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— Review —

ROLE OF ELECTRON WORK FUNCTION
IN SETTING-UP OF ELECTRODE POTENTIAL
AND IN ELECTRODE KINETICS

— Basic Concept Developed by Frumkin —

By

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Abstract

This article concerns the basic concept in electrochemistry developed by A. N. Frumkin which is focussed on the role of electron work function in the setting up of electrode potential and in the kinetics of electron transfer processes. The electrode potential in the absolute scale and also the mechanism of the setting-up of the hydrogen electrode potential of platinum group metals will be discussed. Some of experimental results obtained in our laboratory will be explained on the basis of above concept.

Irving Langmuir¹⁾ pointed out in 1916 that the contact potential between two metals could be converted to electromotive force (E. M. F.). As seen from Fig. 1, plates of two different metals when placed together and then separated acquire electric charges, and an electric field is produced in the space between the two plates and the contact potential appears which equals the difference of electron work functions (W. F.), but there is no difference of the Fermi-levels between the two metals.

If ionized gas is introduced into the space between the two metals, the electric field disappears, and consequently there appears the difference of the Fermi-levels between the two metals which is measured as the E. M. F. In this way the contact potential can be converted to the E. M. F. by introducing ionized gas.

Langmuir suggested that the contact potential would be a major part of the E. M. F. of a chemical cell, although the charging of the double layer at the metal-solution interface could not be neglected.

After Langmuir many electrochemists had special interest in the mechanism of setting-up of the electrode potential in the electrochemical system. But they could get

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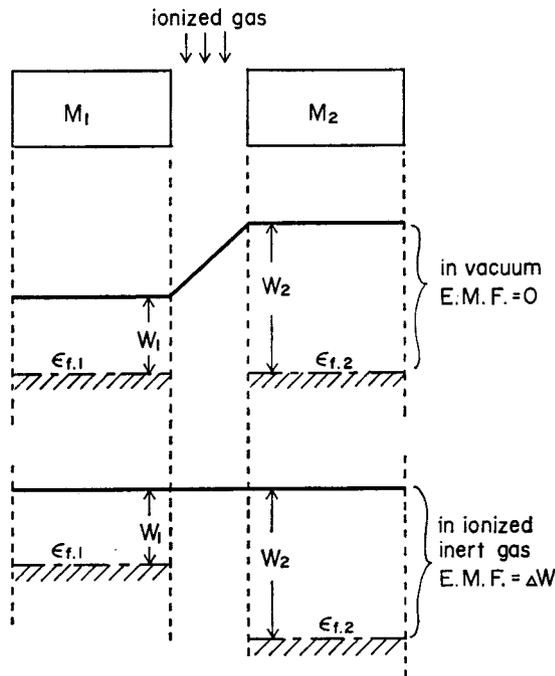


Fig. 1. Langmuir's model for the conversion of the contact potential to the electromotive force.¹⁾

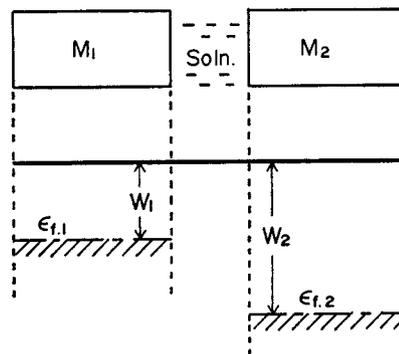


Fig. 2. Frumkin's model for the comparison of the zero charge potential and the contact potential.²⁾

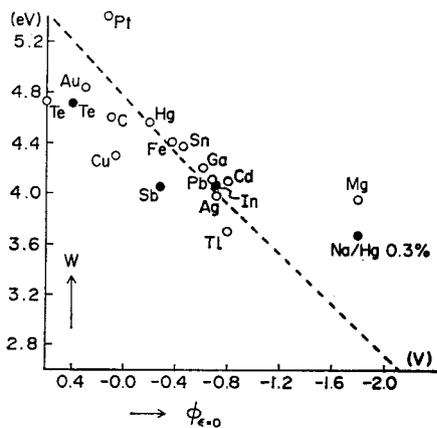


Fig. 3. The relation between the work function W and the zero charge potential, $\phi_{\epsilon=0}$ of metal electrodes³⁾ (numerical values referred to N.H.E.), solid circles in molten salts and open circles in aqueous solutions.³⁾

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no success to find any relation between the contact potential and E. M. F. of a chemical cell until 1928, when Frumkin²⁾ pointed out that the Langmuir's E. M. F. due to contact potential should be compared to the difference of the zero charge potential (Z. C. P.) of the two electrodes referred to a definite reference electrode.

