APPLICABILITY OF STEEL FOR CREATION OF A “SULFIDE AND STEEL” HALF-CELL

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Abstract: An attempt is made in the published article to use a hypothetical “sulfide and steel half-cell” for the rapid determination of the concentration of hydrated sulfide-ion. The potential of such an half-cell was defined as an electromotive force of galvanic cell (EMF or voltage, V) in combination with a silver chloride half-cell (comparisons). A linear relationship was obtained between the sulfide content and the EMF of the above element. Some results on the selectivity of the half-cell under consideration were presented. The temperature dependence of the potential expressed through EMF of the latter is obtained.

Keywords: half-cell; half-cell potential; galvanic cell, sulfide-ion, steel, iodimetric method

Introduction

Ionometry is currently a fairly wide area of science and technology, and plays an important role in analytical chemistry. In particular, to measure the concentration of $S^{2-}$, the “sulfide and steel” half-cells being the most universal and historically the first half-cells with solid membranes for this purpose. Also, sulfide-based half-cells of some doubly charged metal ions are used, the sensitive part of which (membrane) is obtained from mixtures of $[Ag_2S + S^{2-}]$ of the corresponding metal. The most important for practice are copper, lead and cadmium half-cells. In the framework of this article, the author makes an attempt to expand the list of half-cells based on sulfides of doubly charged metal ions by constructing an $S^{2-}$-selective half-cell based on a sample of a common steel st3s (Poland-grade), which contains an average of 97 % iron, without the use of valuable metals. The chemical composition of the steel I used was not specified, since the intermediate goal of this material is to show the suitability for electrochemical measurements not only of a specific steel sample, but also of any steel sample taken arbitrarily.

Methods of experiment

For this experiment, a sample of steel of structural carbon steel of ordinary quality St3 was used.

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A hypothetical “sulfide and steel” half-cell was prepared on a steel plate (with a previously soldered electric wire) with a total surface area of 19 cm² by soaking in “hydrogen sulfide water”, as a result of which the sulfide film was 1.2 μm of thick at the time of experiment. The galvanic cell was designed according to the scheme St₃S(Fe), FeₓSᵧ | S²⁻ test solution || KCl | AgCl, Ag at 25 °C. The half-cell St₃S(Fe), FeₓSᵧ | S²⁻ test solution implies the potential stability over time and its dependence of temperature.

S²⁻ content was evaluated and monitored by the iodimetric method of analyzing. I used this modification of the method: 1.0 ml of S²⁻ containing aqueous solution was taken, 9.0 ml of distilled water was added, and mixed. Determination of the H₂S concentration is performed by titrating 0.05 N I₂ (by using microburettes per 1 ... 2 ml) 10.0 ml of the obtained analyte very pale yellow in color (of 0.05 N I₂). It is V₁. In parallel, titration of 10.0 ml of distilled water is carried out. It is V₀. The calculation is carried out according to the formula \[ C_{S²⁻} = \frac{8000 (V₁ - V₀)}{[mg/L]} \].

Electromotive force (EMF) St₃S(Fe), FeₓSᵧ | S²⁻ test solution || KCI | AgCl, Ag was measured using the LIUMY LM3001.

To determine the temperature dependence of the potential of the “sulfide and steel” half-cell, the latter was designed in a heat-resistant flask to ensure tightness of both the half-cell metal and the test solution in order to avoid concentration of the solution due to evaporation or volatilization of hydrogen sulfide due to hydrolysis of sulfide. In a similar design, the St₃S(Fe), FeₓSᵧ | S²⁻ test solution will have a uniform set temperature, the silver chloride half-cell has the same temperature of 25 °C.

Results and discussion

Based on the obtained results, a graph of the dependence of the element “EMF - S²⁻ test solution concentration” was created (Fig. 1):

![Fig. 1. Illustration of the selectivity of the "sulfide and steel" half-cell (at 25 °C)](https://ssrn.com/abstract=3445013)

Obviously, there is a linear relationship between the S²⁻ -content and the EMF of the above element, expressed as a trend-line. Slight deviations from linearity can be explained by jumps in electrical conductivity, since steel has conductivity, of course, worse than that of silver and platinum (which are usually used for the production of half-cells). The temperature dependence of the half-cell potential of St₃S(Fe), FeₓSᵧ | S²⁻ test solution (expressed through the EMF) (Fig. 2):

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1 KCl | AgCl, Ag is silver-chlorine half-cell
Fig. 2. Illustration of the dependence of the potential of the "sulfide and steel" half-cell in the temperature range, expressed as the EMF

Obviously, when heated to 10 °C, for example, from 23 °C to 33 °C (with a fixed value of \(S^{2-}\) concentration equal to 52.2 mg/L), the EMF changes by about 0.040 V.

**Conclusion:**

As an express method, an half-cell \(\text{St}3s(\text{Fe}), \text{Fe}_x\text{S}_y|S^{2-}\text{test solution}\) is suitable for the estimated determination of the \(S^{2-}\)-concentration. As for all half-cells of the 2nd kind, its drying should be avoided, which is generally accepted. Contact with organic substances should also be avoided, and older publications the adsorption of molecules of organic substances on the surface of steel 3 and, in connection with this, a change in the value of the half-cell potential was proved. For example, when already adding 0.0078 g of EDTA, calculated per 20 mL of the test sulfide-containing solution (1 mM solution with respect to the EDTA - complexone), over time the EMF changed as follows as the adsorption of complexone molecules on the steel surface, which indicates the instability of the potential of the “sulfide and steel” half-cell in the presence of an organic compound having several adsorption centers in the composition of its molecule (Fig. 3):

Fig. 3. Illustration of the time stability of the potential of "sulfide and steel" half-cell, expressed as the EMF over time
This situation arises despite the fact that the $S^2$ concentration in varied both upward and downward.

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