

1. M.Sack, Z.anorg.Chem., **34**, 286 (1903); B.N.Kabanov and A.I.Zak, Dokl.Akad.Nauk SSSR, **72**, 531 (1950).
2. H.Angerstein, Bull.Acad.polon.Sci., Classe III, **3**, 447 (1955).
3. B.N.Kabanov, D.I.Leikis, I.G.Kiseleva, I.I.Astakhov, and D.P.Aleksandrova, Dokl.Akad.Nauk SSSR, **144**, 1085 (1962).
4. R.H.Gerke, J.Amer.Chem.Soc., **45**, 2507 (1923); H.E.Bent and A.F.Forziati, *ibid.*, **58**, 2220 (1936).
5. I.I.Platonova and S.D.Levina, Zhur.Fiz.Khim., **21**, 331 (1947); H.W.Salzberg, J.Electrochem.Soc., **100**, 146 (1953); L.W.Gastwirt and H.W.Salzberg, **104**, 701 (1957); A.N.Frumkin and N.A.Aladzhalova, Zhur.Fiz.Khim., **18**, 493 (1944); E.Lange and R.Ohse, Naturwiss., **45**, 437 (1958); B.Baranowski and M.Smialowski, Bull.Acad.polon.Sci., Classe III, **7**, 663 (1959).
6. A.N.Frumkin, V.S.Bagotskii, Z.A.Iofa, and B.N.Kabanov, "Kinetika Elektroodnykh Protssessov" (Kinetics of Electrode Processes), Moscow, 1952.
7. D.P.Smith, Z.anorg.Chem., **56**, 116 (1908).
8. E.Zintl and W.Haucke, Z.Elektrochem., **44**, 104 (1938); D.P.Shoemaker and R.E.Marsh, Acta Cryst., **5**, 637 (1952); R.Kreman and A.Mehr, Z.Metallk., **12**, 444 (1920), atp.453.
9. W.B.Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys", Pergamon Press, 1958.
10. G.N.Lewis and F.G.Keyes, J.Amer.Chem.Soc., **34**, 121 (1912); G.N.Lewis, J.Amer.Chem.Soc., **34**, 1631 (1912).
11. I.M.Kolthoff and J.J.Lingane, "Polarography" (Translated into Russian), Goskhimizdat, Moscow-Leningrad, 1948.
12. V.N.Korshunov and Z.A.Iofa, Dokl.Akad.Nauk SSSR, **141**, 143 (1961).

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KINETICS OF SOME HETEROGENEOUS REACTIONS AT A SEMICONDUCTOR-ELECTROLYTE INTERFACE

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Much work has recently been done on the kinetics of heterogeneous redox reactions at a semiconductor-electrolyte solution interface¹. Most theoretical work on the kinetics of electrode processes is based on the formulae of the theory of absolute reaction rates². The application of this theory to electron-transfer reactions needs justification. A quantum-mechanical calculation of the probability of an elementary act of ion discharge at an electrode³ has been based on the hypothesis that electron transfer between an ion in an electrolyte solution and an electrode can be regarded as a radiationless electron jump. This theory has subsequently been applied to the kinetics of several electrochemical redox reactions on metals⁴ and semiconductors⁵. The latter paper considered an idealised case in which the whole potential drop was concentrated in the semiconductor. In the present paper we discard this hypothesis, and regard the potential as falling in both semiconductor

and electrolyte. Formulae will be obtained below for the equilibrium potential, the exchange current, and the polarisation characteristic of several systems.

General Kinetic Relations

Let us consider the elementary act of discharge of an ion A^{2+} in the electrolyte:



As shown previously^{3,6}, the energy of the system fluctuates about an equilibrium value I . It is easy to show that the values of I for the initial and final states in reaction (1) can be determined from the respective formulae

$$I_s = -\epsilon_1 + 2e\varphi(x) - \alpha_2, \quad (2)$$

$$I_f = \epsilon_f - U_0 - e\varphi_n + 3e\varphi(x) - \alpha_3, \quad (3)$$

where ϵ_1 is the energy of ionisation of A^{2+} (in the gas phase), α the energy of hydration, $\varphi(x)$ the potential at the position occupied by the ion, and φ_n the internal (voltaic) potential of the semiconductor. The significance of ϵ_f and U_0 is clear from the diagram.

