Effect of Light on a Tin Cathode in Stannous Acid Solution*

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This preliminary experiment study makes it possible to demonstrate that, in the case of the Sn/Sn(II) system, the effect of the light can be at first explained by the lowering of potential barriers.

The study was made using unfiltered light which was simultaneously outside the absorption region of the solution and below the photoelectric threshold of tin.

Comparison has been made particularly of the kinetics of transient states prior to the achievement of equilibrium in the region of very slight overpotential, in the dark and in light.

The extension for our experimental method of the Bockris theory applied to the systems Ag^+/Ag, Ga^{3+}/Ga permits correct interpretation of these kinetic reactions: The tin is discharged and the adion diffuses to the surface of the metal before entering the kink site. The transfer and diffusion parameters are not greatly altered. Only the potential barriers for the discharge and ionization processes (normal to the electrode) are lowered by an equal amount due to the presence of light. This drop in value is essentially equal to the decrease in the potential barrier calculated by diffusion.

Very few experiments have been conducted in connection with the action of light on polycrystalline metallic electrodes. Before making any theoretical interpretation, we decided to make a systematic study of a series of metal (copper, tin, etc.). Here, we will deal with a tin electrode placed in a stannous chloride solution having a pH of 0.5 (phosphoric acid) containing only Sn^{++} ions and yielding neither compounds nor oxides. The assembly is shown in Fig. 1. It is kept at a temperature of $25°\,C \pm 0.01°\,C$, using thermostatic controls.

The spectral distribution of the light source is shown in Fig. 2. The solution has practically no absorption power in this portion of the spectrum. Furthermore, since the photoelectric threshold of tin is 4.39 eV (i. e., $\lambda = 2820$ Angstrom units), this is not due to a pure photoelectric effect.

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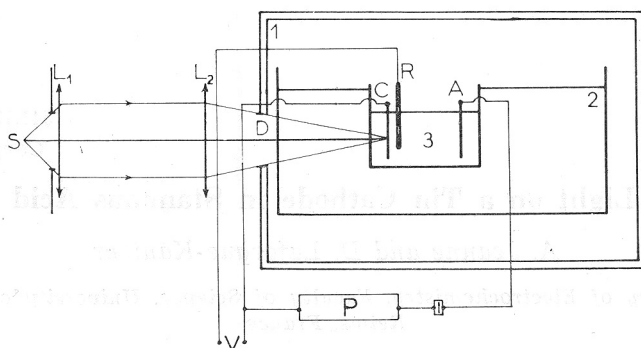
Fig. 1. Apparatus schematic: (1) thermostat (air), (2) thermostat (water), (3) electrolytic cell, (P) potentiostat, (A) anode, (C) cathode, (R) calomel electrode, (D) diaphragm, (S) light source, (L₁), (L₂) lenses, (V) Voltmeter.

The increase in temperature of the electrode, after being illuminated during an experiment, is less than 0.02° C.

1. First, we traced the conventional overpotential curves. All of the results for various surface conditions are contained within the families of curves A and B (Fig. 3) corresponding to darkness and light, respectively.
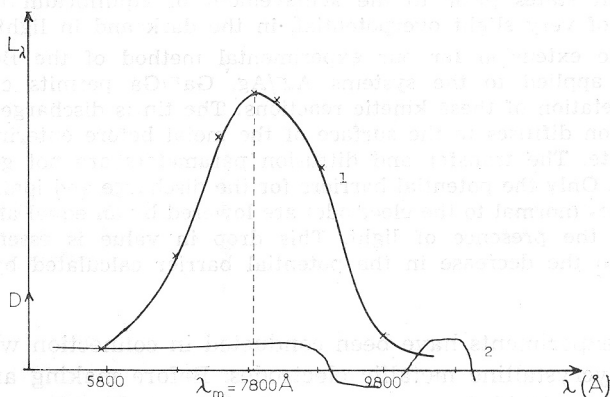

Fig. 2. (1) Spectral distribution of the light source S; (2) Spectral Absorption of the electrolytic solution.