As seen from Fig. 2, if an electrolyte solution is introduced into the space between the two metals in place of ionized gas and each electrode potential is maintained at its zero charge, then it will be found that there is no electric field between the two metals, but there exists the difference of Fermi-levels between the two metals, just like the E. M. F. pointed out by Langmuir. Therefore Frumkin³⁾ compared the Z. C. P. of an electrode in the electrochemical system with the electron work function (W) of the electrode metal measured in vacuum. Fig. 3 shows the relation between the electron W. F. and Z. C. P., $\phi_{\epsilon=0}$, referred to the normal hydrogen electrode (N. H. E.) for various metals.

As seen from this Figure, the Z. C. P. changes approximately linearly with W. F. with a gradient of unity and $W=4.72$ eV at $\phi_{\epsilon=0}=0$,

$$e\phi_{\epsilon=0} = W - 4.72,$$

where e is the elementary charge. The deviation from linear relation in this Figure may be explained by the change of the surface states of the electrodes even at the zero charge, while W. F. is measured in vacuum.

It may be possible to deduce, based on this linear relation, an important basic concept in electrochemistry on the absolute potential of an electrode. If we consider a metal of work function equal to 4.72 eV, we will find the Z. C. P. of this electrode equals zero, in other words, the Fermi-level of this electrode is located at 4.72 eV referred to the energy level of an electron at rest at infinity. So it can readily be understood from this fact that the absolute potential of the N. H. E. equals approximately 4.72 V, because the Z. C. P. is referred to the N. H. E.

If the absolute potential of an electrode is known, it is possible to build up the potential energy curves of an electron transfer reaction on the electrode, on which basis the absolute rate of the electrochemical reaction can be discussed.

Frumkin⁴⁾ has defined the absolute potential of an electrode in modern terminology as the position of the Fermi-level of the electrode referred to the level of an electron at rest at infinity, and he has shown that it may be possible to know the absolute potential when an electrochemical reversible system with respect to metal electrons, $e_{\bar{M}}$, and solvated electrons, $e_{\bar{S}}$, is realized, $e_{\bar{M}} \rightleftharpoons e_{\bar{S}}$.

As seen from Fig. 4, in this reversible system both Fermi-levels in metal and solu-

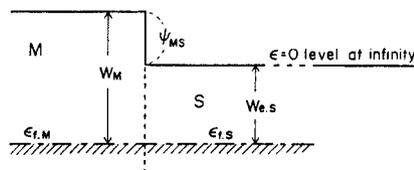
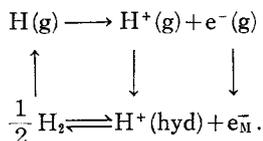


Fig. 4. The potential distribution of a reversible electrode with respect to free metal electrons and solvated electrons.

tion are equalized. Therefore the electron W. F. of the solution ($W_{e,s}$) can be identified numerically with the absolute potential of the electrode. It is not yet possible to measure $W_{e,s}$ directly at the present time, but Frumkin has deduced the absolute potential of the N. H. E. as 4.44 V from the thermodynamical cycle



Therefore the absolute value, E , of any electrode potential, ϕ , referred to the N. H. E. is given by the relation,

$$E = \phi + 4.44 \text{ V}. \quad (1)$$

When the E -value is determined it is possible to build up the potential energy diagram of an electrochemical electron transfer reaction in absolute scale. As an example, the potential energy curves in absolute scale for the proton discharge is shown in Fig. 5,