The current flowing through the system can be written in the form

$$i = i_{ns} - i_{sn} = (i_{ns}^e + i_{ns}^p) - (i_{sn}^e + i_{sn}^p), \quad (4)$$

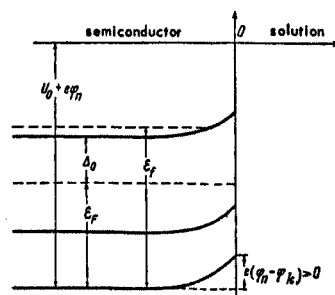
where i_{ns} is the current flowing from the semiconductor to the solution (i.e. associated with transfer of an electron from A^{2+} to the semiconductor), while i_{sn} is the reverse current; the superscripts e and p indicate whether the electrons belong to the conduction band or the valency band respectively:

$$i_{ns} = e \int_0 c_2(x) dx \int W_{sf}(x) [1 - n(\epsilon_f)] \rho_f d\epsilon_f, \quad (5)$$

$$i_{sn} = e \int_0 c_3(x) dx \int W_{fs}(x) n(\epsilon_f) \rho_f d\epsilon_f, \quad (6)$$

$c_2(x)$ and $c_3(x)$ being the concentrations of A^{2+} and A^{3+} ions in the electrolyte distant x from the electrode, $n(\epsilon_f)$ the Fermi partition function, ρ_f the density of levels in the semiconductor, and W_{sf} the probability of electron transfer from the ion A^{2+} to the semiconductor. In the theory of radiationless electron transitions it is shown that the probability of the reverse transfer W_{fs} is linked with W_{sf} by the relation⁶

$$W_{fs} = W_{sf} \exp \left\{ \frac{I_f - I_s}{kT} \right\}. \quad (7)$$



Utilising this formula, we can write the resultant current in the form

$$i = e \int_0^{\infty} dx \int d\epsilon_f \rho_f n(\epsilon_f) c_3(x) W_{fs}(x) \left\{ \frac{c_2(x)}{c_3(x)} \frac{1 - n(\epsilon_f)}{n(\epsilon_f)} e^{I_s - I_f / kT} - 1 \right\}.$$

If a Boltzmann distribution is used for $c_2(x)$ and $c_3(x)$, and the expressions for $n(\epsilon_f)$, I_s , and I_f are written out, we obtain

$$i = \left\{ \exp \left[\frac{e(\varphi_n - \varphi_s) - (a_2 - a_3) - e_f - (e_F - U_0) - kT \ln(c_3/c_2)}{kT} \right] - 1 \right\} i_{sn}, \quad (8)$$

where c_2 (c_3) and φ_s are the concentration of A^{2+} (A^{3+}) ions and the potential in the bulk of the electrolyte, as $x \rightarrow \infty$. By means of Eqn. (8) it is easy to obtain a formula for the equilibrium difference in voltaic potentials at the electrode-solution interface

$$e(\varphi_n^0 - \varphi_s) = (a_2 - a_3) + e_f(e_F - U_0) + kT \ln \frac{c_3}{c_2}. \quad (9)$$

Hence, introducing the overpotential η defined by the formula

$$\eta = \varphi_n - \varphi_n^0, \quad (10)$$

we finally write Eqn. (8) in the form

$$i = i_{sn}(e^{e\eta/kT} - 1). \quad (11)$$

Furthermore, it follows from Eqns. (11) and (4) that

$$i_{ns} = i_{sn} e^{e\eta/kT}. \quad (12)$$

It must be noted that Eqns. (9), (11), and (12) are valid both for semiconductor and for metallic electrodes, as follows from the actual deduction of the formulae.

