A. V. GORODYSKII, Academician of the Academy of Sciences of the Ukrainian SSR, Yu. K. DELIMARSKII,

V. F. GRISHCHENKO

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. GORODYSKII, Academician of the Academy of Sciences of the Ukrainian SSR, Yu. K. DELIMARSKII,
V. F. GRISHCHENKO

CATALYTIC WAVES IN MOLTEN ELECTROLYTES

Polaroscopic studies (^{1,2}) of pure molten chlorides of cadmium, tin, and lead on platinum electrodes reveal waves located on the polarization curves before the voltage of salt decomposition is reached (Fig. 1). A similar phenomenon—additional potentials and waves on polarization curves—was observed in pure or concentrated melts of halides by Harrap (^{3}), Delimarskii, Izbekov, and Chovnykov (^{4,5}), and by Kudra and Gitman (^{6}). On numerous polarograms of dilute melts of heavy-metal halides (^{7,8}), small waves can also be observed, beginning at the very start of the polarograms.

To investigate the nature of these waves, we carried out chronopotentiometric measurements. We studied the time variation of the potential of a platinum indicator cathode relative to an unpolarizable reference platinum electrode. As was found (Fig. 2), the transition time of the chronopotentiograms of cadmium, tin, and lead—the time during which the indicator electrode retains the potential of the unpolarizable electrode—does not depend on the magnitude of the current passed through the cell. This indicates that the concentration of the depolarizer at the electrode surface is proportional to the current passed through the cell, i.e., that the observed waves have a catalytic nature. The product of electrolysis, as a result of interaction with the electrolyte, forms new portions of depolarizer.

Fig. 1. Polarization curves of pure molten chlorides of lead, tin, and cadmium on platinum electrodes at temperatures of 540, 280, and 580°, respectively. The waves under consideration are marked by arrows.

The observed mechanism of the electrochemical reaction can be explained in various ways. In our opinion, the most probable in the present case is the discharge of subcompounds. This assumption allows for the existence of at least negligible amounts of subcompounds in the original individual molten salts.

The subcompound MCl is discharged at the electrode after preliminary

Fig. 2. Transition time of pure molten chlorides on a platinum electrode with a surface area of 1.8 mm^2

Figure 2: Fig. 2. Transition time of pure molten chlorides on a platinum electrode with a surface area of 1.8 mm^2

dissociation to the subion M$^{\cdot}$:

$$\mathrm{MCl} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{M}^{\cdot} + \mathrm{Cl}', \tag{1}$$

$$\mathrm{M}^{\cdot} + \mathrm{e} \rightleftarrows \mathrm{M}. \tag{2}$$

After this, new amounts of the subcompound are formed:

$$\mathrm{M} + \mathrm{MCl}_2 \rightleftarrows 2\,\mathrm{MCl}. \tag{3}$$

The concentration $[\mathrm{MCl}](0,t)$ is determined by the rate of reaction (1) and by the diffusion rate [9,10] of the subcompound from the electrode:

$$i = nFk_1[\mathrm{MCl}](0,t) - nFk_2[\mathrm{M}^{\cdot}](0,t)\cdot[\mathrm{Cl}'](0,t), \tag{4}$$

$$[\mathrm{MCl}](0,t) = \mathrm{MCl}(x,0) + \frac{2i\sqrt{t}}{nF\sqrt{\pi D}} \tag{5}$$

(t is the time from the start of electrolysis, x is the distance from the electrode).

Combining (4) and (5) gives

Fig. 2. Transition time of pure molten chlorides on a platinum electrode with a surface area of 1.8 mm^2

$$[\mathrm{MCl}](0,t) = \frac{i + nFk_2[\mathrm{M}^{\cdot}](0,t)[\mathrm{Cl}'](0,t)}{nFk_1} = [\mathrm{MCl}](x,0) + \frac{2i\sqrt{t}}{nF\sqrt{\pi D}}. \tag{6}$$

At $t = \tau$

$$[\mathrm{M}^{\cdot}](0,\tau) = 0. \tag{7,8}$$

Then

$$[\mathrm{MCl}](0,\tau) = \frac{i}{nFk_1} = \mathrm{MCl}(x,0) + \frac{2i\sqrt{\tau}}{nF\sqrt{\pi D}}. \tag{9}$$

The quantity $[\mathrm{MCl}](x,0)$ can be neglected at a sufficiently large current i. Therefore equation (9) becomes

$$[\mathrm{MCl}](0,\tau) = \frac{i}{nFk_1} = \frac{2i\sqrt{\tau}}{nF\sqrt{\pi D}}. \tag{10}$$

Hence

$$\sqrt{\tau} = \frac{\sqrt{\pi D}}{2k_1} \tag{11}$$

(D is the diffusion coefficient of the depolarizer, k_1 is the rate constant of the preceding reaction).

Equations (10), (11) describe the external aspect of the observed phenomena quite well.

Institute of General and Inorganic Chemistry
Academy of Sciences of the Ukrainian SSR

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