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BEHAVIOUR OF THE IRON ELECTRODE IN ALKALINE SOLUTIONS AT LOW TEMPERATURES

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In studies of the behaviour of the alkaline accumulator^{1,2} it has been noted that the steady-state potential of the iron electrode shifts towards negative values after preliminary cathodic polarisation (partial charging) at low temperatures. This effect was attributed to the presence of surface oxides on the electrode, which would greatly increase the hydrogen overvoltage¹, or to the formation on the electrode surface of an iron-potassium alloy or iron hydride². In view of the contradictory views on this question, we undertook a study of the behaviour of the iron electrode in 5 N KOH in the temperature range between 20° and -20°. The hydrogen overvoltage was measured using a hydrogen electrode in the same solution of alkali and at the same temperature as the test electrode. In studies of the reduction of iron oxides and the anodic dissolution of iron the potentials were measured relative to the steady-state potential of an iron powder electrode in the same solution and at the same temperature. The steady-state potential differed little from the equilibrium potential for the process $\text{Fe} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2$. We assumed

that the steady-state potential remains close to the equilibrium value also when the temperature is altered.

The test electrode consisted of a plate of "Armco" iron on the surface of which a fresh layer of iron was electrodeposited at a current of 0.1 A cm⁻² over a period of 10 min from a bath containing 50 g litre⁻¹ FeSO₄·7H₂O, 50 g litre⁻¹ (NH₄)₂SO₄, and 7.5 g litre⁻¹ of citric acid, giving a uniform, finely crystalline, bright coating. First the cathodic and then the anodic polarisation curve was obtained for this electrode. At large current densities the cathodic curve was recorded rapidly, since the overvoltage of the process increased with time. It is seen from Fig. 1 that the hydrogen overvoltage increases as the temperature is reduced, $(\partial\eta/\partial T)_i = -2$ mV deg⁻¹.

The real activation energy was calculated by the Arrhenius equation from the polarisation curves for the cathodic reaction using the average slopes of $\log i - 1/T$ plots for $\eta = \text{const}$ (Fig. 3). At $\eta = 0.175$ V the real activation energy A in 5 N KOH proved to be 7100 cal mole⁻¹, whereas at $\eta = 0$ the activation energy was $A_0 = 9100$ cal mole⁻¹.

Fig. 1 also shows $\eta - \log i$ curves for the anodic polarisation of iron, from which it is seen that the overvoltage of the process falls as the temperature is reduced contrary to the normal temperature variation of overvoltage. This result is due to the preliminary cathodic polarisation and the short period during which the electrode is maintained without the current flowing after the cathodic curves are recorded. This effect and the charging, $\text{Fe}(\text{OH})_2 + 2e^- \rightarrow \text{Fe} + 2\text{OH}^-$, and discharging, $\text{Fe} + 2\text{OH}^- - 2e^- \rightarrow \text{Fe}(\text{OH})_2$, processes were studied on an iron powder electrode, which was made from pentacarbonyl iron by the method of Platonova and Levina³ and consisted of Fe₃O₄ with added sulphur (0.1% FeS) and nickel (0.3% NiSO₄) compounds which are activators of the above processes^{4,5}. The electrodes were "formed" by passing a current of 0.1 A per gramme of powder. After "forming" the powder electrode had a capacity (for technological purposes) between 0.25 and 0.3 Ah g⁻¹.

The anodic polarisation curves recorded immediately after partial charging without the electrode being first maintained at a steady-state potential, showed, as in the case of the smooth electrode, a positive $(\partial\eta/\partial T)_i$ coefficient. The

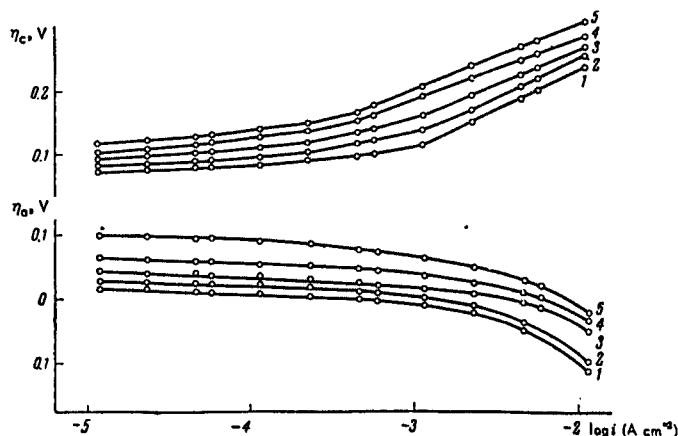


Fig. 1. Cathodic and anodic polarisation curves for a smooth iron electrode with a coating of electrodeposited iron in 5 N KOH at various temperatures (°C): 1) 20; 2) 10; 3) 0; 4) -10; 5) -20.