Kinetics at a Semiconductor Electrode

In order to calculate the current for a semiconductor electrode we integrate with respect to ϵ_f in Eqns. (5) and (6) over both valency and conduction bands. Integration over the valency band alone gives an expression for the "positive hole" current $i^{(p)}$, and over the conduction band the electron current $i^{(e)}$. Eqn. (8), from its derivation, is valid for both components (electron and hole) of the total current. Hence the following relations

$$i^{(e, p)} = i_{sn}(e, p)(e^{e\eta/kT} - 1) = i_{ns}(e, p)(1 - e^{-e\eta/kT}), \quad (13)$$

$$i_{ns}(e, p) = i_{sn}(e, p)e^{e\eta/kT}, \quad (14)$$

analogous to Eqns. (11) and (12), are satisfied for these components.

In order to calculate the current from Eqns. (5) and (6), several simplifying assumptions must be made. Since the probability of electron transfer $W(x)$ diminishes rapidly with increasing distance between the ion undergoing discharge and the electrode, it is natural to introduce the concept of an effective reaction region of thickness l_{eff} , within which discharge takes place. To this approximation Eqn. (6) can be rewritten in the form

$$i_{sn} = e\Gamma_3 \int W_{fs}(\delta) n(\epsilon_f) \rho_f d\epsilon_f, \quad (15)$$

where $\Gamma_3 = l_{eff} c_3(\delta)$, and δ represents the most probable distance from which discharge occurs. In practice δ must be identified with the thickness of the Helmholtz layer (the distance of closest approach of the ion to the electrode), and Γ_3 is to be regarded as the surface concentration of A^{3+} ions on the outside of the Helmholtz layer.

The probability of electron transfer W_{fs} has been calculated³ as

$$W_{fs} = \left(\frac{\pi}{\hbar^2 k T E_s} \right)^{1/2} |L_{sf}|^2 \exp \left\{ - \frac{(I_s - I_f + E_s)^2}{4 E_s k T} \right\}. \quad (16)$$

The significance of L_{sf} (the exchange integral) and E_s (the energy of polarisation) has been discussed previously³⁻⁵, in special detail in Ref. 6.

On the assumption that ρ_f and the preexponential factor of W_{fs} vary little with ϵ_f , Eqn. (15) can be written in the form

$$i_{sn} = B_3 \int n(\epsilon_f) \exp \left\{ - \frac{(I_s - I_f + E_s)^2}{4 E_s k T} \right\} d\epsilon_f, \quad (17)$$

$$B_3 = e\Gamma_3 \rho |L|^2 \left(\frac{\pi}{\hbar^2 k T E_s} \right)^{1/2}.$$

In deriving this formula we have assumed that L_{sf} is only slightly dependent on ϵ_f . However, this hypothesis is definitely not satisfied when $e(\varphi_n - \varphi_k) > \epsilon_f > 0$ and when $e(\varphi_n - \varphi_k) + \epsilon_F + \Delta_0 > \epsilon_f > \epsilon_F + \Delta_0$ (Δ_0 being the half-width of the forbidden gap, and φ_k the semiconductor-electrolyte contact potential - see diagram). Within this range ϵ_f , the electronic transition, is a tunnel effect. Since the Debye thickness in a semiconductor is large, tunnelling can be neglected, and this interval of ϵ_f excluded in the integration in Eqn. (17). Hence the integral with respect to ϵ_f in Eqn. (17) can be written symbolically

$$\int = \int_{\epsilon(\varphi_n - \varphi_k)}^{\epsilon_F - \Delta_0 + e(\varphi_n - \varphi_k)} + \int_{\epsilon_F + \Delta_0 + e(\varphi_n - \varphi_k)}^{U_F + e\varphi_n} \approx \int_{-\infty}^{\epsilon_F - \Delta_0 + e(\varphi_n - \varphi_k)} + \int_{\epsilon_F + \Delta_0 + e(\varphi_n - \varphi_k)}^{\infty} \equiv \int^{(p)} + \int^{(e)}. \quad (18)$$

The lower limit in the first ("positive hole") integral is replaced by $-\infty$, and the upper limit in the second ("electronic") integral by $+\infty$, because the integral in Eqn. (17) converges very rapidly at large negative ϵ_f on account of W_{fs} , and at large positive ϵ_f owing to the presence of $n(\epsilon_f)$. Physically this simply corresponds to the fact that only electrons in the vicinity of the top of the valency band and the bottom of the conduction band are involved in transporting the current.