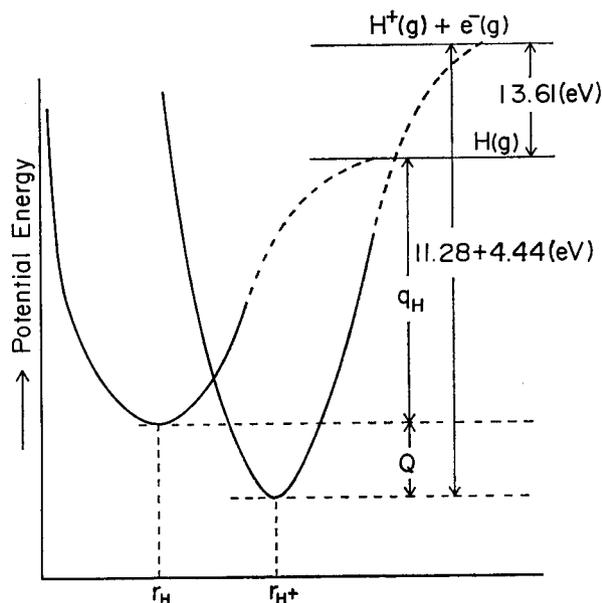


Fig. 5. A schematic representation of the potential energy curves of the initial and final states of the proton discharge; 4.44 V is used for the normal hydrogen electrode potential in the absolute scale.

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The potential energy of the initial state can be expressed as the sum of the real hydration energy of proton, 11.28 eV, and the absolute value of potential, 4.44 eV. The potential energy of the final state depends on the energy of the M-H bond.

It can be seen from Fig. 5 that the position of the Fermi-level reflects directly on the potential energy of the initial state. Frumkin has deduced from this fact an important conclusion for the kinetics of an electron transfer reaction. It can be said that when the electrode potential in the absolute scale is fixed at a constant value, the potential energy curve of the initial state is fixed at a definite position, and any physical nature characteristic to the electrode material, for instance, the W. F., does not reflect on the potential energy curve of the initial state. Therefore, it can be expected that the rate of an electron transfer reaction depends only on the electrode potential, but not on the electrode material when there is no specific adsorption of the reactants and products.

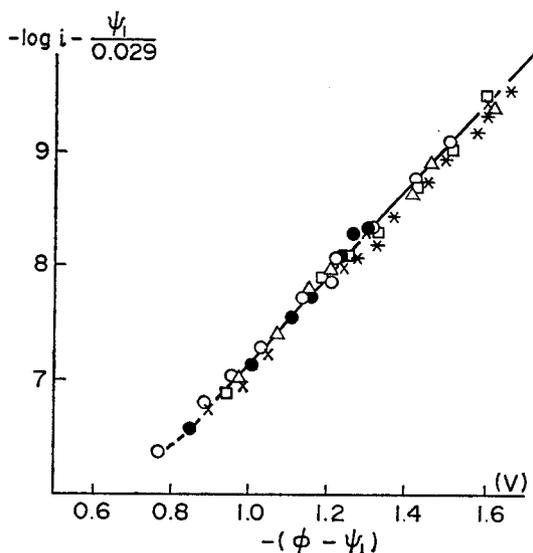


Fig. 6. Polarization curves for Sb, Hg, Bi, Pb, Cd and Sn after the Frumkin correction for the potential drop in the double layer,⁵⁾ in which the potential ϕ is referred to the solution inside.

Frumkin, Nikolaeva-Fedorovich and their coworkers⁵⁾ have shown that the rate of the electroreduction of persulfate ion $S_2O_8^{2-} + 2e_M^- \rightarrow 2SO_4^{2-}$ does not depend on the electrode material of different work function, as shown in Fig. 6. The polarization curves in Fig. 6 are shown after the Frumkin correction for the potential drop in the double layer (D.L.) for Sb, Hg, Bi, Pb, Cd and Sn. It can be seen that there is no effect of the electrode material on the rate of the electron transfer, as pointed out by Frumkin.

It should be stressed that the basic concept developed by Frumkin on the fun-

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damental role of W. F. in the setting-up of the Z. C. P. gives us a possibility to determine the electrode potential in the absolute scale, and that the W. F. of the electrode material has no direct effect on the rate of electron transfer when there is no specific adsorption on the electrode surface.

However, when a specific adsorption of atoms and ions occurs on the electrode surface, the circumstances are quite complicated, because surface potential due to specific adsorption changes seriously the position of Fermi-level of the electrode and consequently the potential energy curves of the initial and final states of an electron transfer reaction are changed by specific adsorption.