overtoltage began to vary with temperature in the normal manner only after part of the "technological" capacity had been discharged and a steady-state potential attained. In order to set up identical conditions for the investigation of the charging and discharging processes in the iron electrode, the cathodic and anodic polarisation curves were obtained in the region of the second third of the "technological" capacity of the electrode, *i.e.* after the electrode had been discharged to the extent of one third of its initial capacity. The anodic polarisation curve was recorded first. Then, after the electrode had been completely discharged and recharged to the extent of one third of its capacity, a steady-state potential was established and the cathodic polarisation curve recorded (Fig. 2). The plots of $\log i$ against $1/T$ for $\eta = \text{const}$ (Fig. 3) were constructed on the basis of the η - $\log i$ curves and the activation energies, whose values are listed in the Table, calculated.

As noted in the literature^{1,2}, after partial charging at low temperatures the steady-state potential of the electrode shifts towards more negative values. In our experiments after partial charging at -20° the steady-state potential was 76 mV more negative than the potential of the electrode which had not been charged. However, this difference rapidly disappeared on anodic polarisation at low current densities after a discharge equivalent to a decrease of the capacity as small as 0.005 Ah g^{-1} . An additional arrest of the potential associated with the decomposition of surface compounds was not observed.

The more negative steady-state potentials of the iron electrode after partial charging at low temperatures is clearly related to the higher surface concentration of hydrogen on the metal, which increases as the temperature falls. It has been shown⁶ that, with increase in the pressure of hydrogen over the iron electrode and hence with increase of the concentration of hydrogen on the electrode surface, the steady-state potential shifts towards negative values. This

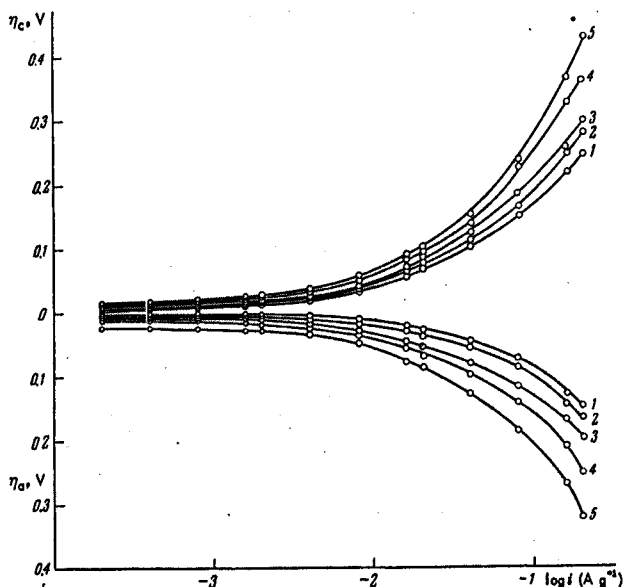


Fig. 2. Cathodic and anodic polarisation curves for an iron powder electrode in 5 N KOH at various temperatures ($^\circ\text{C}$): 1) 20; 2) 10; 3) 0; 4) -10; 5) -20.

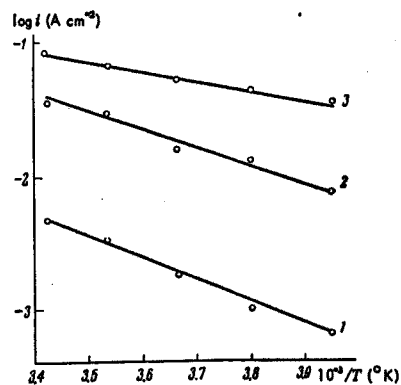


Fig. 3. Variation of the logarithm of the rate of the process with the reciprocal of temperature: 1) evolution of hydrogen (smooth electrode); 2) anodic dissolution of iron (powder electrode); 3) reduction of ferrous hydroxide (powder electrode). [The assignment of the legend to the curves is not clear in the Russian original: it has been made here with reference to the Table (Ed. of Translation).]