"Metallised" Surface

Let us begin calculation of the current with the simplest case, in which the semiconductor surface is "metallised" as a result of intersecting a Fermi level of the valency band or the conduction band. The criterion of "metallisation" can be written

$$e|\varphi_n - \varphi_k| - \Delta_0 > 4kT. \quad (19)$$

The integral occurring in Eqn. (17) can in this case be evaluated by Laplace's method (which is analogous to the saddle point method for functions of a real variable). The resulting formula is

$$i_{sn} = \frac{2\pi e \rho}{\hbar} |L|^2 \sqrt{\frac{2kT}{E_s}} \sqrt{\frac{c_2}{c_3}} \Gamma_3 \exp \left\{ - \frac{[E_s + e\eta + e(\varphi_s - \varphi(\delta))]^2}{4 E_s k T} \right\}. \quad (20)$$

Confining ourselves to the region of not too high overpotentials $e\eta < 2\sqrt{kTE_s}$ (~ 1 eV), and assuming that when $i \neq 0$ the Boltzmann equilibrium distribution function from Eqns. (11) and (20) is valid for Γ_3 , we obtain

$$i = i_0 (e^{e\eta/2kT} - e^{-e\eta/2kT}) e^{5e/4} [\varphi(\delta) - \varphi(\delta)] / 2kT, \quad (21)$$

where the exchange current i_0 is determined from the formula

$$i_0 = \frac{2\pi e p_{\text{eff}}}{h} |L|^2 \sqrt{\frac{2kT}{E_s}} \sqrt{c_2 c_3} e^{-E_s/4kT} \exp\left\{\frac{5e[\varphi_s - \varphi^0(\delta)]}{2kT}\right\}, \quad (22)$$

and $\varphi^0(\delta)$ corresponds to the equilibrium potential at the point $x = \delta$ when $\eta = 0$.

On comparing Eqns. (21) and (22) with previous results⁴, we see that the expressions for the currents in the case of a semiconductor having a "metallised" surface and in the case of a metal electrode are formally identical. However, the quantities $\varphi^0(\delta)$ and $\varphi(\delta)$ in Eqns. (21) and (22) and in the corresponding equations of Ref. 4 differ both quantitatively and in the dependence of $\varphi(\delta)$ on overpotential. (This is linked with the different potential distributions in these two systems.) It is only when the potential drop in the electrolyte occurs almost entirely in the Helmholtz layer, i.e. at high concentrations, that a "metallised" semiconductor behaves in just the same way as a metallic electrode.

"Non-Metallised" Surface

When the surface of the semiconductor is not "metallised", i.e. when the inequality

$$\Delta_0 - e|\varphi_n - \varphi_k| > 4kT \quad (23)$$

is satisfied, $n(\epsilon_f)$ in Eqn. (15) can be replaced by unity for electrons in the valency band, while the Boltzmann distribution can be written instead of $n(\epsilon_f)$ for electrons in the conduction band. In the calculation of $i_{sn}^{(e)}$ and $i_{sn}^{(p)}$ use was made of the asymptotic formula⁷

$$\int_0^\infty e^{-u^2} du \approx \frac{e^{-t^2}}{2t}, \quad t \gg 2. \quad (24)$$

