

A METHOD OF MEASURING THE ELECTROCHEMICAL ADSORPTION AND REACTION HEATS

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If through the interface of a solid electrode and an electrolyte an alternating current $j = j_0 + \Delta j \sin \omega t$ is transmitted the electrode will then vibrate mechanically at the same frequency ω , owing to its periodic thermal expansion. With $j_0 = 0$ (adsorption, reversible reactions), the Joulean heating ($\sim j^2$) of the solution is completely ineffective: its frequency is equal to 2ω . Its influence is insignificant also in other cases since the thermal conductivities of electrode and solution differ by two orders of magnitude. In the charging of a double layer the oscillation effects of the surface tension (γ) with an amplitude of 0.5 V about the zero point and the heat oscillations (ϑ) are comparable only at 10 kcal/Farad; therefore, in many cases, ϑ does not influence measurements of γ [1]. When ϑ is to be measured, the effect of γ is (a) eliminated by increasing the concentration of the reacting substances so that the potential amplitude is reduced leaving Δj unchanged (additional means: etching of the electrode) or (b) separated by using electrodes in the form of plates of different thicknesses (thus making use of the fact that heat penetrates rapidly into the depth of plates) and also by measuring at the zeros of the amplitude of γ . Formulas [2] yield e.g. for Pt at 1 kc the following values of the phase shifts α (between the effects γ and ϑ for equal phases j): $\alpha = 0.43 \pi$ with a thickness of 0.1 mm, and $\alpha = 0.07 \pi$ with 0.5 mm. An electrode in the form of a 10μ Pt foil welded on a glass plate guarantees a natural calibration of the device: the vibrations of the electrode are recorded first in the process considered (γ or ϑ , Δj being of the order of 10^{-2} A/cm²), and then when heating by alternating current has set in due to (frequency $\omega/2$) only passing briefly through the foil. At 20°C and 1 kc the electrochemical reaction heats are measured on the Pt electrode for the systems $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and I_3^-/I^- , and also heat of the adsorption of hydrogen ions on Pt, from sulfuric acid, at various potentials ranging from +0.25 to 0 V (sat. hydr. electr.).

LITERATURE CITED

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2. A. Ya. Gokhshtein, *Dokl. Akad. Nauk SSSR*, **174**, 394 (1967); *Fiz. i Tekh. Poluprv.*, **1**, 1486 (1967).