), given by

$$Y_{e^*} = \frac{e}{2\rho}\left(\frac{1}{D_i}-1\right)^2 + \frac{e^2}{\rho}\left(\frac{1}{D_i}-1\right) + \frac{ee^*\varphi_0(D_a)}{D_i}$$

where $e^*\varphi_0(D_a)/D_i$ is the electrostatical potential at the centre of the sphere due to the charge accumlated at the boundary of the ellipsoid; the latter surface charge remains the same as induced by the prescribed charge e^* irrespective of the charge afterward introduced so long as the mean configuration of the surroundings is fixed to e^*.

Introducing further into (9.12) the detailed expressions for Y_∞ and Y_1, we have, that

$$Y_{M,\Sigma}^{H_2^+} + Y_{W,\Sigma,e^*}^{H_2^+} = \frac{e}{D_i}\left[\frac{e^*\varphi_0(20)+e^*\varphi_0(\infty)}{2} - e^*\varphi_0(1)\right] + \frac{(e^*)^2}{2}\int\left[\frac{\varphi_+(\infty)\omega_f(\infty)}{2} - \varphi_f(1)\omega_f(1)\right]df, \qquad (16.5)$$

and further according to (16.3), (16.4) and (16.5) that

$$V_{\Sigma,e^*}^{H_2^+ +\ominus} = -e\phi + e\zeta_0 + V_{K,\Sigma}^{H_2^+} + \sum_j \theta_j U_{H_2^+}^{i} + \frac{e}{D_i}\left[\frac{e^*(\varphi_0(20)+\varphi_0(\infty))}{2} - e^*\varphi_0(1)\right] + \frac{(e^*)^2}{2}\int\left[\frac{\varphi_f(\infty)\omega_f(\infty)}{2} - \varphi_f(1)\omega_f(1)\right]df \qquad (16.6)$$

where ϕ is the work function of the electrode. The potential surface of the critical state is thus constructed from potential energies $V_{\Sigma,e^*}^{H_2}$ and $V_{\Sigma,e^*}^{H_2^+ +\ominus}$ in accordance with §15 at several different values of Σ and e^* for the case of the electrode polarised against a normal calomal electrode by -0.41 and at -1.26 Volt in N/10 HCl solution at 19°C, θ_j and ζ_0 required for the evaluation of $V_{\Sigma,e^*}^{H_2}$ and $V_{\Sigma,e^*}^{H_2^+ +\ominus}$ being taken from Table V.

The investigation of the results thus obtained shows that the surface in the configuration space having an energy relation

$$V_{\Sigma,e^*}^{H_2} = V_{\Sigma,e^*}^{H_2^+ +\ominus} \qquad (16.7)$$

has such properties that it separates the partial configuration space of the elementary system into two parts respectively corresponding to the initial and final state and that the potenital energy is nimimum along every coordinates included in the surface and maximum along the normal.

On this ground (16.7) was taken the equation of the critical surface.

§ 17. q_K^*; III The Mean Position and the Partition Function of The Critical Complex at a Prescribed Values of e^* and Σ.

The factor $\sum_i e^{-\varepsilon_0^*/kT}$ for the critical complex is calculated by approximating the potentials $V_{\Sigma,e^*}^{H_2}$ and $V_{\Sigma,e^*}^{H_2^++\ominus}$, with respective quadratic functions of coordinates around the minimum point of critical surface, (16.7), as that

$$V_{\Sigma,e^*}^{H_2} = V_{0,\Sigma,e^*}^* + \sum_n a_n^{H_2} q_n + \frac{1}{2}\sum_{l,m} a_{l,m}^{H_2} q_l q_m , \qquad (17.1)$$

$$V_{\Sigma,e^*}^{H_2^++\ominus} = V_{0,\Sigma,e^*}^* + \sum_n a_n^{H_2^+} q_n + \frac{1}{2}\sum_{l,m} a_{l,m}^{H_2^+} q_l q_m , \qquad (17.2)$$

where q_n's are coordinates making the minimum point as their origins. Eq. (16.7) may now expressed as that

$$\sum_n (a_n^{H_2^+} - a_n^{H_2^+})\, q_n + \frac{1}{2}\sum_{l,m} (a_{l.m}^{H_2^+} - a_{l,m}^{H_2})\, q_l q_m = 0 \qquad (17.3)$$

whereas V_{Σ,e^*}^* by

$$V_{\Sigma,e^*}^* = V_{\Sigma,e^*}^{H_2^++\ominus} - \chi_0 \left(V_{\Sigma,e^*}^{H_2^++\ominus} - V_{\Sigma,e^*}^{H_2}\right) , \qquad (17.4)$$

with the former as the constraint, χ_0 being a constant determined from the condition that V_{Σ,e^*}^* is minimum at the origin or that

$$\left(\frac{\partial V_{\Sigma,e^*}^*}{\partial q_n}\right)_{q_n=0} = 0 , \qquad n = 1, 2 \cdots\cdots . \qquad (17.5)$$

The result is that

$$V_{\Sigma,e^*}^* = V_{0,\Sigma,e^*}^* + \sum_{l,m} \left[a_{l,m}^{H_2^+} - \chi_0 (a_{l,m}^{H_2^+} - a_{l,m}^{H_2})\right] q_l q_m \qquad (17.6)$$

and

$$\chi_0 = \frac{a_n^{H_2^+}}{a_n^{H_2^+} - a_n^{H_2}} , \qquad n = 1, 2 \cdots\cdots . \qquad (17.7)$$

The $V_{\Sigma,e^*}^* - V_{0,\Sigma,e^*}^*$ or the excess of the potential energy on the critical surface over the minimum value V_{0,Σ,e^*}^* is now given by (17.6) as a

homogeneous quadratic function of coordinates with the constraint (17.3). The second order term in (17.3) may however be neglected, so that

$$V_c \equiv \sum_n (a_n^{\mathrm{H}_2{}^*} - a_n^{\mathrm{H}_2}) q_n = 0 \ , \tag{17.8}$$

so far as we remain with the approximation with the potential energy on the critical surface of neglecting terms of higher than the second order, since the latters give rise to terms of only the third and higher terms when any one of coordinates in (17.6) were substituted by (17.3).

In terms of the coordinate system introduced in §12, Lagragean equation of motion for the elementary system at the critical state,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right) - \frac{\partial L}{\partial q_k} = -\chi\left(\frac{\partial V_c}{\partial q_k}\right) , \qquad k = 1, 2 \cdots\cdots \tag{17.9}$$

takes the form,

$$(I_{\mathrm{I}}^* + I_{\mathrm{II}}^*)\,\ddot{\theta} = 0 \, , \tag{17.10}$$

$$\frac{I_{\mathrm{I}}^* I_{\mathrm{II}}^*}{I_{\mathrm{I}}^* + I_{\mathrm{II}}^*}\,\ddot{\theta} + A_{\theta\theta}\,(\theta - \theta_0) = 0 \tag{17.11}$$

and

$$\left.\begin{aligned}
&(m_{\mathrm{I}} + m_{\mathrm{II}})\,\ddot{r} + (m_{\mathrm{I}} - m_{\mathrm{II}})\,\ddot{\bar{r}} + A_{rr}\,(r - r_0) + A_{r\xi}\,(\xi - \xi_0) = -\chi A'_r \\
&(m_{\mathrm{I}} - m_{\mathrm{II}})\,\ddot{r} + (m_{\mathrm{I}} + m_{\mathrm{II}})\,\ddot{\bar{r}} + A_{\bar{r}\bar{r}}\,(\bar{r} - \bar{r}_0) + A_{\bar{r}\bar{\xi}}\,(\bar{\xi} - \bar{\xi}_0) = 0 \\
&(m_{\mathrm{I}} + m_{\mathrm{II}})\,\ddot{\xi} + (m_{\mathrm{I}} - m_{\mathrm{II}})\,\ddot{\bar{\xi}} + A_{\xi\xi}\,(\xi - \xi_0) + A_{r\xi}\,(r - r_0) = -\chi A'_\xi \\
&(m_{\mathrm{I}} - m_{\mathrm{II}})\,\ddot{\xi} + (m_{\mathrm{I}} + m_{\mathrm{II}})\,\ddot{\bar{\xi}} + A_{\bar{\xi}\bar{\xi}}\,(\bar{\xi} - \bar{\xi}_0) + A_{\bar{r}\bar{\xi}}\,(\bar{r} - \bar{r}_0) = 0 \\
&A'_r\,(r - r_0) + A'_\xi\,(\xi - \xi_0) = 0
\end{aligned}\right\} \tag{17.12}$$

where χ is the indeterminate multiplier for the constraint force derived from (17.8), and