We omit the calculations, and merely give the results

$$i_{sn}^{(p)} = \frac{e p_{\text{eff}}}{h} |L|^2 \sqrt{\frac{4\pi kT}{E_s}} \sqrt{c_2 c_3} e^{3e[\varphi_s - \varphi^0(\delta)]/4kT} \times \exp\left\{-\frac{|E_s + \Delta_0 - e(\varphi_n^0 - \varphi_s) - e[\varphi(\delta) - \varphi_k]|^2}{4E_s kT}\right\}, \quad (25)$$

$$i_{sn}^{(e)} = i_{sn}^{(p)} \exp\left\{-\frac{|E_s + \Delta_0(\varphi_n^0 - \varphi_s) + e[\varphi(\delta) - \varphi_k]|}{E_s kT}\right\} \times \exp\{-e[\varphi_n - \varphi(\delta) - \varphi_k]/kT\}. \quad (26)$$

[Eqn. (26) obviously contains several errors (Ed. of Translation)]. Introducing the notation $\eta_g = \varphi(\delta) - \varphi^0(\delta)$ and $\eta_k = \varphi_k - \varphi_k^0$ and remembering that E_s is large (of the order of 10 eV), we can approximately rewrite Eqns. (25) and (26) in the form

$$i_{sn}^{(p)} = i_0^{(p)} e^{-3e\eta_g/2kT} \exp\left\{-\frac{e\eta_k}{2kT}\right\}, \quad (27)$$

$$i_{sn}^{(e)} = i_0^{(e)} e^{-5e\eta_g/2kT} \exp\left\{\frac{e\eta_k}{2kT} - \frac{e\eta}{kT}\right\}, \quad (28)$$

where the positive-hole exchange current is

$$i_0^{(p)} = \frac{e p_{\text{eff}}}{h} |L|^2 \sqrt{\frac{4\pi kT}{E_s}} \sqrt{c_2 c_3} e^{3e[\varphi_s - \varphi^0(\delta)]/2kT} \times \exp\left\{-\frac{|E_s + \Delta_0 - e(\varphi_n^0 - \varphi_k)|^2}{4E_s kT}\right\}, \quad (29)$$

and the electron exchange current is linked with this by the relation

$$i_0^{(e)} = i_0^{(p)} \exp\left\{-\frac{e(\varphi_n^0 - \varphi_k^0)}{kT} \left[1 + \frac{\Delta_0}{E_s}\right]\right\}. \quad (30)$$

Comparison of Eqns. (27) and (28) with the corresponding formulae in Ref. 5 shows that taking into account the fall in potential in the electrolyte leads formally to the appearance in the expressions for the positive-hole and electron currents of the factors $\exp(-e\eta_k/2kT)$ and $\exp(e\eta_k/2kT)$ respectively.

Comparison with the Tafel Equation

It is interesting that expressions have been obtained which are analogous to the Tafel equation in electrochemistry, which is usually deduced from Brønsted's empirical relation

$$E^*(\eta) - E^*(\eta = 0) = -\beta[\Delta I(\eta) - \Delta I(\eta = 0)],$$

where E^* is the activation energy, in our case the exponent in Eqn. (16) multiplied by kT . This relation is equivalent to Polanyi's rule for gas reactions². This rule does in fact hold in the theory developed in the present paper, and it is found that $\beta = \frac{1}{2}$ for both metals and semiconductors, a result to be expected on the basis of the model adopted. Actually, β is a coefficient of proportionality between the change in the heat of reaction (change in difference between minima on the potential-energy curves of the system in initial and final states) and the change in the activation energy (change in the distance from point of intersection of potential-energy curves to minimum on the corresponding curve) on application of overpotential. In the present model the potential-energy curves are parabolas with both metallic and semiconductor electrodes.

In the case of a metallic electrode the value of β mainly determines the dependence of current on overpotential (if the ψ_1 effect is separated from the dependence of the concentration of ions in the solution on the overpotential), since in this case the current is determined by the probability of electron transfer from the solution to a Fermi level in the metal.

With a semiconductor electrode (having a "non-metallised" surface) the current is greatly affected by the electronic levels and by the concentration of electrons in the semiconductor.