We observed that if the solution alone is illuminated, there is no change in electrode potential. Therefore, the phenomenon does appear to be localized in the vicinity of the electrode.

Moreover[1] we discovered that if the light acts on the diffusion potential barrier, it lowers the latter by about 500 calories for the source employed.

2. We paid particular attention to the electron transfer region. A straightforward analysis of the overpotential curves yields a transfer coefficient α that is very close to unity ($\alpha = 0.98$) for all of the curves, whereas the sum ($\alpha + \beta$) takes on values of several times unity which vary from one experiment to another.
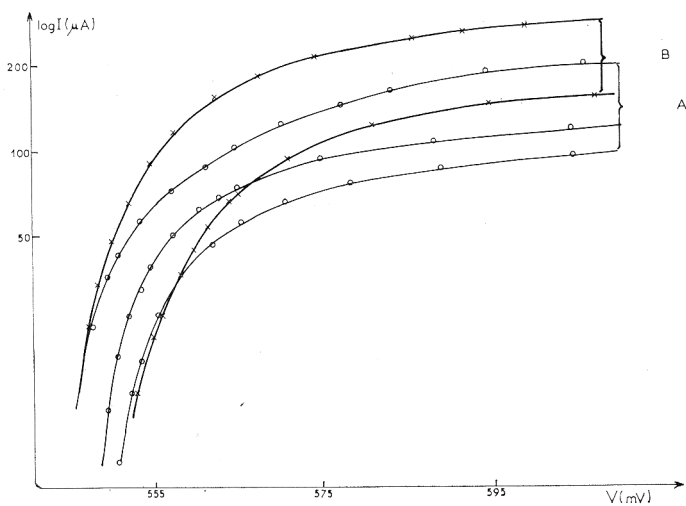
Fig. 3. Comparative study between darkness curves A and light curves B.

On the other hand, recordings of electrode potential show that the equilibrium potential for a given intensity is attained very slowly and that the kinetics of this process are altered by illumination (Fig. 4).
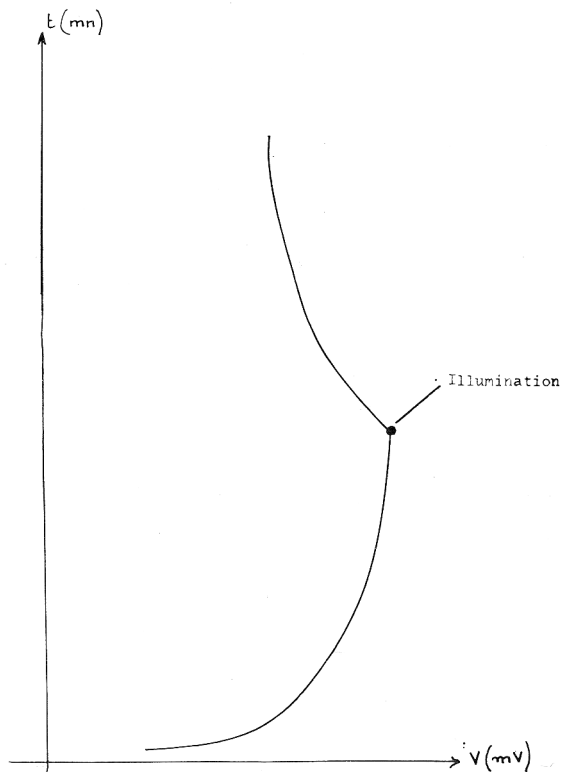

Fig. 4. Experimental curves of the Sn^{II}/Sn kinetics (a = darkness; b = light).

We therefore studied this kinetic process and were able to explain it perfectly by means of the so-called crystallization theory developed by Bockris. The essential idea is that, once the ion is discharged, it diffuses over the surface of the electrode before entering the crystal lattice at certain favored points.