$$I_i^* = m_i r_0^2 \, , \tag{17.13}$$

$$A_{l,m} = \left[a_{l,m}^{\mathrm{H}_2{}^*} - \chi_0\,(a_{l,m}^{\mathrm{H}_2{}^*} - a_{l,m}^{\mathrm{H}_2})\right] , \tag{17.14}$$

and

$$A'_n = a_n^{\mathrm{H}_2{}^*} - a_n^{\mathrm{H}_2} \, , \tag{17.15}$$

suffix 0 signifying values of coordinates at the minimum point. The (17.10) leads to the free rotation with the moment of inertia $I_{\mathrm{I}}^* + I_{\mathrm{II}}^*$, (17.11) to the deformation vibration of the frequency $\nu_1^* = \frac{1}{2\pi}\sqrt{\frac{A_{\theta\theta}(I_{\mathrm{I}}^* + I_{\mathrm{II}}^*)}{I_{\mathrm{I}}^* I_{\mathrm{II}}^*}}$ and (17.12) to the three fold modes of vibration. The latter can be solved for the frequency ν^* of the small normal vibrations by putting coordinates and χ proportional to $e^{2\pi i \nu^* t}$. The secular equation is

$$\begin{vmatrix} -\lambda(m_I+m_{II})+A_{rr} & A_{r\xi} & -\lambda(m_I-m_{II}) & 0 & A'_r \\ A_{r\xi} & -\lambda(m_I+m_{II})+A_{\xi\xi} & 0 & -\lambda(m_I-m_{II}) & A'_\xi \\ -\lambda(m_I-m_{II}) & 0 & -\lambda(m_I+m_{II})+A_{\bar{r}\bar{r}} & A_{\bar{r}\bar{\xi}} & 0 \\ 0 & -\lambda(m_I-m_{II}) & A_{\bar{r}\bar{\xi}} & -\lambda(m_I-m_{II})+A_{\bar{\xi}\bar{\xi}} & 0 \\ A'_r & A'_\xi & 0 & 0 & 0 \end{vmatrix} = 0 \tag{17.16}$$

where $\lambda = 4\pi^2\nu^{*2}$.

Solving (17.16) we obtain three normal vibrational frequencies ν_2^*, ν_3^* and ν_4^*. Eigenwerts may be derived from the above classical results arriving at the factor $\sum_i e^{-\varepsilon_i/kT'}$, i.e.,

$$\sum_i e^{-\varepsilon_i/kT} = \frac{\sqrt{2\pi(I_I^*+I_{II}^*)kT'}}{sh} \prod_k^{1\cdots4} \left(2\sinh\frac{h\nu_k}{2kT'}\right)^{-1} e^{-V^*_{0,\Sigma}/kT'}. \tag{17.17}$$

A numerical example is shown below in Table VI and in Fig. 4 for the cases of an electrode polarised in N/10 HCl solution by -0.41 and by -1.26 Volt against the normal calomel electrode at 19°C with respective prescribed values of L, Ω and $\mathfrak{e}^*$ which happens to be those corresponding to q^*_{Σ,Σ_0} with the critical complex consisting of two protium nuclei as well as for that consisting of a protium and a duterium nuclei assuming with UREY[29] that the isotopic replacements does not vary interatomic potentials involved.

TABLE VI

Critical Complex	η_c Volt/mol	L_0 Å	Ω_0	$\mathfrak{e}^*/\mathfrak{e}$	χ_0	$I_I^* + I_{II}^*$	ν_2^* cm^{-1}	ν_3^*	ν_4^*	ν_1^*
(H, H)	-0.41	4.30	0.00	0.42	0.634	5.72×10^{-41}	3448	1427	126	124
	-1.26	4.20	0.00	0.53	0.521	6.16×10^{-41}	3338	1516	163	105
(H, D)	-0.41	4.30	0.00	0.42	0.634	8.58×10^{-41}	2994	1126	103	107
	-1.26	4.20	0.00	0.53	0.521	9.24×10^{-41}	2905	1231	134	91

Fig. 5 shows the modes of motion associated with the elementary reaction, $H_2^+ + \ominus \rightarrow H_2$ and with the individual vibrations deduced from (17.12) for the cases of (H, H) and (H, D) at $\eta_c = -1.26$, e. V.

§ 18. q_K^* ; IV The Free Energy of the Critical Complex with the Prescribed Values of $\sum$ and $\mathfrak{e}^*$.

Free energy $Y^*_{0,\Sigma,\mathfrak{e}^*}$ of the critical complex with the prescribed

29) UREY and RITTENBERG, J. Chem. Phys., 1 (1933), 137.

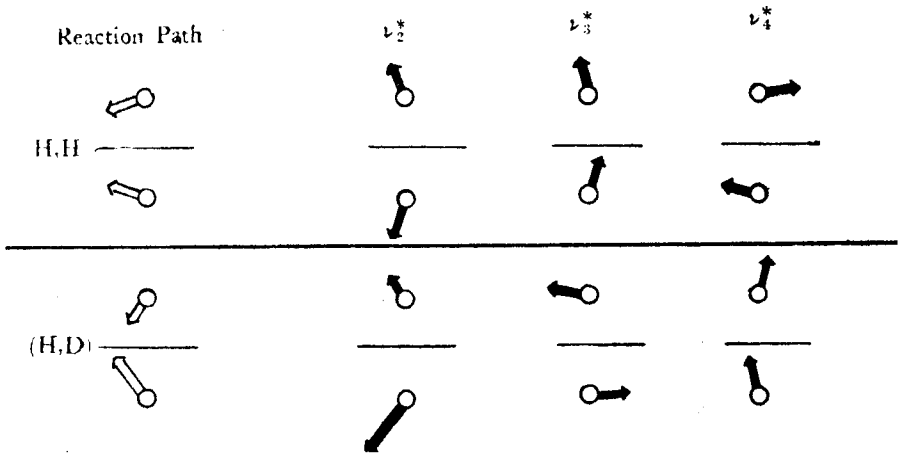

Fig. 5

values of Σ and e^* consists according to §15 of two parts, i. e.

$$Y^*_{0,\Sigma,e^*} = Y'_{\Sigma,e^*} + V^*_{0\,\Sigma' e^*} \tag{18.1}$$

where Y'_{Σ,e^*} is the reversible work required to set up the dipole orientation appropriate to e^*, and V^*_{0,Σ,e^*} that required to bring up the elementary system to the critical state at the fixed configuration of the surroundings worked out in the preceeding paragraph. The first part of the work further consists of that required to introduce the point charge e^* into the cage without external restriction on the dipole orientation and of that required to withdraw the charge leaving the surroundings at the mean configuration appropriate to the charge e^* in the cage. These constituents of the work, Y'_{Σ,e^*} are however given respectively by (9.38) putting $e = e^*$ there and by (16.5) changing the sign of $Y^{H_2\dagger}_{M,\Sigma^2} + Y^{H_2\dagger}_{W,\Sigma}$ and putting $e = e^*$. We have now

$$Y'_{\Sigma,e^*} = \frac{(e^*)^2}{4}\int \varphi_f(20)\,\omega_f(20)\,df \tag{18.2}$$

and by (18.1) and (18.2) also

$$Y^*_{0,\Sigma,e^*} = \frac{(e^*)^2}{4}\int \varphi_f(20)\,\omega_f(20)\,df + V^*_{0,\Sigma,e^*}. \tag{18.3}$$

§ 19. q^*_K ; V The Determination of $q^*_{K,\Sigma}$ and of q^*_K .

We now arrive at $q^*_{K,\Sigma}$ with the expression,

$$q^*_{K,\Sigma} = \Big(\sum_i e^{-\varepsilon^*_i/kT}\Big)_{\Sigma_0,e^*} e^{-Y^*_{0,\Sigma}/kT},$$

by locating the minimum $Y^*_{0,\Sigma}$ of Y^*_{0,Σ,e^*} with respect to e* according to (18.3) just derived, where $\left(\sum_i e^{-\varepsilon_i^*/kT'}\right)_{\Sigma_0,e_0^*}$ is the factor $\left(\sum_i e^{-\varepsilon_i^*/kT'}\right)$ calculated according to §15 at the minimum point of Y^*_{0,Σ,e^*} with respect to Σ and e*. Fig. 6 shows the plot of Y^*_{0,Σ,e^*} against e*/e at $\Omega = 0$ and at different values of L for an electrode polarised in N/10 HCl solution by −1.26 Volt and by −0.41 Volt respectively against the normal calomel electrode at 19°C, from which the minimum of Y^*_{0,Σ,e^*} is determined.