Firstly, the presence of a forbidden gap results in electronic transitions taking place mainly to levels immediately adjacent to the bottom of the conduction band or to the top of the valency band, which in fact corresponds to the appearance of an effective activation energy differing for electron exchange with the two bands. From Eqns. (25) and (26) the effective activation energy is

$$E_{\text{eff}}^{(p)} = \frac{|E_s + \Delta_0 - e(\varphi_n^0 - \varphi_s) - e[\varphi(\delta) - \varphi_k]|^2}{4E_s}$$

for a positive-hole current, and

$$E_{\text{eff}}^{(e)} = \frac{|E_s + \Delta_0 + e(\varphi_n^0 - \varphi_s) + e[\varphi(\delta) - \varphi_k]|^2}{4E_s}$$

for an electron current. Hence it is evident that, when a positive space charge is present in a semiconductor, the electron exchange current is smaller than the positive-hole current, and conversely if the space charge is negative.

Secondly, the current is proportional to the concentration of electrons or holes at the bottom of the conduction band and at the top of the valency band. Therefore, besides the usual activation dependence of current on overpotential (associated with the quantity β), there will also be a concentration dependence, which is an exponential function of η — see Eqn. (26). The overall dependence of current on

overpotential is determined experimentally. It is therefore convenient to characterise the current by the parameter⁹

$$\alpha = -\frac{kT}{e} \frac{d \ln i_n}{d\eta}. \quad (31)$$

For the electron current $i_n^{(e)}$ at high electrolyte concentrations, for example, α becomes

$$\alpha^{(e)} = 1 - \frac{1}{2} \frac{d\eta_k}{d\eta}.$$

For the positive-hole current $\alpha^{(p)} = 1 - \alpha^{(e)}$. This quantity depends on the distribution of potential in the system and may depend on η .

In the case of a metal electrode (in the absence of a ψ_1 effect) the parameter α defined in Eqn. (31) is identical with β . This is not the case with a semiconductor (see below).

The formulae obtained in this section apply generally to systems containing a semiconductor electrode. In order to assess the influence of the potential drop on the current, let us examine actual systems.

Calculation of Kinetic Parameter α for Some Real Systems

Since experiments are usually made with high electrolyte concentrations, it may be supposed that the whole potential drop in the electrolyte occurs within the Helmholtz layer. We shall consider only systems in which the semiconductor surface is "non-metallised", i.e. to which the inequality (23) applies. The current will then depend on η and η_k , the latter being a function of η and being determined by the actual form of the potential distribution.

Let us consider the system formed by an intrinsic semiconductor with an aqueous electrolyte solution. We shall assume that the deviation of the system from equilibrium on application of an overpotential η is small and that, as before, equilibrium formulae can be applied to the distribution of potential. In the absence of specific adsorption, we can write for the distribution of potential

$$A \sinh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT} = \frac{e(\varphi_k^0 - \varphi_s)}{2kT} + \frac{e\eta_k}{2kT}, \quad (32)$$

where

$$A = \frac{e}{kT} \frac{\epsilon_n}{\epsilon_r} \delta \sqrt{\frac{8\pi kT n_0}{\epsilon_n}},$$

ϵ_n and ϵ_r being the dielectric constants of the semiconductor and of the Helmholtz layer, δ the thickness of the Helmholtz layer, and n_0 the concentration of carriers in the semiconductor. Hence

$$\frac{d\eta_k}{d\eta} = \frac{A \cosh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT}}{1 + A \cosh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT}}, \quad (33)$$

which shows that α is a function of η . However, the derivative $d\eta_k/d\eta$ is very small, its maximum value for germanium being about 0.06. Thus in this case the effect of the potential drop on the current is very slight, and the values of α for the electron and positive-hole currents are practically 1 and 0 respectively.

