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Kinetic Relationships of the Formation of Antimony Sulfide

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Abstract — The kinetics of deposition of antimony sulfide from solutions of sodium thiosulfate was studied. The reaction orders with respect to the components and the activation energy of the process were determined.
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As shown in [1], sodium thiosulfate undergoes hydrolysis [reaction (1)]:

$$S_2O_3^{2-} + H_2O = S^{2-} + SO_4^{2-} + 2H^+. \quad (1)$$

This reaction can be used for deposition of metal sulfides.

Along with reaction (1), thiosulfate can decompose in acid solutions with the formation of sulfur and sulfite ion [2]:

$$S_2O_3^{2-} = S + SO_3^{2-}. \quad (2)$$

Sulfite ion, being a residue of a weak acid, binds hydrogen ions into a weakly dissociated species HSO_3^-, which can serve as pH regulator. In this study we examined the kinetics of chemical deposition of antimony sulfide using sodium thiosulfate as a sulfidizer [3] and as a pH regulator in acid solutions.

On combining solutions of antimony trichloride and sodium thiosulfate, a transparent solution is formed; it gradually becomes turbid owing to formation of an orange-red precipitate in the bulk of the solution and of a thin orange-red film on a glass support. An X-ray diffraction analysis showed that both the precipitate and the film consist of orthorhombic antimony sulfide Sb_2S_3. The diffraction pattern of the antimony sulfide film contains only a (212) reflection (Fig. 1); apparently, the film consists of very fine particles and is essentially X-ray amorphous.

A typical kinetic curve of the accumulation of the solid phase (Fig. 2) is *S*-shaped. The rate of the heterogeneous reaction depends on the temperature, surface area of the solid phase *S*, and concentrations of the reactants raised to the power equal to the reaction order with respect to the corresponding reactant [4, 5].

The goal of this study was to determine the form of the rate equation. As the surface area of the solid phase varied in the course of the process, which could not be taken into account, we examined the reaction kinetics under the conditions of controllable surface area provided by glass powder (particle size 100 μm) preliminarily coated with a layer of antimony sulfide.

The total *controllable* surface area *S* onto which antimony sulfide was deposited was determined by multiplying the weight of the glass powder portion (m) by the surface area of 1 g of the powder (S_0), i.e., $S = mS_0$. Assuming the glass density equal to 2.7 g cm^{-3}, we obtained for spherical particles 100 μm in diameter the specific surface area S_0 equal to 222 cm^3 g^{-1}. Experiments were performed with continuous stirring to keep the powder particles in the suspended state. In preliminary experiments we found what portion of the glass powder was sufficient to ful-

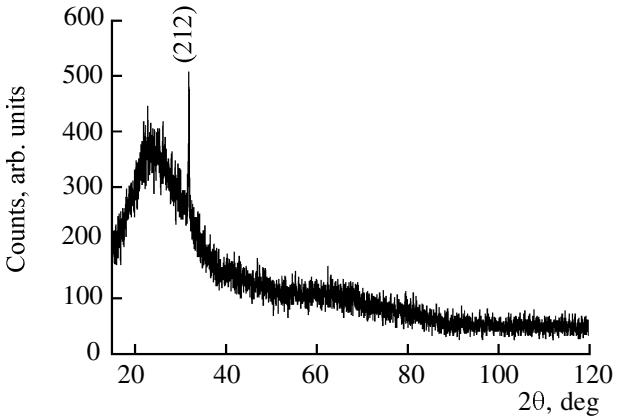

Fig. 1. X-ray diffraction pattern (Cu$K_{\alpha_{1,2}}$) of an antimony sulfide film. The Sb_2S_3 film has an orthorhombic structure and is essentially X-ray amorphous.

ly suppress the solid phase nucleation in the bulk of the reaction mixture: 15 g per 100 ml of the reaction mixture. We found that the process rate was directly proportional to the surface area of the solid phase. The kinetic curve obtained under the conditions of the controlled surface area of the solid phase in the reaction mixture is shown in Fig. 3; it is seen that the system comes to equilibrium. Treatment of the experimental data by standard methods [6] showed that the kinetic curves are well described by an equation of a reversible first-order reaction with respect to antimony concentration:

$$dx/d\tau - kS(x_\infty - x) = k_{exp}(x_\infty - x), \quad (3)$$

where x_∞ is the amount of the antimony salt converted to the solid phase on reaching the equilibrium; x, amount of the antimony salt converted to the solid phase by the time τ from the reaction start; and k_{exp}, experimental rate constant. Its dependences on the temperature, surface area of the solid phase, sodium thiosulfate concentration, and pH allow determination of all the parameters of the rate equation.