Frumkin and his school^{6-8,19)} have extended their work on the elucidation of the mechanism of the setting-up of the electrode potential to the electrochemical reversible systems in which there occurs a specific adsorption on the electrode surface, the hydrogen electrode being taken as an example. It is not difficult to realize the reversible electrode of the proton discharge and the ionization of adsorbed hydrogen atoms for the platinum group metals. As is known, the electrode potential of this reaction can be expressed by the Nernst equation in terms of the electrochemical potentials of the hydronium ion, $\bar{\mu}_H$, and adsorbed hydrogen atom, μ_H , and it does not depend on the electrode material,

$$d\phi = -d\bar{\mu}_e = d\bar{\mu}_H - d\mu_H. \quad (3)$$

Hereafter the chemical potential will be expressed in volts.

Now the question of our interest is what is the role of the adsorbed hydrogen atom and the free charge on the electrode surface in the setting-up of the electrode potential, *i. e.*, to express the electrode potential in terms of the concentration of the adsorbed hydrogen atom A_H and the free charge density ϵ ;

$$d\phi = XdA_H + Yd\epsilon, \quad X \equiv \left(\frac{\partial \phi}{\partial A_H} \right)_\epsilon, \quad Y \equiv \left(\frac{\partial \phi}{\partial \epsilon} \right)_{A_H}. \quad (4)$$

in which A_H and ϵ are taken as the independent variables in place of μ_{H^+} and μ_H .

Even if the electrode potential is fixed at a constant value, we can expect different concentration of adsorbed hydrogen atoms depending on the electrode material and also different ϵ -value depending on the specific adsorption of anions and cations in the solution. Frumkin and his school have solved this problem in the case of reversible hydrogen electrodes of Pt-group metals $H^+ + e_M^- \rightleftharpoons H(\text{ads})$.

This reversible system can be compared to a black box, as shown in Fig. 7. Suppose

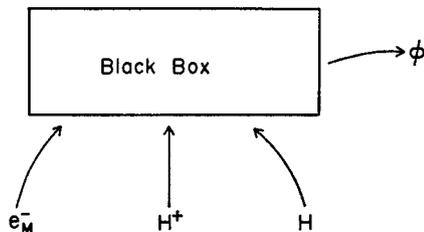


Fig. 7. Pt-H electrode compared to a black box in Gibbs' thermodynamical treatments.

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that a definite quantity of electrons, or hydronium ions H^+ , or hydrogen atoms H are introduced into this black box, and then the corresponding change of the electrode potential is measured under the equilibrium condition.

Frumkin has shown that the change of the electrode potential with the addition of these species can be explained on the basis of the Gibbs thermodynamics,

$$d\sigma = - \sum_j \Gamma_j d\bar{\mu}_j, \quad j = e^-, H^+, H \text{ and ions}, \quad (5)$$

where σ is the interfacial tension and Γ_j is the adsorbed quantity of j -component. In this treatment the material balance among the adsorbed quantities of the electron, proton and hydrogen atom should be taken into consideration together with the electric neutrality at the metal-solution interface, because there occurs transfer among the reaction species through the reaction, $\Gamma_e + \Gamma_H = A_H - \epsilon$, $\Gamma_{H^+} + \Gamma_H = \Gamma_{H^+}^I + A_H$, $\epsilon = \Gamma_{A^-} - \Gamma_{e^+}$, where $\Gamma_{H^+}^I$ is the adsorbed quantity of H^+ at the solution side of the D. L. which can be neglected in the presence of excess salt.

Three basic measurements for the determination of ϵ and A_H have been developed by Frumkin and his school.

1) First it will be shown the change of the electrode potential with the addition of electron to the black box. Let us start from a reversible electrode of Pt-black under the atmospheric hydrogen pressure. If the hydrogen gas is displaced by nitrogen gas, a reversible electrode with respect to H is obtained and the electrode potential is slightly displaced toward anodic direction due to slight change of A_H .

If metal electrons is extracted from this black box by supplying a small anodic current, and the change of the electrode potential with time is measured, then a relation between Γ_e and ϕ_r is obtained, in which ϕ_r corresponds to the electrode potential referred to the reversible hydrogen electrode under the atmospheric hydrogen pressure.