The situation may change if a large concentration of ionised levels is present on the surface of the semiconductor. Let us consider for simplicity the case in which

a constant concentration N_d of donor levels of energy E_d is present on the surface. The distribution of potential can then be represented by the equation

$$A \sinh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT} + A_d \left(1 - \frac{1}{1 - \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\}} \right) = \frac{e[\varphi_k^0 - \varphi_s]}{2kT} + \frac{e\eta_k}{2kT}, \quad (34)$$

where $A_d = 2\pi e^2 N_d \delta / kT \epsilon_r$;

$$\begin{aligned} \frac{d\eta_k}{d\eta} = & \left[A \cosh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT} + \right. \\ & \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\} \\ & + 2A_d \frac{\exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\}}{\left[1 + \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\} \right]^2} \left. \right] \times \\ & \times \left[1 + A \cosh \frac{e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{2kT} + \right. \\ & \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\} \\ & + 2A_d \frac{\exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\}}{\left[1 + \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\} \right]^2} \left. \right]^{-1}. \end{aligned} \quad (35)$$

It is evident from Eqn. (35) that, if

$$2A_d \frac{\exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\}}{\left[1 + \exp \left\{ \frac{E_d - e_F + e[\varphi_n^0 - \varphi_k^0] + e(\eta - \eta_k)}{kT} \right\} \right]^2} \gg 1, \quad (36)$$

then $d\eta_k/d\eta \approx 1$, and hence $\alpha = \frac{1}{2}$: i.e. with respect to the dependence of current on overpotential the semiconductor will behave as a metallic electrode. It must be noted that the inequality (36) contains η , and therefore, although it may be satisfied for some values of η , it may not be satisfied with others, and the opposite inequality may even apply. The semiconductor will then behave as in the absence of surface levels.

SUMMARY

1. Minute examination based on the theory developed in previous papers has given an expression for the equilibrium voltaic potential difference at an electrode-solution interface which is identical with the expression obtained thermodynamically⁴.
2. In the case of a semiconductor electrode having a "metallised" surface the expressions for the current are formally identical with the corresponding expressions for a metallic electrode.
3. In the case of a semiconductor having a "non-metallised" surface, allowance for the potential drop in the electrolyte results in the appearance of the factors $\exp(-e\eta_k/2kT)$ and $\exp(e\eta_k/2kT)$ in the respective expressions for positive-hole and electron currents. The value of η_k depends on the actual distribution of potential in the system. With an intrinsic semiconductor having no surface levels, the effect of the potential drop on the current is slight, and the Tafel constants α for the electron and hole currents are 1 and 0 respectively. In the presence of a large concentration of surface levels, $\alpha = \frac{1}{2}$, and in this respect the semiconductor behaves as a metallic electrode.

4. Brønsted's rule applies to the reactions considered, with $\beta = \frac{1}{2}$ for both metallic and semiconductor electrodes.

1. H. Gerischer, Z. phys. Chem. (Frankfurt), **26**, 223, 325 (1960); **27**, 48 (1961); J. F. Dewald, in "Semiconductors" (edited by N. B. Hannay) (Translated into Russian), Inostr. Lit., 1962, [Chapter XVII].
2. S. Glasstone, K. H. Laidler, and H. Eyring, "Theory of Rate Processes" (Translated into Russian), 1948.
3. R. R. Dogonadze and Yu. A. Chizmadzhev, Dokl. Akad. Nauk SSSR, **144**, 1077 (1962).
4. R. R. Dogonadze and Yu. A. Chizmadzhev, Dokl. Akad. Nauk SSSR, **145**, 849 (1962).
5. R. R. Dogonadze and Yu. A. Chizmadzhev, Dokl. Akad. Nauk SSSR, **150**, 333 (1963).
6. V. G. Levich and R. R. Dogonadze, Coll. Czech. Chem. Comm., **26**, 193 (1961).
7. N. N. Lebedev, "Spetsial'nye Funktsii i Ikh Prilozheniya" (Special Functions and Their Application), 1953.
8. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetika Elektrokhimicheskikh Protseessov" (Kinetics of Electrode Processes), 1952.
9. H. Gerischer, Z. phys. Chem. (Frankfurt), **27**, 48 (1961).