TABLE I

State of Surface	S_1		S_2			S_3	
I_{p+1} (µA)	104	85	104	86	69	103	85
$\eta_{p+1}\infty$ (mV)	21.0	14.5	14.7	10.6	8.0	11.5	8.8
$\eta_p\infty$	14.5	10.8	10.6	8.0	6.5	8.8	6.8
$\Delta\eta_{t=0} - \Delta\eta_\infty$ (mV)	5.2	3.6	3.7	2.5	2.0	2.2	1.5
$r \cdot 10^3$ (s^{-1})	3.43	3.22	4.25	4.20	4.12	4.11	4.12
$(\alpha + \beta') \cdot S \cdot \mid M\eta\infty \mid \frac{p}{s} \cdot 10^7$	3.9	4.9	4.5	5.5	5.5	7.5	8.0
$\dfrac{I_{i+1}}{I_{j+1}}$	$\dfrac{104}{85} = 1.22$		$\dfrac{104}{86} = 1.20$	$\dfrac{85}{69} = 1.24$		$\dfrac{103}{85} = 1.21$	
$\dfrac{\eta_{i+1}}{\eta_{j+1}}$	$\dfrac{14.5}{10.8} = 13.4$		$\dfrac{10.6}{8} = 13.2$	$\dfrac{8}{6.5} = 1.23$		$\dfrac{8.8}{6.8} = 1.29$	
$(\alpha + \beta')$			1.8	1.8	1.7	1.7	

The equations established by Bockris[2-4] and which we have adapted to our experimental method (by successive intensity steps)[5] are applicable only in the region of very low overpotential where the combination of transfer and diffusion processes in the solution is negligible.

Let $\mid M_0 \mid_S$ be the surface concentration of adions having a valence z at time t = 0 (origin of axes) and let $\mid M_{\eta, t} \mid$ be their concentration at variable time t for the same overpotential η.

$$\frac{d\mid M_{\eta, t}\mid}{dt} = \frac{i_{p+1}}{zF} - J$$

where

J is the diffusion flux

i_{p+1} is the current density of the p + 1th intensity step.

$$J = r [\mid M_{\eta, t}\mid_S - \mid M_{\eta, 0}\mid_S]$$

where r is the diffusion velocity constant of the adions.

Making all of theses calculation yields the expressions for the partial ionization and discharge current $\overrightarrow{i}$ and $\overleftarrow{i}$ which are expressed as a function of the transfer coefficients and to which Bockris has given the physical meaning shown in Fig. 5.

The written equations permit determining the coefficients α and β'. The results are perfectly coherent for conditions of darkness: $\alpha \simeq 1$; $\beta' \simeq 0.7$.
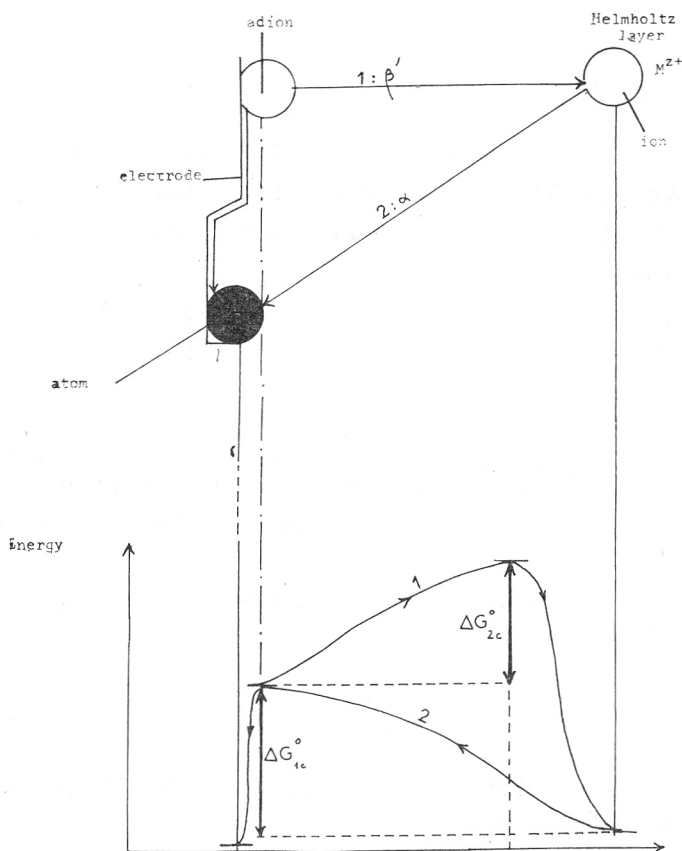
Fig. 5. Diagrammatic representation (Darkness): (1) oxydation; (2) reduction.