Fig. 8 shows the polarization of the hydrogen electrode obtained in this way by the electricity supplied from outside, which

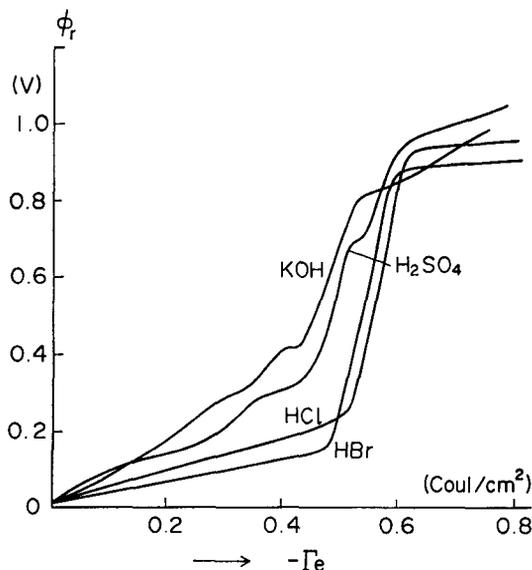


Fig. 8. The potential change of Pt-H electrode caused by extraction of electrons from the electrode,⁶⁾ where ϕ_r is referred to the reversible hydrogen electrode.

is called the charging curve.⁹⁾ It is found that the electricity supplied is stored on the electrode surface in the form of H(ads) and ϵ , and the polarization of an reversible electrode is quite different from that of an ideally polarized electrode such as Hg. As is known, in the 1-st gradual slope the electricity is consumed mainly for the ionization of H(ads) (the hydrogen region), in the 2-nd part for the charging up of the D. L. (the double layer region) and in the 3-rd part for the formation of adsorbed oxygen (the oxygen region). Our main interest will be focussed on the establishment of the electrode potential in the 1-st region. As seen from Fig. 8, the polarization is different in different solutions, *i. e.* different concentrations of H(ads) as well as ϵ can be expected at constant potential.

2) Next it will be shown how to determine the value of ϵ . As shown by Frumkin, ϵ equals Γ_{H^+} at the presence of excess salt, so it is sufficient to measure Γ_{H^+} in order to know ϵ . Frumkin, Petrii and coworkers have developed the potential titration method for the determination of Γ_{H^+} under atmospheric H_2 -pressure.

When a reversible electrode of very small area is used under atmospheric hydrogen pressure, a usual titration curve is obtained as shown by curve 1 in Fig. 9.¹¹⁾ In this case the change of the solution pH is caused practically by the alkaline solution added to the cell.

If an electrode of large surface area is introduced into this cell, a titration curve 1' is obtained and the solution pH is changed in this case not only by the added alkali, but also by the proton produced by the ionization of H(ads). Therefore, the difference of the quantity of alkali at the same electrode potential between the two curves gives the proton desorbed from the electrode, *i. e.* Γ_{H^+} . In this way the free charge density, ϵ_0 , on the electrode surface under atmospheric hydrogen pressure at $\phi_r=0$ can be determined.

3) In order to determine the free charge density ϵ at any electrode potential ϕ_e , Frumkin, Petrii and their coworkers^{10,12)} have devised a new experimental method which is called the pH-dependence of ϕ_r at constant Γ_0 . This new parameter will be denoted by γ ,

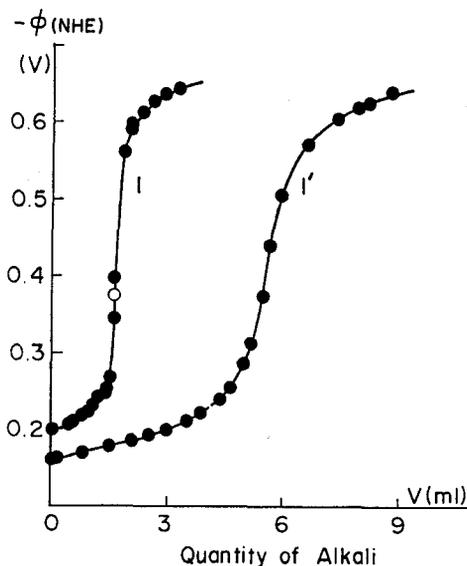


Fig. 9. Potential titration curves of Pt-H electrodes with a small surface area (1) and a large surface area (1') under 1 atm. pressure of H_2 , where ϕ is referred to N. H. E.¹¹⁾

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$$\gamma \equiv \left(\frac{\partial \phi_r}{\partial \mu_{H^+}} \right)_{\Gamma_e} \quad (6)$$

The experimental condition of constant Γ_e can be obtained from the charging curve when the supply of the electricity is stopped.

When a small amount of alkali solution is added to the cell at a constant Γ_e , the displacement of the electrode potential toward negative side is observed. In this way γ is found as a function of ϕ_r , as seen from Fig. 10.