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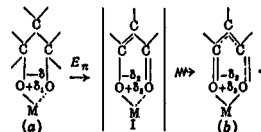
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X-RAY SPECTRA OF QUASIAROMATIC COPPER COMPLEXES

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The present paper reports the use of X-ray spectra to study the structural characteristics of chelate compounds.

The formation of chelate compounds involves a fundamental change in the nature of the chemical bonds in the original molecules¹⁻⁵. Thus the conversion of a ring not containing conjugated bonds (a) into a ring containing conjugated bonds (b) is accompanied by a tendency for bond lengths to become equal, with a change in the character of the O-M bonds ($\delta_3 < \delta_1$):



The energy of formation E_1 of the metal-non-metal bond in ring (a) is determined by the dipole and donor-acceptor interactions E_d and E_α :

$$E_1 = E_\alpha + E_d, \quad (1)$$

and in ring (b) by

$$E_2 = E_\alpha + E_d + E_\pi. \quad (2)$$

The energy E_π of π -electron interaction will be regarded

as the change in energy of the metal-non-metal bond occurring on passing from ring (a) to ring (b), in the latter of which the π electrons of the system and two p electrons from the oxygen atom forming the O-M bond have been delocalised by participation in vacant orbitals of the metal atom. Ring (b), containing a metal-non-metal bond, can be termed "quasiaromatic" because in it six electrons have been delocalised, and can utilise six molecular orbitals (three bonding and three antibonding), including p (or d) orbitals of the metal atom⁶⁻¹⁰.

Quasiaromatic rings containing metal-non-metal bonds and those containing hydrogen bonds are similar in character^{1,2}, but delocalisation of the electrons is more effective in the former because the vacant orbitals are lower on the metal atom than on a hydrogen atom.

As noted above, the term E_π in Eqn. (2) represents the change in all types of interaction accompanying formation of a quasiaromatic metal ring. In order to obtain an approximate quantitative idea of the energy E_π for different compounds, let us suppose that the value of $E_d + E_\alpha$ in Eqn. (2) remains practically constant for a series of similar compounds (for example those in Table 1). We then have $E_\pi = E_2 - E_1$. Since E_π depends on conjugation in the quasiaromatic ring, it may be expected to increase with increase in electron density on the C=C and C=O bonds occurring in this ring. This density can be measured by the "bond order" ($N_{C=C}$, $N_{C=O}$). Under otherwise identical conditions, the "bond order" will depend on the nature of the substituents attached to the $R_1-C=O$ and $R_2-C=C-R_3$ groups. If R_1 does not change, the change in E_π is determined solely by $N_{C=C}$, the order of the C=C bond on the basis of which the ring has been built. Quasiaromatic rings containing a hydrogen bond show a linear relation between E_π ($\Delta\nu$, cm^{-1}) and $N_{C=C}$.^{4,9} Quasiaromatic rings containing a metal atom may be supposed to exhibit a similar relation between these quantities.

The increase in energy E_π associated with participation of vacant orbitals (p or d) of the metal atom will obviously diminish the polarity of the $O^{\delta-}-M^{\delta+}$ bond, and hence the effective charge on the metal atom. The values of E_π and E_α probably vary in the opposite sense to $N_{C=C}$. The known physicochemical properties (solubility, volatility, reactivity, etc.) of chelate compounds support this conclusion. Hence in a series of chelate compounds (Table 1) a relation should exist between the change in effective charge on the metal atom and the value of E_π associated with the multiplicity of the C=C bond.

In the present work an investigation has been initiated of the above relationship and of analogies between metal-non-metal and hydrogen bonds revealed in the X-ray spectra.

EXPERIMENTAL

Method

The variation in effective charge in the test compounds can be determined from their X-ray spectra.

Many investigations of the X-ray spectra of chemical compounds have established empirical rules relating these spectra with the nature of the chemical bond in the compounds. During recent years many workers have developed a theory of X-ray spectra and examined the relation between the latter and parameters of the chemical bond.