The parameter r is constant for a given surface condition and is of the order of 4×10^{-3} s^{-1}.

The physical meaning of the coefficients α and β' permits determining the position of intermediate complexes on the diagram. The ion discharge occurs in the vicinity of the electrode, whereas, in the ionization process, the ion which leaves the electrode crosses its barrier not far from the Helmholtz layer.

The Table II display the results obtained for the case of illumination. The coefficients α, β and r remain fairly constant (to within 5%). Moreover, the calculations show that:

$$\Delta\eta_{t=\infty} - \Delta\eta_{t=0} = \frac{RT}{4 F^2} - \frac{I_{p+1}}{Sr \left| M_{\eta,\,0} \right|_S^P (\alpha + \beta')}$$

where S is the active surface of the electrode $(I_{p+1} = S \cdot i_{p+1})$

If we assume that the active surface S is not altered by illumination, we obtain:

$$\frac{\Delta\eta_{(t=0)} - \Delta\eta_{(t=\infty)}}{[\Delta\eta_{(t=\infty)} - \Delta\eta_{(t=0)}]_e} \simeq \frac{\left| M_0 \right|_S^e}{\left| M_0 \right|_S}$$

TABLE II

State of Surface	S_1^e		S_2^e			S_3^e
I (μA)	103	70	118	86	69	130
$(\Delta \eta_\infty - \Delta \eta_{t=0})^e$ (mV)	0.83	0.63	2.34	1.05	0.72	0.95
$r_e \cdot 10^3$ (s⁻¹)	3.97	3.95	3.98	4.25	4.20	4.8
$r \cdot 10^3$ (s⁻¹)			4.2			5
$(\Delta \eta_{t=0} - \Delta \eta_\infty)$	2.2		2.5			
E	2.6		2.4			

The plots of $\log [\Delta \eta_{(t=\infty)} - \Delta \eta_{(t=0)}$ form a family of straight lines. By extrapolating these straight lines to time $t = 0$ is it found that the above ratio is fairly constant, regardless of the surface condition of the electrodes, and is equal to 2.5.

Furthermore, the exchange current in the absence or in the presence of light is of the following form:

$$I_0 = SzFK_C \left| M^{z+} \right|_{OS} \exp \frac{(-\alpha zF \Delta \phi)}{RT} = Sz FK'_C \left| M_O \right|_S \exp \frac{(\beta' zF \Delta \phi)}{RT}$$

Experiments show that the equilibrium potential is the same under illumination or in darkness. Therefore,

$$\frac{\left| M_O \right|_S^e}{\left| M_O \right|_S} = \frac{\dfrac{K_C^e}{K_C}}{\dfrac{K'_C^e}{K'_C}} = 2.5$$

Furthermore, for the same surface conditions

$$\frac{\left| M_O \right|_S^e}{\left| M_O \right|_S} = \frac{I_0^e}{I_0} \cdot \frac{K'_C}{K'_C^e}$$

