MEASUREMENT OF THE HEAT OF IRREVERSIBLE ELECTRODE PROCESSES

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If a process is reversible, a periodic current $j = \Delta j \cos \omega t$ with a frequency $\omega/2\pi$ generates mechanical oscillations of the electrode for an unlimited time (t); the amplitude of the oscillations is proportional to the heat W evolved during this process [1]. Superimposition of a direct current on an alternating current, so that the total current flows in only one direction, $j = j_0 + \Delta j \cos \omega t$ $(\Delta j \le j_0)$, permits such measurements for an irreversible process as well. The reagent concentration near the electrode c (or the superficial adsorbate density) decreases to zero over the transition period. At $\Delta j = 1$ mA/cm^2 and an initial c = 0.1 M, τ is of the order of a second. A frequency of 10^3-10^4 Hz is then sufficient for measurement of W at the instant when the current is switched on and for recording of the W−t curve. The cathodic and anodic W−t curves recorded by this method at an activated platinum or gold electrode in 0.2 M $K_3Fe(CN)_6$ + 0.2 M $K_4Fe(CN)_6$ solution originate (W_c, W_a) at the same level, $W_0 = 0.4$ V, as when no direct current is applied, $W_c = W_a = W_0$. As t increases, the cathodic curve rises and the anodic curve falls, the deviation from W_0 reaching 20% at the end of the transitionperiod. In the cathodic curve, W then increases abruptly to $W \approx 2W_0$, which is the heat at which water discharges and releases hydrogen (an irreversible process).

The initial W on application of direct current differs from W_0 at inactivated platinum (and at other metals under definite conditions): $W_0 - W_a \approx W_c - W_0$. As was shown by experiments with different c and ω the difference among W_c, W_a, and W_0 results from the fact that the exchange current is small and the overvoltages $\Delta\eta$ and $\Delta\eta_0$ corresponding to the currents Δj and j_0 are large under the conditions in question. This is responsibe for the appearance of a substantial alternating superficial-voltage component in the overall signal (because of $\Delta\eta$), its variation when the current j_0 is applied, and the change in its sign (because of η_0). Solvent discharge occurs earlier at the same j_0 when the exchange current decreases.

LITERATURE CITED

1. A. Ya. Gokhshtein, Dokl. Akad. Nauk SSSR, 183, 859 (1968); Élektrokhimiya, 5, 637 (1969); 6, 979 (1970).

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