Frumkin¹⁰ has derived an expression for γ on the basis of Gibbs thermodynamics,

$$\gamma = (\partial \epsilon / \partial \phi_r)_{\mu_{H^+}} / (\partial \Gamma_e / \partial \phi_r)_{\mu_{H^+}} \quad (6a)$$

which also equals $(\partial \epsilon / \partial \Gamma_e)_{\mu_{H^+}}$. As seen from the expression of γ , at $\gamma=0$, ϵ is maintained at constant with the change of ϕ_r , in other words, the change of the electrode potential is caused by the adsorbed hydrogen atom only. It can be seen from Fig. 10 that the electrode potential is established by H (ads) only at the neighbourhood of the reversible potential under atmospheric hydrogen pressure.

On the other hand, at $\gamma = -1$, $\epsilon = \Gamma_e$, *i. e.*, in this potential region, the change of the electrode potential is caused by charging up of the double layer, just like the ideally polarized electrode. It can be seen from Fig. 7 that at $\phi_r = 0.6$ V there appears a double layer region when the electrode potential is changed from the hydrogen to the oxygen region.

It should be emphasized in the potential region where γ equals zero that the two components of the electrode potential due to the adsorbed hydrogen atom and free charge are mutually independent and can be expressed by the following equations on the basis of Gibbs thermodynamics,¹³

$$XdA_H = -d\mu_H, \quad (7a)$$

$$Yd\epsilon = d\mu_{H^+}. \quad (7b)$$

Equation (7b) shows that the free charge density is kept constant insofar as the pH of solution is maintained at constant.

The left hand side of Eq. (7a) shows the change of the electrode potential due to the hydrogen adsorption, *i. e.*, the displacement of the Fermi-level due to the adsorp-

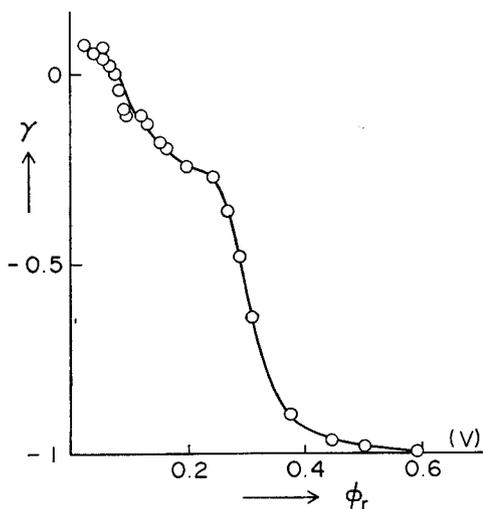


Fig. 10. The pH-dependence of ϕ_r at isoelectric conditions of Pt-H electrode in 0.01 n HCl+KCl solution.¹²⁾

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tion of hydrogen, while on the other hand, the right hand side of Eq. (7 a) $\Delta\mu_{\text{H}}$ practically equals the change of the energy of the Me-H adsorption bond, the entropy term being neglected. The left hand side of Eq. (7 a) may reflect on the potential energy of the initial state of the proton discharge as the change of the energy of the metal electron ;



On the other hand $\Delta\mu_{\text{H}}$ may reflect on the potential energy of the final state of the proton discharge. In this way Eq. (7 a) means a compensation effect of the adsorbed hydrogen atom on the potential energies of the initial and final states of the proton discharge. Therefore it can be expected that the electrode potential component due to the adsorbed hydrogen atom does not affect the rate of the proton discharge in the potential region where γ equals zero.

The compensation effect of an intermediate species produced by an electron transfer step described above, has recently been verified in our laboratory in the case of the hydrogen electrode in alkaline solutions¹⁴, in which the electron transfer step is the discharge of the alkali metal ion and the intermediate alkali metal atom is produced as the result, and the electrode potential is established by the alkali intermediate and the free charge on the electrode surface, as in the case of H(ads) and ϵ of the hydrogen electrode.

The time constant τ_1 of the discharge of the alkali metal ion remains constant in the range of overvoltage η from 0 to a few hundred millivolts, as exemplified in Fig. 11 in the case of Au.¹⁵ In the overvoltage region where τ_1 remains constant the overvoltage is caused by the adsorbed alkali metal atoms and the free charge density on the electrode surface is practically kept constant, *i. e.*, γ defined with respect to the alkali metal ion discharge equals practically zero. The constancy of the time constant means the compensation effect of the intermediate alkali atom on the potential energies of the initial and final states of the discharge of the alkali metal ion.