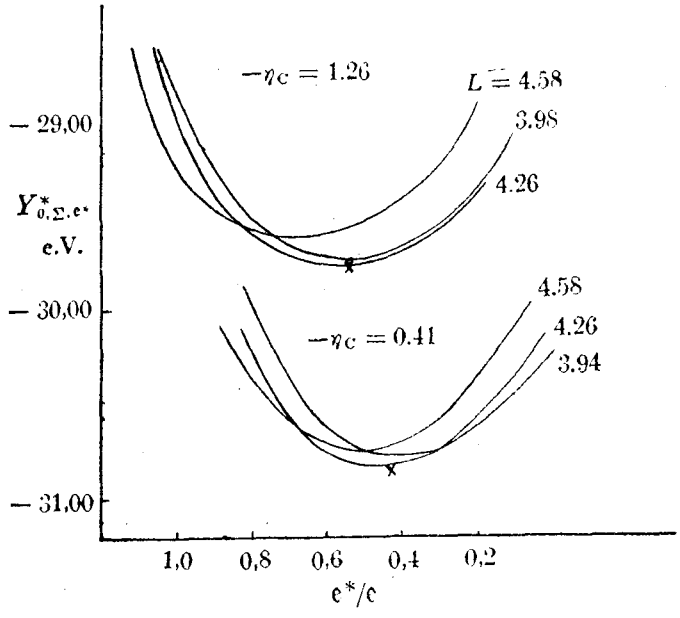

Fig. 6

The q^*_K is henceforth determined by integration of $q^*_{K,\Sigma}$ according to (3.5) approximating $Y^*_{0,\Sigma}$ in the above expression by a quadratic function of Σ around Σ_0 of the form,

$$Y^*_{0,\Sigma} = Y^*_{0,\Sigma_0} + \Gamma^*_L (L-L_0)^2 + \Gamma^*_\Omega (\Omega-\Omega_0)^2 \qquad (19.1)$$

arriving finally at the expression that

$$q^*_K = \frac{\sqrt{2\pi(I^*_I + I^*_{II})kT'}}{sh} \prod_k^{1,\ldots 4} \left(2\sinh\frac{h\nu^*_k}{2kT'}\right)^{-1} \frac{\rho_\Sigma \pi kT}{\sqrt{\Gamma^*_L \Gamma^*_\Omega}} e^{-Y^*_{0,\Sigma_0}/kT'}. \qquad (19.2)$$

Table VII shows the numerical results of the calculation with the above example of the electrode potential.

TABLE VII

$-\eta_c$ Volts	e*/e	Σ_0		$-Y^{*}_{0,\Sigma_0}$ e.V.	q^{*}_{K}	Y'_{Σ,e^*} e.V.
		L_0 Å	Ω_0			
0.41	0.42	4.30	0.00	30.86	7.65×10^{523}	0.316
1.26	0.53	4.20	0.00	29.76	1.43×10^{505}	0.511

CHAPER III. THEORETICAL CALCULATION OF THE OBSERVABLE QUANTITIES.

§ 20. Outlines.

Having developed the reaction rates in terms of the q^{δ}_{K}'s and of Θ_{δ}'s in Chapter I, and evaluated latters in Chapter II, we are now in the position to calculate the reaction rate and any observable quantities derivable from the latter at given conditions, for instance the absolute values of anodic and cathodic current densities and their variation with polarization and temperature, the ratio of the relative rate of discharge of protium and deuterium from a solution by electrolysis or the isotopic seperation factor defined by,

$$S = \frac{d[\mathrm{H}]}{[\mathrm{H}]_l} \Big/ \frac{d[\mathrm{D}]}{[\mathrm{D}]_l} \tag{20.1}$$

and its temperature coefficient, where $d[\mathrm{H}]$ anb $d[\mathrm{D}]$ are the rates of discharge of hydrogen and deuterium respectively and $[\mathrm{H}]_l$ and $[\mathrm{D}]_l$ atomic concentrations of hydrogen and deuterium in the solution respectively.

In the following paragraphs we will draw theoretical conclusions on the above quantities to compare them with experiments.

§21. The Absolute Value of the Current Density.

Observable current density i is given, according to the present theory, by the difference of negative and positive current densities given, respectively, by (6.3) and (6.4) as that

$$i = |\vec{I} - \overleftarrow{I}| = 2\mathrm{e}\frac{kT'}{h} G\Theta_0 \frac{q^{*}_{K}}{Q^{\mathrm{H}_2}_{g}} |N_{g,0} e^{-2\mathrm{e}\eta/kT'} - N_g| , \tag{21.1}$$

which is called the cathodic or anodic current density according as $\vec{I} > \overleftarrow{I}$ or $\vec{I} < \overleftarrow{I}$. The observable anodic or cathodic current will however consist almost exclusively of negative or positive current respectively except

in the region of small polarization as seen from the equation derived from (6.3) and (6.4), i. e.

$$\vec{I}/\overleftarrow{I} = (N_{g,0}/N_g)\, e^{-2e\eta/kT'}, \qquad (21.2)$$

which shows in particular that the current in the reverse direction at room temperature reduces to one per cent of the total as soon as η departs from zero by 0.06 Volts.

The cathodic current of an electrode polarized in N/10 HCl solution by -1.26 Volt or by -0.41 Volt against the normal calomel electrode at 19°C for example is hence, assuming one atmospheric pressure of hydrogen gas around the electrode, directly given by $\vec{I}$ in (6.3), η against a reversible hydrogen electrode of one atmospheric pressure in the same solution being $-1.26+0.34=-0.92$ and -0.07 Volt, respectively.

With the data for θ_0, q_K^* and $Q_g^{H_2}$ prepared for the special example in the preceeding paragraphs with $G = 11 \times 10^{15}$, we have

$i = 2 \times 10^{-5}$ Amp/cm^2 at $\eta_c = -1.26$ Volt.

$i = 4 \times 10^{-15}$ Amp/cm^2 at $\eta_c = -0.41$ Volt.

The experimental result, $i = 3 \times 10^{-4}$ Amp/cm^2 at $\eta_c = -1.26$ Volt was obtained by BOWDEN and RIDEAL[30] which is to be compared with the theoretical value at the lower electrode potential whereas no experimental data seems to have hitherto been obtained for the current at the higher one as well as for the anodic current to be compared with, presumably because the latter have so far escaped experimental investigation on account of the contamination with that due to the ionization of the mercury electrode itself.

It might however be possible whether the above agreement, close enough for an a priori calculation of this sort, is due to a fortuitous choice of rather uncertain interatomic or molecular potentials. To examine this point the above theoretical calculation of the current density was repeated by doubling the potential fnnction $V_{OH_2}^H$ given by (10.3) as that

$$V_{OH_2}^H = 2\left(\frac{30}{r^7} - \frac{16}{r^6}\right) \text{ e. V},$$

which would make a difference of 0.2 Volt in the energy of H_2^+ at its stable configuration determined in §12. The latter amount corresponds, if imposed upon the energy of either the critical or the initial complex, to the variation of the rate by $10^{3.5}$ factor. The result is shown in Table VIII together with the original ones in the parentheses side by side.

30) BOWDEN and RIDEAL, Proc. Roy. Soc., A **120** (1928), 86.

The $V^{H_2}_{0,K,\Sigma_0}$ or $V^{H_2{}^+ + \ominus}_{0,K,\Sigma_0}$ is the minimum value respectively of $V^{H_2}_{K,\Sigma,e^*}$ or of $V^{H_2{}^+ + \ominus}_{K,\Sigma,e^*}$ as given by (16.1), or (16.3) with respect to the coordinates of the elementary system at the configuration of the cage and that of the surroundings corresponding to the maximum value of q^*_{K,Σ,e^*} with respect to Σ and e^*.

TABLE VIII

η_c Volt	Θ_0	Θ_H	Θ_{H_2}	Θ_{H^+}	$\Theta_{H_2{}^+}$	$V^{H_2}_{0,K,\Sigma_0}$ e.V.
	0.330	2×10^{-4}	2×10^{-3}	3×10^{-5}	0.670	−30.62
−1.26						
	(0.094)	(8×10^{-10})	(2×10^{-14})	(2×10^{-17})	(0.906)	(−30.92)
η_c Volt	$V^{H_2{}^+ \ominus}_{0,K,\Sigma_0}$ e.V.	U^{H_2} e.V.	$U^{H_2{}^+}$ e.V.	Y^*_{0,Σ_0} e.V.	e^*/e	i Amp.
	−30.32	0.415	0.275	−29.65	0.60	1×10^{-6}
−1.26						
	(−30.36)	(0.562)	(0.372)	(−29.76)	(0.53)	(2×10^{-5})

The Table VIII shows that in the case of $\eta_c = -1.26$ Volt the increase in the potential $V^H_{OH_2}$ results in the increase in $V^{H_2}_{0,K,\Sigma_0}$'s as well as in the decrease in $\sum_j \Theta_j U^j_{H_2}$ both effect on $V^*_{0,K,\Sigma_0 e_0 *}$ almost cancelling each other. In the case of $\eta_c = -0.41$ Volt, Θ_δ's and in consequence $\sum_j \Theta_j U^j_{H_2}$ practically vanish irrespective of the potential $V^H_{OH_2}$.