From the overpotential curves for equilibrium conditions, we obtain (see Fig. 6):

$$\frac{I_0^e}{I_0} = 2.44 = E$$

Therefore $K'_C/K_C^e \simeq 1$ which means that the lowering of the potential barriers is practically the same. Indeed, if the height of both potential barriers

is decreased by ΔG, the difference ΔG_2^0 is constant and we find from the following equation

$$2.3 \log E = \Delta \left(\frac{\Delta G}{RT}\right) \text{ that}$$

$$\Delta G = 536 \text{ calories}$$

We verify this set of results by similarly studying the return to equilibrium when the illumination is removed.
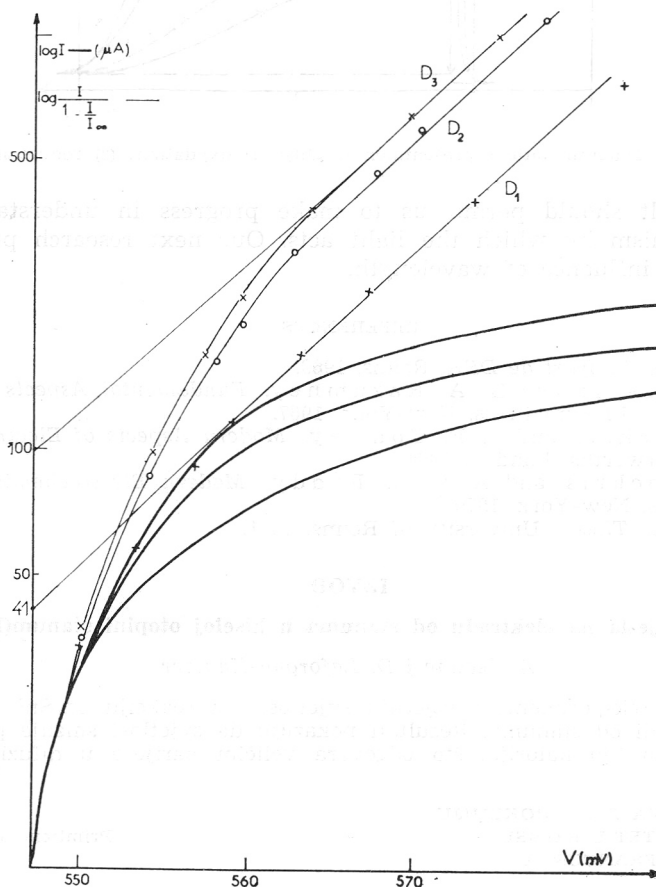

Fig. 6. Cathodic overpotential curves.

This coherent set therefore permits us to assert that, in this system at least, the light lowers both potential barriers by essentially the same amount and does not affect any of the other kinetic parameters (Fig. 7).

This drop in potential barrier has been calculated to be approximately 540 calories, the actual value depending on the light intensity. It is practicaly equal to the barrier drop in the diffusion region.
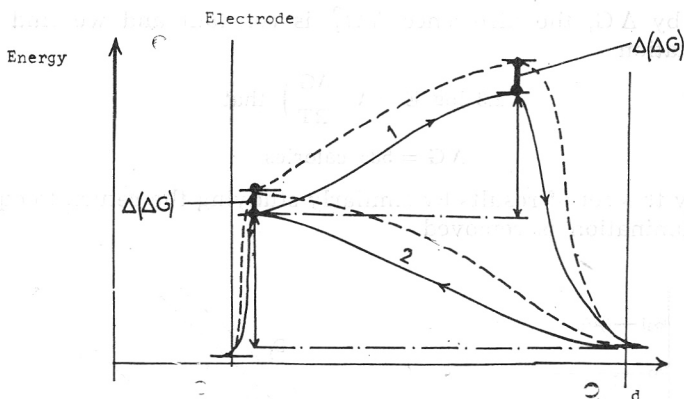
Fig. 7. Diagrammatic representaion (Light): (1) oxydation; (2) reduction.

This result should permit us to make progress in understanding the actual mechanism by which the light acts. Our next research project will deal with the influence of wavelength.

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IZVOD

Utjecaj svijetla na elektrodu od stanuma u kiseloj otopini stanum(II) iona

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Opisani su eksperimenti o utjecaju svjetlosti na reakciju Sn/Sn^{2+} na polikristalinoj elektrodi od stanuma. Rezultati pokazuju da svjetlost snizuje potencijalnu barijeru za oko 540 kalorija, što odgovara veličini barijere u difuzionom sloju elektrode.

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