Now ϕ_r -dependence of ϵ will be discussed based on Eq. (6 a) and the values of γ in Fig. 10. The denominator of γ in Eq. (6 a) $\left(\frac{\partial \Gamma_e}{\partial \phi_r}\right)_{\text{H}^+}$ can be estimated from the char-

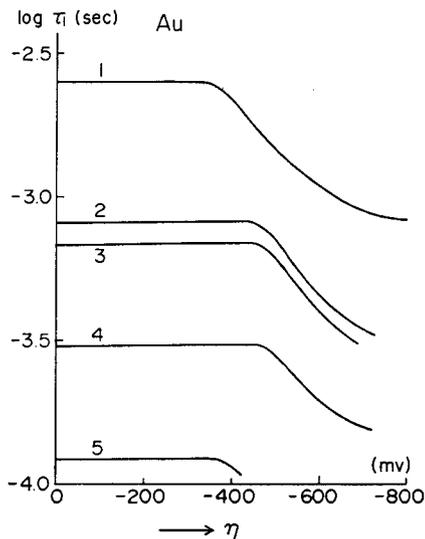


Fig. 11. The overvoltage dependence of the time constant of the electron transfer step of Au-H electrode in aq. NaOH,¹⁵ 1-0.007 *n*, 2-0.02 *n*, 3-0.001 *n* + 0.1 *n* Na₂SO₄, 4-0.5 *n*, 5-1 *n*.

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ging curve as a function of ϕ_r . Therefore the value of ϵ can be obtained from the graphical intergration of the numerator as,

$$\int_0^{\phi_r} \left(\frac{\partial \epsilon}{\partial \phi_r} \right)_{\mu_{H^+}} d\phi_r = \epsilon - \epsilon_0,$$

using the integral constant ϵ_0 obtained by the potentiometric titration method under atmospheric hydrogen pressure.

An example of ϵ determined in this way will be shown in Fig. 12 as a function of ϕ_r in the case of Rh in 0.1 n KCl with pH in the range from 3-11 (curves from 1 to 9).¹⁰ It can be seen from Fig. 12 that in acidic solution the increase of ϵ in the H-region is rather remarkable due to the specific adsorption of Cl^- ion, and then the charging of the double layer appears together with the adsorption of oxygen, and the competition of the adsorption of oxygen and Cl^- occurs with the increase of ϕ_r .

In acidic solution there appears two Z. C. P. at the hydrogen and oxygen regions which may result from the difference of the W. F. between the two adsorption states. In alkaline solutions ϵ is always negative and there appears no Z. C. P. This may be explained by the oxygen adsorption even in the hydrogen region.

Comparing Figs. 8 and 12, the relation between A_H and ϕ_r , (or ϕ) can be obtained, as shown in Fig. 13.¹⁷ Using two fundamental relations $A_H \sim \phi$ and $\epsilon \sim \phi$, the two components of the electrode potential X and Y which are caused by $\text{H}(\text{ads})$ and ϵ can be determined separately. Frumkin, Petrii and their coworkers have determined the values of X and Y in various systems of hydrogen electrodes of Pt-group metals. Some examples of the values of X and Y are shown in Fig. 14 in the case of Pt¹⁹. The upper diagram in this Figure shows X and Y in

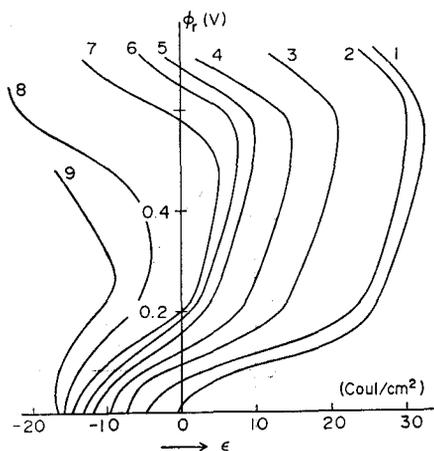


Fig. 12. The relation between the free charge density and the electrode potential on Rh-H electrode in KCl solutions of pH from 3 (curve 1) to 11 (curve 9).