So far as the above control is concerned, one might expect that the close agreement at the lower electrode potential is rather due directly to the logical consequence of the present theory than to the fortuitous choice of the individual potential function, whereas the inaccuracy of the latters, if any, at higher electrode potential, would more or less disfigure the theoretical value of the current density.

§22. Variation of the Cathodic Current with Polarization—The Tafel's Relation.

It has long been known that the cathodic current varies with the electrode potential over a range of cathodic polarization according to the relation.

$$\ln \vec{I} = -\frac{\alpha}{RT} F\eta + \text{const.}, \qquad (22.1)$$

as found by Tafel and estabilished by exhaustive experiments by BOWDEN

and RIDEAL,[31] where α is a proper fraction remaining constant nearly at 0.5 over a considerable range of polarization. FRUMKIN[32] has raised an analogous empirical relation due to Brönsted about the specific rate of proton transfer and the electrolytic dissociation constant K of acids or bases involved in the reaction, i.e.

$$\ln k = \alpha' \ln K + \text{const.}, \qquad (22.2)$$

where α' is a constant proper fraction with a series of acids or bases, pointing out that the free energy of the electrolytic dissociation $-RT\ln K$ here plays a similar part as η in the Tafel's relation. The striking analogy seems to have suggested, that it is the proton transfer from the electrode to the solution, i.e. ionization of the adsorbed hydrogen atoms or the reversed process, which governs the rate of the electrode process. With this conception VOLMER,[33] GURNEY,[34] FOWLER,[35] HORIUTI and POLANYI[36] have given more or less quantitative explanation to the relation, which, although appreciably different in form, consists essentially in deriving the fact, from the standpoint of Arrhenius theory of reaction rate, that the energy increase at the initial state was only partially effective to decrease the activation energy of the reaction, and in expressing the latter partial effectiveness by the proper fraction α in Tafel's relation.

On studying the problem more precisely by means of hydrogen isotopes, OKAMOTO and present authors have later arrived at a revised poit of view, discarding the above mechanism that the observed electrode reaction proceeds either by the catalytic or the electrochemical mechanism,*) which in earlier forms of representation, were thought inadequate only because they were incapable to account for the Tafel's relation on the basis of the simple kinetic theory of reaction.

OKAMOTO and present authors have however developed the statistical mechanical theory of the catalytic mechanism leading to the conclusion

*) Catalytic mechanism was already suggested by Tafel [Z. physik Chem., **34** (1900), 200; ibid., **50** (1905), 649.] himself and the electrochemical mechanism in different but somewhat common form by HEYROWSKY [Rec. Trav. Chim., **46** (1927), 582] and by BOWDEN [Proc. Roy. Soc., A **126** (1929), 107].

31) BOWDEN and RIDEAL, loc. cit.

32) FRUMKIN, Z. phys. Chem., A. **164** (1933), 121.

33) VOLMER, Z. phys. Chem., **150** (1930), 209.

34) GURNEY, Proc, Roy, Soc., A **134** (1931), 137.

35) FOWLER, Trans. Farad. Soc., **28** (1932), 368.

36) HORIUTI and POLANYI, Acta Physicochim., U.S.S.R. **2** (1935), 505.

that $\alpha = 2$ when the surface of the electrode is only slightly occupied by hydrogen atom and that $0 < \alpha < 1$, as observed over a certain range of polarization, when moderately occupied and that $\alpha = 0$ when fully occupied.

We are now going to draw conclusion from our statistical mechanical theory of the electrochemical mechanism upon the dependence of the negative current $\vec{I}$ on the polarization in terms of the differential coefficient $-\frac{kT'}{e}\frac{d\ln\vec{I}}{d\eta}$ at a constant temperature which equals to the Tafel's constant α according to §20 and to (22.1). The latter differential cofficient is given by (6.3), as that

$$-\frac{kT'}{e}\frac{d\ln\vec{I}}{d\eta} = -\frac{kT'}{e}\frac{d\ln q_K^*}{d\eta} - \frac{kT'}{e}\frac{d}{d\eta}\ln\frac{\Theta_{H_2^+}}{q_K^{H_2^+}p_m^{\ominus}} \qquad (22.3)$$

where the factor $\Theta_{K(0)}/p^{H_2^+}$ in (6.1. $\vec{v}$) is conveniently replaced by $\Theta_{H_2^+}/q_K^{H_2^+}$ according to (4.5). The first term may be written, according to (18.1) and (19.2), in the form

$$-\frac{kT'}{e}\frac{d\ln q_K^*}{d\eta} = -\frac{dV_{0,\Sigma,e^*}^*}{d\eta} + \frac{1}{e}\frac{dY'_{\Sigma,e^*}}{d\eta} \qquad (22.4)$$

neglecting the variation of the form of the energy surfaces, $V_{\Sigma,e^*}^* = V_{\Sigma_0 e_0^*}^*(q_1, q_2 \cdots\cdots)$, and of $Y'_{\Sigma,e^*} = Y'_{\Sigma,e^*}(\Sigma, e^*)$ or that of the factor $\left(\sum_i e^{-\varepsilon_i/kT}\right)_{\Sigma_0 e^*}$, Γ_2^* and Γ_L^* with electrode potential η. The differential coefficient of V_{Σ,e^*}^* with respect to η may in general be written in accordance with (17.4) in the form,

$$\frac{dV_{\Sigma,e^*}^*}{d\eta} = \frac{\partial V_{\Sigma,e^*}^*}{\partial\eta} + \frac{\partial V_{\Sigma,e^*}^*}{\partial\chi_0}\frac{\partial\chi_0}{\partial\eta} + \sum_i \frac{\partial V_{\Sigma,e^*}^*}{\partial q_i}\frac{\partial q_i}{\partial\eta} + \frac{\partial V_{\Sigma,e^*}^*}{\partial\Sigma}\frac{\partial\Sigma}{\partial\eta} + \frac{\partial V_{\Sigma,e^*}^*}{\partial e^*}\frac{\partial e^*}{\partial\eta}. \qquad (22.5)$$

We obtain therefrom the differential coefficient of V_{0,Σ_0,e^*}^* with respect to η by introducing the condition that V_{Σ,e^*}^* lies on the surface,

$$V_{\Sigma,e^*}^{H_2^+ + \ominus,*} = V_{\Sigma,e^*}^{H_2,*}, \qquad (22.6)$$

and that $V_{\Sigma_0,e_0^*}^*$ is the minimum of V_{Σ,e^*}^* with respect to coordinates as well as to Σ and to e^* according to §19, or, that

$$\frac{\partial V_{\Sigma,e^*}^*}{\partial q_i} = 0, \qquad i = 1, 2 \cdots\cdots$$

$$\frac{\partial V_{\Sigma,e^*}^*}{\partial\Sigma} = 0, \qquad (22.7)$$

$$\frac{\partial V^{*}_{\Sigma,e^{*}}}{\partial e^{*}} = 0 \qquad (22.7)$$

at $V^{*}_{0,\Sigma_0,e_0^{*}}$.

The second term on the right of (22.5) vanishes according to (17.4) and (22.6) and subsequent ones according to (22.7) resulting that

$$\frac{dV^{*}_{\Sigma_0,e_0^{*}}}{d\eta} = \frac{\partial V^{*}_{\Sigma_0,e_0^{*}}}{\partial \eta}$$

or according to (17.4), (16.1) and (16.6) that

$$\frac{dV^{*}_{\Sigma_0 e_0^{*}}}{d\eta} = -\left(e\frac{d\zeta_0}{d\eta} + \frac{dU^{H_2^{+}}}{d\eta} - \frac{dU^{H_2}}{d\eta}\right)\chi_0 + e\frac{d\zeta_0}{d\eta} - e\frac{dU^{H_2^{+}}}{d\eta}. \qquad (22.8)$$

From the similar reasoning we can show that the second differential coefficient in (22.4) vanishes, remembering that $Y'_{\Sigma,e^{*}}$ difined in §18 depends only on Σ and e^{*}.