Integration of Eq. (3) brings it to the form convenient for graphic determination of the rate constant k:

$$\log(x_\infty - x) = (kS/2.3)\tau + \log x_\infty. \quad (4)$$

The experimental data processed with Eq. (4) are satisfactorily fitted by a straight line (Fig. 4), which indicates that the reaction is first-order with respect to the antimony salt.

To determine the reaction orders with respect to sodium thiosulfate and hydrogen ions, we made a series of experiments in which the sodium thiosulfate concentration was constant and pH was varied by adding HCl. In another series of experiments, vice versa, the pH was constant and the initial concentration of sodium thiosulfate was varied. The experimental data were processed with Eq. (5):

$$\log k_{exp} = A + n_i \log C_i, \quad (5)$$

where k_{exp} are the experimental constants of Eq. (3) calculated from the slopes of the straight lines in the corresponding experimental series.

Graphic determination of the kinetic orders with respect to hydrogen ions, $r_{H^+} = 0.0$, and to sodium thiosulfate, $r_{Na_2S_2O_3} = -2.0$, is illustrated by Figs. 5 and 6.

The reaction rate constant k' related to the unit surface area of the solid phase and unit concentration of each component is 1.02×10^{-3} mol^2 l^{-2} min^{-1} cm^{-2}

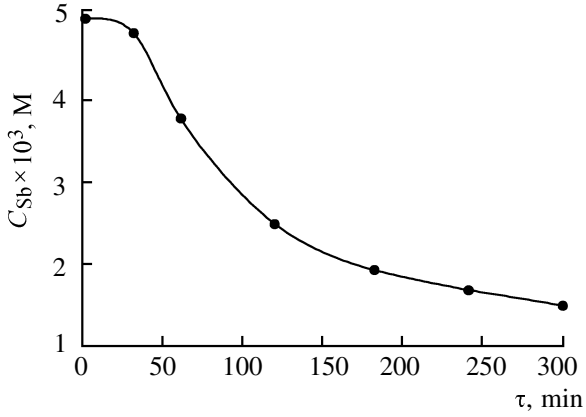

Fig. 2. Kinetic curve of the accumulation of the solid phase at 30°C, pH 2.1, $C_{Na_2S_2O_3}$ 1.5×10^{-2} M.

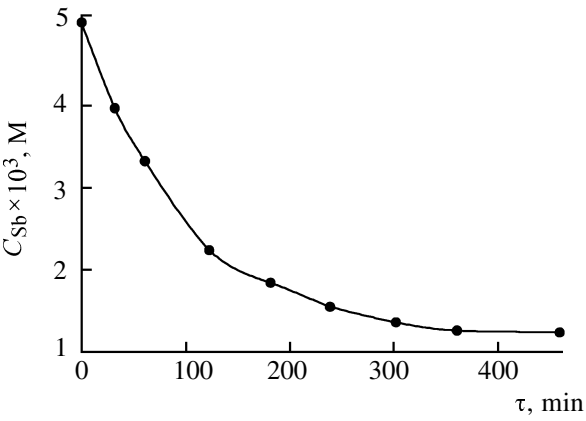

Fig. 3. Kinetic curve recorded under the conditions of controllable surface area (S 10^4 cm^2) at 30°C, pH 2.1, $C_{Na_2S_2O_3}$ 1.5×10^{-2} M.

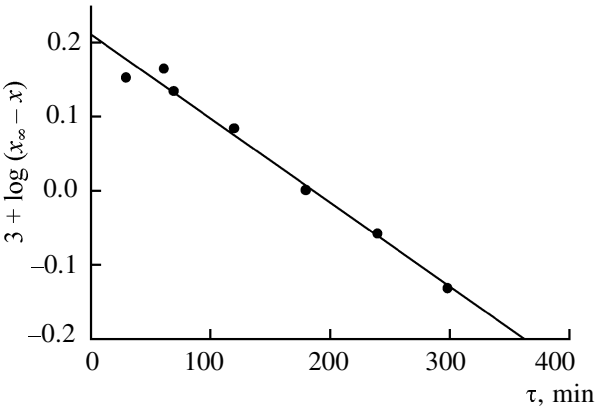

Fig. 4. Graphic solution of Eq. (3) for the kinetic curve shown in Fig. 2.