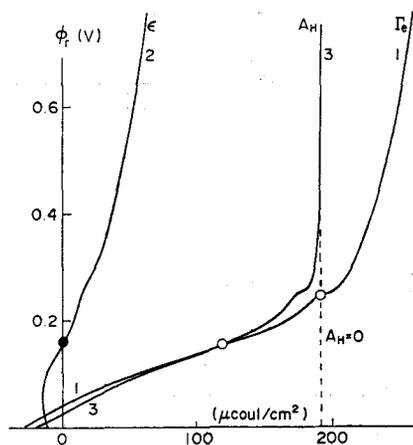


Fig. 13. The ϕ_r -dependence of ϵ , A_H and Γ_e in 0.10 n $\text{HCl} + 1$ n KCl .¹⁷

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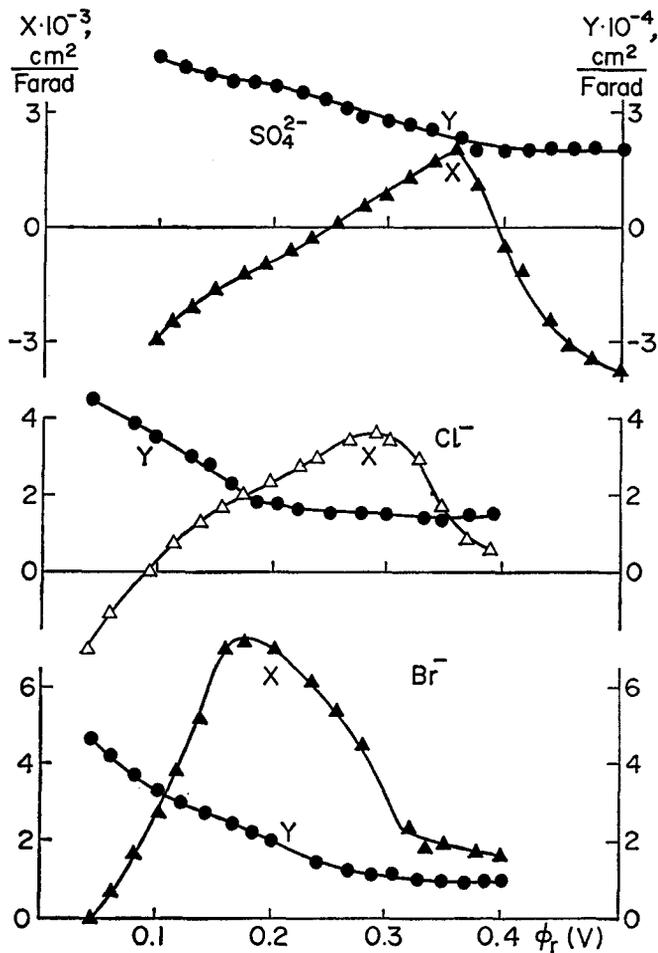


Fig. 14. The contribution of adsorbed hydrogen atom (X) and free charge density ϵ (Y) to Pt-H electrode potential in sulfate, chloride and bromide solutions.¹⁸⁾

sulfate solution, the middle in chloride solution and the lower in bromide solution.

The quantity X can be compared with the W. F. change by the adsorption of H-atom in vacuum system, because both quantities mean the change of the position of the Fermi-level by the adsorption of H-atom.

The negative sign of X in the hydrogen region means the displacement of the electrode potential toward negative side or the decrease of W. F. by H-atom adsorption, so that the M-H bond turns its positive end toward the solution side; on the contrary, when X is positive the negative end toward the solution side.

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On the other hand, in the oxygen region X means $-\left(\frac{\partial\phi}{\partial A_0}\right)$; therefore the negative sign of X means the displacement of the electrode potential toward positive side or the increase of the W.F., as is expected from oxygen adsorption. It can be seen from Fig. 14 that the effect of oxygen adsorption appears at the potentials in the range from 0.2~0.4 V and also the M-H bond is affected by the anion adsorption.

Y is the reciprocal of the differential capacity of the D. L. It can be seen from Fig. 14 that Y -values are decreased by the hydrogen adsorption, but its reason is not clear at present.

The expression for the electrode potential established by Frumkin and his school as a function of A_H and ϵ ,

$$d\phi = XdA_H + Yd\epsilon$$

should be evaluated as the extension of the thermodynamical Nernst Equation into the molecular interpretation of the electrode potential.

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