Expressing the second term in (22.3) in accordance with (14.4) in the form,

$$-\frac{kT'}{e}\frac{d}{d\eta}\ln\frac{\Theta_{H_2^{+}}}{q_K^{H_2^{+}} p_m^{\ominus}} = -\frac{kT'}{e}\frac{d\ln\Theta_{H_2^{+}}}{d\eta} - \frac{d\zeta_0}{d\eta} - \frac{dU^{H_2^{+}}}{d\eta}, \qquad (22\cdot 9)$$

(22.3) may be written by (22.4), (22.8) and (22.9) as that

$$-\frac{kT'}{e}\frac{d\ln\vec{I}}{d\eta} = \left(-\frac{d\zeta_0}{d\eta} - \frac{dU^{H_2^{+}}}{ed\eta} - \frac{dU^{H_2}}{d\eta}\right)\chi_0 - \frac{kT'}{e}\frac{d\ln\Theta_{H_2^{+}}}{d\eta}, \qquad (22.10)$$

χ_0 in the expression is directly given in Table VI and differential coefficient are derivable from numerical results given in Table V as follows.

$-\eta_c$	χ_0	$d\zeta_0/d\eta$	$\frac{dU^{H_2^{+}}}{ed\eta}$	$\frac{dU^{H_2}}{ed\eta}$	$\frac{kT'd\log\Theta_{H_2^{+}}}{ed\eta}$	$(-d\zeta_0/d\eta - dU^{H_2^{+}}/d\eta + dU^{H_2}/d\eta)$	$\frac{-d\ln\vec{I}}{ed\eta}$
0.41	0.63	−1.30	−0.101	−0.153	−0.650	1.25	1.44
1.26	0.52	−1.22	−0.45	−0.680	−0.030	0.99	0.55

The last term on the right of (22.10) is, as given in the 6th colomn of the above table, approximately unity or zero according as the electrode potential is higher or lower, whereas the coefficient of χ_0 in the parenthesis given in the 7th column equals approximately unity throughout. As χ_0 is a proper fraction in both cases, we arrive

at the final result that $-\frac{kT}{e}\frac{d\ln\vec{I}}{d\eta}$ is unity plus a proper fraction for $\eta_c = -0.41$ Volt or a proper fraction for $\eta_a = -1.26$ Volt, as shown in the 8th column in the table.

The important features of the present conclusion that χ_0 is a proper fraction and that $-\frac{kT}{e}\frac{d\ln\theta_{H_2^+}}{d\eta}$ is approximately unity or zero according as the electrode potential is higher or lower, from which the above final results are arrived at, may be qualitively but more directly derived as below along the fundamental line of our treatment.

That χ_0 is a proper fraction follows directly from the property of the surface (16.7) which qualifies it for being a critical surface in conformity with our claim that the transition $H_2^+ + \ominus \rightarrow H_2$ or the reverse one governs the rate; i. e., since χ_0 is given by

$$\chi_0 = \frac{\left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial n}\right)}{\left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial n}\right) - \left(\frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial n}\right)} \quad *), \qquad (22.11)$$

and $\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}/\partial\eta$ is different in sign from $\partial V_{\Sigma,e^*}^{H_2}/\partial n$ according to §17, χ_0 should necessarily be a proper fraction.

Another feature of the present result that $-\frac{kT}{e}\frac{d\ln\theta_{H_2^+}}{d\eta}$ is unity or zero according as the electrode potential is higher or lower, may be directly deduced as follows by disregarding the diffuse potential or $\zeta_0 - \zeta_b$, an approximation which is exaxt, when the concentration of free

*) According to (17.4) and (17.5) is given by,

$$\frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial q_i} - \chi_0\left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i} - \frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial q_i}\right) = 0 \qquad i = 1, 2 \cdots\cdots$$

where q_i's will be here any set of Cartesian coordinates. Multiplying the equation through with $\left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i} - \frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial q_i}\right)$ and summing up for all i's, we have

$$\chi_0 = \sum_i \frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i}\left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i} - \frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial q_i}\right) \Big/ \sum_i \left(\frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i} - \frac{\partial V_{\Sigma,e^*}^{H_2}}{\partial q_i}\right)^2,$$

which lead to (22.11) by virue of the relations,

$$\frac{\partial\left(V_{\Sigma,e^*}^{H_2^+ + \ominus} - V_{\Sigma,e^*}^{H_2}\right)}{\partial n} = \sqrt{\sum_i \left\{\frac{\partial\left(V_{\Sigma,e^*}^{H_2^+ + \ominus} - V_{\Sigma,e^*}^{H_2}\right)}{\partial q_i}\right\}^2}$$

and

$$\partial V_{\Sigma,e^*}^{H_2^+ + \ominus} \Big/ \partial n = \sum_i \frac{\partial V_{\Sigma,e^*}^{H_2^+ + \ominus}}{\partial q_i}\frac{\partial\left(V_{\Sigma,e^*}^{H_2^+ + \ominus} - V_{\Sigma,e^*}^{H_2}\right)}{\partial q_i} \Big/ \sqrt{\sum_i \left\{\frac{\partial\left(V_{\Sigma,e^*}^{H_2^+ + \ominus} - V_{\Sigma,e^*}^{H_2}\right)}{\partial q_i}\right\}^2},$$

where n is the normal to the surface, $V_{\Sigma,e^*}^{H_2^+ + \ominus} = V_{\Sigma,e^*}^{H_2}$.

ions in the solution is sufficiently large to cancel the potential rise or drop at the adsorption layer.[37)38)] According to (4.5), (5.4), (5.6), (13.2), (14.4) and (14.6) we have, with the above approximation that

$$U^{H_2^+} + e\eta - kT'\theta_0 + kT' \ln \theta_{H_2^+} = kT' \ln \frac{q_K^{H_2^+}}{p_{g,0}^{H_2}},$$

where the right hand side is a constant independent of η. The equation shows that when the adsorption layer is only slightly occupied at higher electrode potential, and hence θ_0 is approximately unity and $U^{H_2^+}$ zero according to (13.2), $\theta_{H_2^+}$ varies proportional to $e^{-e\eta/kT'}$, resulting that $-\frac{kT'}{e}\frac{d \ln \theta_{H_2^+}}{d\eta} = 1$. It shows on the other hand that when the adsorption layer is moderately occupied exclusively by H_2^+ at lower electrode potential so that both θ_0 and $\theta_{H_2^+}$ lies in the neighbourhood of unity and $U^{H_2^+}$ consists practically of $\theta_{H_2^+} U_{H_2^+}^{H_2^+}$ according to (13.3), $\theta_{H_2^+}$ varies approximately in accordance with the equation,

$$\theta_{H_2^+} U_{H_2^+}^{H_2^+} + e\eta = \text{const.},$$

since then $kT' \ln \frac{\theta_{H_2^+}}{\theta_0}$ lies constantly in the neighbourhood of zero.

The situation that the rate of increase of adsorbed elementary systems along with the drop of electrode potential appreciably falls off before the adsorption layer is fully occupied, to which also the forthcoming of Tafel's constant in the case of catalytic mechanisms owes,[39)] seems rather characteristic to the elementary systems involving hydrogen atoms, whose electron density only slowly decreases with distance from the nucleus owing to the smallest nuclear charge and in consequence a far reaching repulsive potential to resist the concentration. This point will be dealt with more in detail in our later paper including the case of the chemical adsorption of hydrogen on nickel. Our final result of $-\frac{kT'}{e}\frac{d \ln \vec{I}}{d\eta}$ for $\eta_e = -1.26$, which gives the theoretical value of Tafel's constant $\alpha = 0.55$ according to §21, may be compared with the experimental value, $\alpha = 0.52$ obtained by BOWDEN and RIDEAL[40)] at the same external conditions, whereas that for the higher electrode potential with the experimental value $\alpha = 1.5$ obtained by HORIUTI and MITUYA.*)

*) The subsequent paper of this Journal.

37) STERN, Z. Elektrochem., **30** (1924), 508.

38) FRUMKIN., loc. cit.

39) OKAMOTO, HORIUTI and HIROTA, Sc. Pap. I.P.C.R., Tokio, **29** (1936), 223.

40) BOWDEN and RIDEAL, loc. cit.

§ 23. Isotopic Separation Factor.

An expression of the separation factor for a solution of dilute heavy water will be derived below from the definition (21.1), according to the present theory of the reaction rate.