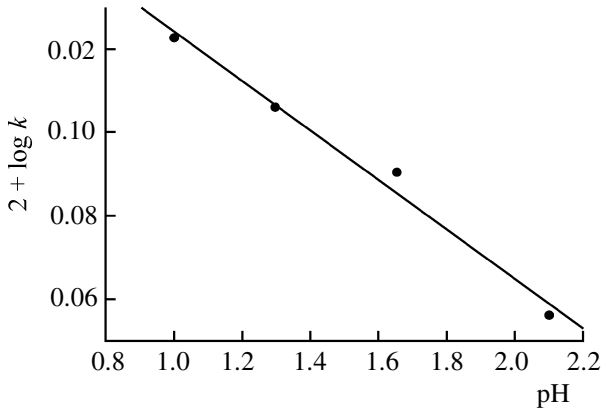

Fig. 5. Determination of the kinetic order of the reaction with respect to hydrogen ions at S 10^4 cm^2, T 30°C, and $C_{Na_2S_2O_3}$ 1.5×10^{-2} M.

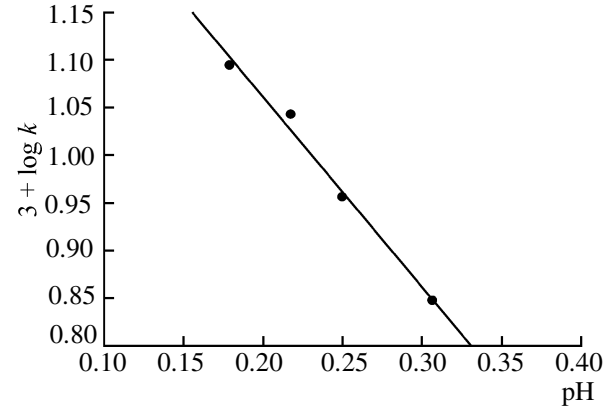

Fig. 6. Determination of the kinetic order of the reaction with respect to sodium thiosulfate at S 10^4 cm^2, T 30°C.

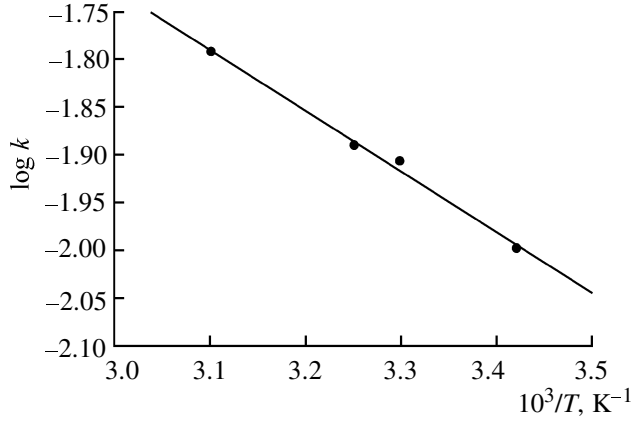

Fig. 7. Graphic determination of the activation energy of the process from the Arrhenius plot.

at 303 K. The reaction kinetics were studied in the temperature range 20–50°C. The activation energy calculated by the Arrhenius equation $\log k' = \log k_0 - E/(2.3RT)$ is 12.6 kJ mol^{-1}, and the preexponential factor, 2.5×10^{-3} mol^2 l^{-2} s^{-1} cm^{-2} (Fig. 7). Thus, the rate equation can be given in the following form:

$$dC_{SbCl_3}/d\tau = 2.5 \times 10^{-3}\exp(-12\,600/8.314T)SC^{-2}_{Na_2S_2O_3}C_{SbCl_3}. \quad (6)$$

EXPERIMENTAL

Samples of antimony sulfide were prepared by chemical deposition from aqueous solutions. The chemical method for preparing metal sulfides in the form of powders and films on the surface of an inert solid support (e.g., glass plates or glass powder) consists in performing the reaction between a soluble metal salt and a sulfidizing agent in aqueous solutions. As sulfidizing agent we chose sodium thiosulfate. Chemical deposition of antimony sulfide was performed in the system $SbCl_3$–$Na_2S_2O_3$–HCl–H_2O.

The kinetics of the accumulation of the solid phase were monitored by taking samples and titrating them with $KBrO_3$ according to [7].

When solutions of antimony trichloride and sodium thiosulfate are combined, a complex compound $Na_2[Sb(S_2O_3)_3]$ interrfering with the antimony determination is formed. To decompose this compound, we added concentrated HCl to the sample, boiled the solution to induce sulfur precipitation, filtered the sample through a dense filter, and titrated the filtrate with a $KBrO_3$ solution in the presence of Methyl Orange. The pH was monitored with a P-340 device.

For primary structural certification of the antimony sulfide samples, we recorded their X-ray diffraction patterns with a DRON-UM-1 diffractometer (Cu$K_{\alpha 1,2}$ radiation) in the 2θ range from 15° to 120° with the step Δ2θ 0.03°.

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