TABLE.

Process	η , V	A , cal $\times$ mole^{-1}	A_0 , cal $\times$ mole^{-1}
$\text{Fe}(\text{OH})_2 + 2e \rightarrow \text{Fe} + 2\text{OH}^-$	0.150	2750	6200
$\text{Fe} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2 + 2e$	0.050	6150	7300

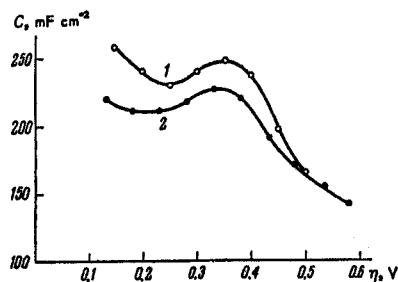


Fig. 4. Differential capacitance curves for a smooth iron electrode in 5 N KOH: 1) 19.2° ; 2) -21.5° .

finding is confirmed by our data on the differential capacitance at 19° and -21.5° of a smooth electrode made from pure zone-refined iron (Fig. 4).

The differential capacitance was measured at a frequency of 800 c/s with an impedance bridge based on a circuit with series-connected resistance and capacitance. The results were then recalculated for a parallel capacitance-resistance circuit⁷. On decrease in temperature, the differential capacitance falls somewhat but the overall

shape of the $C-\eta$ curves remains unchanged. If a chemical compound formed and were decomposed on the surface of the metal at low temperatures, corresponding changes in the capacitance curves would be expected (the presence of peaks, change in the shape of the curve). The small fall in capacitance is probably related to the fact that at low temperatures the relative surface concentration of the electrochemically active atomic hydrogen diminishes, although the overall adsorption of hydrogen increases.

SUMMARY

1. Steady-state polarisation curves have been obtained for the anodic oxidation (activation) of an iron powder electrode and the cathodic reduction of iron oxides in 5 N KOH at temperatures between 20° and -20°.
2. The real activation energy was calculated: for the first process, $A = 7300 \text{ cal mole}^{-1}$ and for the second $A = 6200 \text{ cal mole}^{-1}$.
3. Partial charging of the electrode at -20° results in a displacement of the steady-state potential by 76 mV towards negative values. This effect vanishes after brief anodic polarisation (involving the removal of less than 0.005 Ah g^{-1} of the "technological" capacity).
4. The hydrogen overvoltage of a smooth electrolytically iron-plated electrode in 5 N KOH increases at a rate of 2 mV deg^{-1} as the temperature is reduced. The activation energy $A = 9100 \text{ cal mole}^{-1}$.

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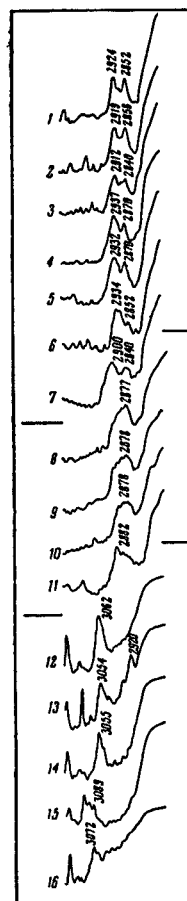
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A CHARACTERISTIC FEATURE OF THE RAMAN SPECTRA OF CERTAIN HYDROCARBONS

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Our studies of the Raman spectra of organic compounds have shown that hydrocarbons can be rapidly and reliably classified according to the stretching frequencies of their C-H groups†. High resolution and extensive processing



Photomicrograms of the C-H bands in the Raman spectra of hydrocarbons:

- 1) cyclohexane; 2) methylcyclohexane; 3) methylcyclohexanol; 4) cyclopentane; 5) methylcyclopentane; 6) piperidine; 7) tetrahydrofuran; 8) n-hexane; 9) n-heptane; 10) n-octane; 11) iso-octane; 12) benzene; 13) toluene; 14) pyridine; 15) furan; 16) thiophen. The positions of the maxima are indicated in cm^{-1} .

† Considerable difficulties are encountered in infrared absorption spectroscopy in the region of 3 μm .