Ignoring the possibility of formation of D_2O as well as of D_2 molecules for the solution of dilute heavy water (20.1) may be written in the form,

$$S = \frac{\vec{v}_{H_2}}{\vec{v}_{HD}} \frac{[HDO]_l}{[H_2O]_l} , \tag{23.1}$$

where $\vec{v}_{H_2}$ and $\vec{v}_{HD}$ are the rates of evolution of H_2 and HD molecules by neutralization and $[H_2O]_l$ and $[HDO]_l$ molecular concentrations of H_2O rnd HDO molecules, respectively. Expressing $\vec{v}_{H_2}$ according to (6.1 $\vec{v}$) (3.12) and (4.7) by

$$\vec{v}_{H_2} = \frac{kT'}{h} G\Theta_0 \frac{q^{\ddagger}_{K,H_2}}{(p^H)^2} , \tag{23.2}$$

and $\vec{v}_{HD}$ similarly by

$$\vec{v}_{HD} = \frac{kT'}{h} G\Theta_0 \frac{q^{\ddagger}_{K,HD}}{p^H p^D} , \tag{23.3}$$

we have

$$S = \frac{p^D}{p^H} \frac{q^{\ddagger}_{K,H_2}}{q^{\ddagger}_{K,HD}} \frac{[HDO]_l}{[H_2O]_l} , \tag{23.4}$$

where p^D is the similar quantity for deuterium ion as p^H for protium ion, suffixes H_2 or HD denoting specially the pair of nuclei involved.

The quotient p^D/p^H in the expression may be reduced to observable quantities by the relation between the function p^δ's, i. e.

$$p_g^{HDO} p_l^{H^+} = p_g^{H_2O} p_l^{D^+} , \tag{23.5}$$

of the interchange equilibrium between solution and its vapour, i. e.

$$HDO_g + H_l^+ = H_2O_g + D_l^+ ,$$

where the suffix g and l denote the state in gas and solution, respectively; we obtain from the latter equation according to (4.7) that

$$\frac{p^D}{p^H} = K_E \frac{Q_g^{HDO}}{Q_g^{H_2O}} \frac{[H_2O]_l}{[HDO]_l} ,$$

where $Q_g^{H_2O}$ or Q_g^{HDO} is the partition function of H_2O or HDO molecule in gaseous state, respectively, and

$$K_E = \frac{[HDO]_l [H_2O]_g}{[HDO]_g [H_2O]_l} , \tag{23.6}$$

the equilibrium constant of the exchange reaction,

$$HDO_g + H_2O_l = H_2D_g + HDO_l .$$

The q^*_{K,H_2} and $q^*_{K,HD}$ in (23.4) differ from each other only by the factor $\sum_i e^{-\varepsilon_i^*/kT}$ in (7.3), hence we have

$$q^*_{K,H_2}/q^*_{K,HD} = \sum_i^{H_2} e^{-\varepsilon_i^*/kT'} \Big/ \sum_i^{HD} e^{-\varepsilon_i^*/kT'}, \qquad (23.7)$$

so far as we remain with UREY's postulate[41] that the interatomic potential is unchanged by isotopic replacement as well as with our approximation, 2° in §7, and that in §15. By (23.4), (23.6) and (23.7) we have finally

$$S = K_E \frac{Q_g^{HDO}}{Q_g^{H_2O}} \frac{\sum_i^{H_2} e^{-\varepsilon_i^*/kT'}}{\sum_i^{HD} e^{-\varepsilon_i^*/kT'}}. \qquad (23.8)$$

K_E is determined by UREY and TEAL[41], HORIUCHI and OKAMOTO[42] and over a wide range of temperature by IKUSIMA and AZAKAMI[43] with the following results;

t°C	0°C	18°C	50°C	100°C	160°C
K_E	1.109	1.076	1.048	1.023	1.002

$Q_g^{HDO}/Q_g^{H_2D}$ is calculable by the expression

$$\frac{Q_g^{HDO}}{Q_g^{H_2O}} = 2 \frac{\left\{ m_3^{\frac{3}{2}} (I_A I_B I_C)^{\frac{1}{2}} \prod_i^i e^{-h\nu_i/2kT} / (1 - e^{-h\nu_i/kT}) \right\}_{HDO}}{\left\{ m_3^{\frac{3}{2}} (I_A I_B I_C)^{\frac{1}{2}} \prod_i^i e^{-h\nu_i/2kT} / (1 - e^{-h\nu_i/kT}) \right\}_{H_2O}}$$

with following numerical values,

Molecular Weight m		H_2O	HDO	Molecular Weight m		H_2O	HDO
		18	19			18	19
Moment of Inertia (gm, cm²)[44]	I_A	1.03×10^{-40}	1.18×10^{-40}	Ground Frequencies (cm^{-1})[45]	ν_1	3654	2720
	I_B	2.07×10^{-40}	3.74×10^{-40}		ν_2	3756	3750
	I_C	3.10×10^{-40}	4.92×10^{-40}		ν_3	1596	1403

*) The factor 2 is the ratio of the symmetry number of HDO to that of H_2O.

41) UREY and TEAL, J. Chem. Phys., 2 (1934), 421.
42) HORIUTI and OKAMOTO, Bull. Chem. Soc. Japan, 10 (1935), 305.
43) IKUSHIMA and AZAKAMI, J. Chem. Soc. Japan, 59 (1938), 40 (in Japanese).
44) BAKER and SLEATER, J. Chem Phys.. 3 (1935), 660.
45) Calculated from spectroscopic data of BAKER and SLEATER (loc. cit.) and MECKE [Z. phys. Chem., 81 (1933), 445].

The seperation factor due to the electrochemical mechanism may now be theoretically evaluated by computing the last quotient in (23.8) according to the results in §17.

WOLFENDEN and WALTON[46] have on the other hand observed the seperation factor for various metal electrodes over a wide temperature range arriving at remarkable results that the metal electrodes fell into two groups with regard to the magnitude of temperature coefficient of the seperation factor in close agreement with those of the catalytic and the electrochemical mechanism; i.e. the seperation factor for those metal electrodes to which the catalytic mechanism was attributed decreased adpreciably with rise of temperature whereas that of the electrochemical mechnisim decreased only slightly or even increases with temperature.

Table IX shows the theoretical values calculated according to (23.8) at the condition of the above experiments in comparison with the experimental data, as well as those for the silver electrode, which belongs to the group of the catalytic mechanism, quoted from the theoretical result due to one of the present authors.[47]

TABLE IX

temp t°C	Mercury (Electrochemical)		Silver (Catalytic)	
	Calc.	Obs.	Calc.	Obs.
19 °C	3.3	3.1	6.1	6.8
100 °C	2.5	3.1	4.2	4.6

The theoretical value accounts for the absolute value satisfactorily whereas the temperature coefficient at least qualitivaly.

Appreciably small rate with which the seperation factor due to the electrochemical mechanism decreases comfirmed by theory and experiment may be qualitively accounted for as follows with special reference to the isotopic difference of the zero point energy at the critical state. As seen from the result obtained in §18, the vibration appropriate to ν_2^* is nearly the motion along Hg—OH_2 axis of the cage and its frequency is exceptionally large even among those of the catalytic mechanism. The latter fact may be attributed to the special circusmstances of the electrochemical mechanism. At the critical state H—H or H—D is

46) WOLFENDEN and WALTON, Nature. **138** (1936), 468. Trans. Farad. Soc., **34** (1938). 436.
47) T. KEII, "Catalyst", **3** (1948), 30 (in Japanese).

situated with more or less effective charge between Hg and OH_2 with its axis perpendicularly bisected by the Hg—OH axis at the potential hollow of the potential curves Hg—H_2^* and H_2^*—OH_2. Since the potential hollows are mainly due to the charge of the H_2^*, they simply overlap to result in a pronounced dip and hence in a big resultant curvature at the bottom. The two potentials Hg—H^+ and H^+—OH_2 having now big enough curvature at the bottom for themselves, we must expect for the case of electrochemical an exceptionally large curvature of potential surface in the direction of H—OH_2 axis and in consequence a large vibrational frequency.

Big frecuencies at the critical state accompanies now a big isotopic difference of the zero point energy at the critical state, which in turn reduces the value of seperation factor and its temperature coefficient from the following reason. The first and the second factors in (23.8) are merely a function of temperature, independent of the mechanism and the kind of the electrode metal: their speciality is included solely in the last factor, which may be approximately written in the form

$$\left(\sum_i e^{-\varepsilon_i^*/kT}\right)_{H_2} \Big/ \left(\sum_i e^{-\varepsilon_i^*/kT}\right)_{HD} = Ae^{-(\varepsilon_{0,H_2}^* - \varepsilon_{0,HD}^*)/kT},$$

where A is a constant nearly equal to unity due to non-vibrational mode of motion and soft vibrations and $\varepsilon_{0,H_2}^* - \varepsilon_{0,HD}^*$ which is positive, is the sum of the zero point energy difference of stiff vibrations. The large value of the latter reduces according to the expression appreciably the absolute value of S and its rate of decrease with temperature, contributing a positive value to $RT^2 \dfrac{\partial \ln S}{\partial T}$.

As remarked above $\varepsilon_{0,H_2}^* - \varepsilon_{0,HD}^*$ should vary from metal to metal even in the case of electrochmical mechanism. In the case of mercury electrode the potential of hydrogen atom due to mercury atom is as well known exceptionally shallow, contributing very little to the curvature at the critical state in the above sense and hence to the zero point energy.

From this reason we might expect for other electrodes of electrochemical mechanism a greater value of the curvature and hence the zero point energy difference so that the sign of the temperature coefficient of the separation factor is even reversed to assume a positive value as actually observed by WOLFENDEN and WALTON for Sn.[48]

48) WOLFENDEN and WALTON, loc. cit.

SUMMARY

One of two alternative mechanisms, the electrochemical mechanism, which was suggested for being responsible for the hydrogen electrode process, $2H^+ + 2\ominus = H_2$ [$\ominus$; —metal electron] in the previous work [HORIUCHI and OKAMOTO; Scient. Pap. Inst. Phys. Chem. Res. Tokio, 28 (1936), 231] on the cathodes of Hg, Sn and Pb (in acid solution) was statistical mechanically worked out to compare the theoretical conclusions arrived at with exeriments: the electrochemical mechanism proceeds in two steps, i.e. $2H^+ + \ominus \rightarrow H_2^+$ or the formation of hydrogen molecule ion H_2^+ adsorbed on the electrode surface and $H_2^+ + \ominus \rightarrow H_2$ or the neutralization of H_2^+, the latter step governing the rate. The alvervative was the catalytic mechanism suggested for being operative on the cathodes of Ni, Au, Cu, Fe and Pb (in alkaline solution), which proceed through the intermediary of neutral hydrogen atoms adsorbed on the electrode surface, their recombination to form H_2 being the rate-determining step.

Specifying the model of the hydrogen electrode by a set of several postulates the rate of the governing step, i.e. the neutralization of H_2^+ was statistical-mechanically formulated according to the general theory of the reaction rate [HORIUCHI; Bull. Chem. Soc. Japan, 13 (1938), 210: HIROTA and HORIUCHI, Sci. Pap. I.P.C.R. Tokio, 34 (1938), 1174], making thereby an extensive use of the four conjugated statistical-mechanical functions p^δ, q_σ^δ, $\Theta_{\delta(0)}$ and $\Theta_{\sigma(0)}$ introduced by one of the present anthers [HORIUCHI, this journal, 1 (1948~1951), 8.]. The model was such that each mercury atom on the boundary forms a cage being accompanied by one nearest water molecule, which is either empty or occupied by any one of H, H^+, H_2^+ and H_2 as well as the critical complex of the geverning step or the intermediate between H_2^+ and H_2.

The procedure of calculation was elaborated as far as possible allowing for every factor coming into question in order to render the whole theory possibly the logically closed from although the present knowledge of the interatomic potentials, which are the fundamental material of the calculation and determine the accuracy of the ultimate numerical result, might seem not deserving such an elaboration. The dipole orientation of water molecules around the cage due to the interaction with the charge of H^+, H_2^+ as well as that of the critical complex inside the cage was thus allowed for, leading in the last case to the effective charge of the critical complex about half an elementary charge.

Using the expression thus formulated the current density of hydrogen electrode, its variation with the electrode potential, and the electrolytic seperation factor of deuterium by the mercury electrode was calculated and compared with experiments.

For a mercury cathode in N/10 HCl solution polarised at 19°C against calomel electrode by 1.26 or 0.41 Volt the current density was calculated at 2×10^{-5} or 4×10^{-15} amp/cm^2 respectively, the former being compared with BOWDEN and RIDEAL's obsevation, 3×10^{-4} amp/cm.^{2} It was shown moreover by shifting the repulsive potential between hydrogen atom and the constituent water molecule of the cage, whose estimation seems most uncertain among the materials of the calculation, by 0.2 Volt that the current density varies by a factor of 10 or $10^{3.5}$ respectively for the cathodic polarization 1.26 or 0.41 Volt and this contrast was shown by tracing the procedure of calculation to be due to the abundant or scanty occupation of the cages by H_2^+.

The observed variation of the current density i with the electrode potential η summarised by the Tafel's emipirical equation,

$$\log i = -\frac{\alpha}{RT'} F'\eta + \text{const},$$

where α is the empirical constant 0.52 as precisely determined by BOWDEN and RIDEAL [Proc. Roy. Soc., A 120 (1928)], F' Faraday, R gas constant and T' the absolute temperature, was successfuly accounted for by the theory, α being calculated at 0.55.

The isotopic separation factor was calculated 3.3 at 19°C and 2.5 at 100°C respectively, WOLFENDEN and WALTON's measurement at both the cited temperatures being constantly 3.1. The cause for such small separation factor confirmed both by the theory and the experiment compared with that (7~) of the catalytic mechanism, was discussed with special reference to the nature of the electrochemical mechanism, thus affording the theoretical ground to the former rather intuitive attribution [HORIUCHI and OKAMOTO, Scient. Pap. Inst. Phys. Chem. Res. Tokio, 28 (1936), 231] of its values particularly to the respective alternative mechanisms.

Appendix, Glossary of Notations

The parenthesized number refers to the equation of definition.

a_0	First Bohr orbit.
a	Anharmonic constant.
a	Suffix designating outward.
A	The area of the section of the ellipsoid replaced for the cage perpendicular to Hg—OH axis.
$A_{l,m}$	Force constant defined by (17.14).
B	The base of generalised sense due to Brönsted.
c	Light velocity.
C	A macroscopic assembly without any microscopic constraint.
C^δ	C argumented by one elementary system δ.
$C^\delta_{\sigma(\delta)}$	C^δ with the constraint that a cavity σ inside C^δ is vacant.
$C_{\sigma(0)}$	C with the constraint that a cavity σ inside C is vacant.
D	Dissociation energy of diatomic molecule.
D	Suffix designating the dielectric constant of the medium.
D_i	The dielectric constant inside the cage.
D_a	The dielectric constant outside the cage.
D_s	The dielectric constant outside the adsorption layer.
$d\tau$	Volume element.
df	Surface element of the ellipsoid replaced for the cage.
d[H], d[D]	The rate of discharge of protium, deuterium.
e	Elementary charge.
e*	The effective charge of critical complex.
$E_i(-Z)$	Function of Z; $= -\int_Z^\infty Z^{-1}e^{-Z}dZ$.
F	The free energy of hydration (footnote §9).
G	The total number of cages in unit surface area of the electrode.
h	PLANK's constant.
$\boldsymbol{H}$	Hamiltonian operator.
$\boldsymbol{H}_0$	Unperturbed Hamiltonian operator.
H_{AA}, H_{AB}	The energy matrix; (under (12.5)).

i	Suffix designating inward.
i	Observable current density.
$i,j,k,l,m,n,$	Running indices.
$I_{\mathrm{I}},I_{\mathrm{II}},I_{\mathrm{A}},I_{\mathrm{B}},I_{\mathrm{C}}$	Moment of inertia.
$\vec{I}$	Negative current; (6.3).
$\overleftarrow{I}$	Positive current; (6.4).
j	Rotational quantum number.
J	Exchange energy.
k	BOLTZMANN's constant.
$k_{rr},\ k_{\overleftarrow{rr}},\cdots$	Force constant.
K	Suffix designating the cage.
$K_{(0)}$	Suffix designating the empty cage.
$K_{(\delta)}$	Suffix designating the cage occupied by δ.
$K_{(\delta),\Sigma}$	Suffix designating the $K(\delta)$ at a particular configuration $\sum$.
K	Internal field strength (footnote §9).
K	Coulombic energy.
K_E	Equilibrium constant of the exchange reaction (23.6).
K_0	Function used in the quantum mechanical calculation defined by (13.19).
K_2	Function used in the quantum mechanical calculation defined by (13.20).
l	Suffix designating a quantity inside the solution.
L	Distance between the centres of the mercury atom and the water molecule composing the cage.
m	Mass of particule.
m	Suffix designing a quantity inside metals.
n	Normal.
N_A	Avogadro's number.
$N_g^{\mathrm{H_2}}$	Concentration of hydrogen molecules in gas.
N_i	Concentration of ions in solution.
$N_{i,b}$	Concentration of ions at the bulk of the solution.
$\circ$	Suffix designating quantities appropriate to the reversible hydrogen electrode (subscript).

$\circ$	Suffix, designating minimum.
p^{δ}	The statistical mechanical function of δ; (2.1).
$p_m^{\ominus}$	p^{δ} of a metal electron; (3.17).
P	Defined by (9.7).
$P_n(\xi), Q_n^{\nu}(\eta),$	Spherical functions.
q_l, q_m	Coordinates.
q_{σ}^{δ}	The statistical mechanical function; (2. 3).
q_K^{δ}	q_{σ}^{δ} for $\sigma \equiv K$.
$Q_g^{H_2}$	Partition function of a hydrogen molecule in gas.
$Q_g^{H_2O}$	Partition function of a water molecule in gas.
$\mathfrak{Q}$	Partition function of the assembly.
r	Distances.
r_0	Distance between the point charge and the surface element of the ellisoid replaced for the cage.
r_0	Equilibrium distance of diatomic molecule.
$R(r_1), R(r_2)$	The eigenfunction of the 6*s* electron; (9. 5).
R_a, R_b	Coulombic potential of the positive particule constituting the cage due to the proton situated at a (b); (12. 2).
s	Symmetry number of molecule.
S	A statistical mechanical function defined by (4. 13).
S	The isotpic separation factor. (20. 1).
T	Absolute temperature.
T	Kinetic energy.
U^{δ}	The potential of δ in a cage due to elementary systems inside the surrounding cages; (3. 1), (13. 2).
U_j^i	The potential of an elementary system of i–th kind situated in a particular cage K_i due to j–th ones supposed fully to occupy the surrounding cages (13. 3).
$u_j^i(k)$	The individual potential of i–th elementary system due to that of j–th kind situated inside k–th cage K_k.
u	Atomic orbital of hydrogen atom.
v_K	The volume of a cage.
$\vec{v}$	Reaction rate; (2. 7).

$\vec{v}$	Reaction rate $H_2^+ + \ominus \longrightarrow H_2$. (6.1 $\vec{v}$).
$\overleftarrow{v}$	Reaction rate $H_2^+ + \ominus \longleftarrow H_2$. (6.2 $\overleftarrow{v}$).
V	Electrode potential; (3.13).
V_{Σ}^{δ}	Potential of δ inside the cage.
$V_{K,\Sigma}^{\delta}$	The sum of the mutual potential of the particles composing δ and that due to the cage at a configuration $\sum$; (7.4).
$V_{W,\Sigma}^{\bar{\delta}}$	Potential of $\bar{\delta}$ due to the WEBB's model; (7.4).
$V_{M,\Sigma}^{\delta}$	Potential of δ due to mercury electrode; (7.4).
V_{E}^{δ}	Potential of δ inside a cage due to other elementary systems inside the surrounding ones; (7.4).
V_a	Excess of potential of the critical complex above the minimum.
w_A, w_B	The potential between the proton and the cage; (12.8) (12.9).
W	Eigenwert.
W_0	Unperturbed eigenwert of the system, $Hg+H+H^+ + OH_2$. (12.12).
W_i	Eigenwert; (12.1).
W_{H_g}	The unperturbed eigenwert of the system, $Hg+H^+$.
W_A	The eigenwert of the system, $Hg-H_A+H_B-OH_2$, A and B signifying the position of the respective hydrogen nucleous.
W_B	The eigenwert of the system, $Hg-H_B+H_A^+-OH_2$.
$r, \bar{r}, \xi, \bar{\xi}, \theta, \bar{\theta}$	Linear combinations of cylindrical coordinates.
x_0	The distance of the adsorption layer from the equivalent conductor.
x_1	The distance of the nearest approach of chlorine ion to the equivalent conductor.
x, y, z	Cartesian coordinates.
x_I, y_I, θ_I	The cylindrical coordinates.
$Y_{0,\Sigma}^{\delta}$	The free energy of the elementary system δ inside the cage at rest; (7.3), (8.1).
$Y_{0,K,\Sigma}^{\delta}$	The part of $Y_{0,\Sigma}^{\delta}$ corresponding to the interaction of particles with each other and with the cage; (8.1).
$Y_{0,\Sigma,e^*}^{\delta}$	The reversible work of bringing up the critical complex

from the state of referrence to the mean configuration inside the cage with the dipole orientation appropriate to e*.

$Y^{\delta}_{W,\Sigma}$ The part of $Y^{\delta}_{0,\Sigma}$ corresponding to the interaction of δ with the WEBB's model.

$Y^{\delta}_{M,\Sigma}$ The part of $Y^{\delta}_{0,\Sigma}$ corresponding to the interaction of δ with the electrode.

Y^{δ}_{E} The part of $Y^{\delta}_{0,\Sigma}$ corresponding to the interaction of δ with the surrounding elementary systems.

$Y^{\delta}_{I,\Sigma}$ The part of $Y^{\delta}_{0,\Sigma}$ corresponding to the interaction of δ with the electrode and the WEBB's model around the cage (8.1).

Y_D The electrostatical work required to bring up the cage with δ inside from vacuum into the medium of dielectric constan D.

Y_{e*} The reversible work required to bring up the elementary charge from infinity up to the centre of the spherelet inside an ellipsoid with the WEBB's model of the particular orientation appropriate to e* outside.

$Y'_{\Sigma,e*}$ The reversible work required to set up the dipole orientation appropriate to e* of the WEBB's model; (18.2).

α Tafel's constant.

α_x, α_y, α_z Force constants; (9.39), (10.5).

α' Empirical constant in (22.2).

α, β Variation parameters; (uuder (12.2)).

r Variation constant; (9.2).

Γ^{δ}_{L} Coefficient of L^2 in the quadratic expanssion of the free energy of δ inside the cage; (8.2).

Γ^{δ}_{Ω} Coefficient of Ω^2 in the quadratic expression of the free energy of δ inside the cage; (8.2).

δ An elementary system.

δ^*, Critical complex.

δ^{I} Initial complex.

Δ Overlap integral.

Δ The function defined used in the quantum-mechanical calculation by (13.22).

Δ'	The function defined used in the quantum-mechanical calculation by (13. 22).
ε_i	The energy of the i–th quantum state.
ε_i^*	The energy of the i–th quantum state of critical complex.
ζ	Electrostatical potential inside the solution.
ζ_0	Electrostatical potential at the adsorption layer.
ζ_b	Electrostatical potential in the bulk of solution.
ζ_1	Electrostatical potential at the nearest approach distance of chlorine ion.
η	Electrode potential referred to reversible hydrogen electrode (Overvolatge.); (5. 2).
η_c	The electrode potential referred to N/10 calomel electrode.
$\theta_{K(\delta)}$, θ_δ	Probability defined by (2. 4) of σ being occupied by a piece of δ.
$\theta_{K(0)}$, θ_0	Probability defined by (2. 5) of σ being unoccupied.
κ	Transmission coefficient; (§6).
$k_{\mathrm{H}}^{\mathrm{H}}$	Interaction potential between the two neutral hydrogen atoms; (Tab. III).
$k_{\mathrm{H}^+}^{\mathrm{H}}$	Interaction potential between a neutral hydrogen atom and a proton; (13. 5).
$k_{\mathrm{H}_p}^{\mathrm{H}^+}$	Interaction potential between a proton and the distorted hydrogen atom in the hydrogen molecule ion; (13. 15).
$\bar{k}_j^i$	Interaction potential between elementary systems i and j averaged over the azimuthal angle of either one.
$\bar{\bar{k}}_j^i$	Interaction potential between elementary systems i and j averaged over the azimuthal angle of the both.
λ	Eigenwert of vibration.
μ	Reduced mass.
$\bar{\mu}$	Dipole moment of water.
μ^3	Chemical potential.
ν_i	Vibrational frequency of i–th mode.
ν_i^*	Vibrational frequency of the i-th mode of critical complex.
ν_0	Foundamental frequency of diatomic molecule.
ξ, η, ϕ	Confocal elliptic coordinates.

Π Product.

ρ The radius of the spherelet in the elliposed.

ρ_{Σ} The probability for finding the configuration of the unoccupied cage at a certain configuration Σ reckoned to its unit extension.

ρ_e The charge density in solution.

σ Small cavity of molecular dimension.

$\sigma_{(0)}$ Small cavity of molecular dimension unoccupied.

$\sigma_{(\delta)}$ Small cavity of molecular dimension occupied by δ.

$\sum_i$ Summation.

Σ The configuration of cage.

φ The unperturbed eigenfunction of atom core of mercury; (9.5).

ϕ Azimuthal angle.

ϕ The work function of mercury.

χ Indeterminate multiplier for the constraint force; (17.9).

χ_0 Indeterminate multiplier for the intersection of potential surfaces of H_2 and H_2^+; (17.7).

ψ' Eigenfunction of the cage; (under (12.5)).

ψ'_A The eigenfunction of the system, $Hg-H_A+H_B^+-OH_2$. A and B signifying the position of respective hydrogen nucleus.

ψ'_B The eigenfunction of the system, $Hg-H_B+H_{A]}^+-OH_2$.

Ψ_0 The unperturbed eigenfunction; (9.4).

Ψ Eigenfunction; (9.2).

Ω The solid angle extended by the dipole of the water molecule of the cage; (3° §1).

$\ominus$ Metal electron.

The Research Institute for Catalysis
Hokkaido University
Sapporo, Japan