

KINETICS OF AMALGAM DECOMPOSITION IN A HORIZONTAL DECOMPOSER*

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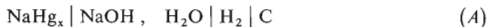
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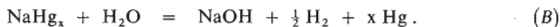
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The decomposition rate of sodium amalgam in a horizontal flow-through decomposer was measured at various temperatures (70–90°C), concentrations of the amalgam (0.01–0.6 wt. % Na) and soda lye (10–41 wt. % NaOH), and at various rates of flow of the amalgam (12–43 cm³/cm s). From the comparison of experimental and theoretical values it follows that the decomposition reaction is at low amalgam concentrations controlled by the transport of sodium from the bulk of the amalgam to the amalgam-electrolyte interface; at higher amalgam concentrations the evolution of hydrogen on graphite and passage of current through the electrolyte played an important role. The decomposition rate was proportional to the rate of amalgam flow raised to a power of 0.5–0.8. The dependence of the decomposition rate on the concentration of NaOH showed a flat maximum at about 20 wt. % NaOH. The Arrhenius activation energy of the decomposition did not exceed the value of 4 kcal/mol.

An amalgam decomposer used in the industrial production of chlorine and soda lye operates as a short-circuited galvanic element



with an amalgam anode and a graphite cathode. The electric current passing through this cell is proportional to the rate of the decomposition reaction



The local current densities, the total cell current and hence also the rate of the amalgam decomposition are determined by the electromotive force of the cell, the anodic and cathodic overvoltage, the specific resistance of the hydrogen-electrolyte emulsion between the electrodes, the contact resistance between the amalgam and the graphite, as well as by the geometry of the cell.

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The electromotive force of the amalgam-hydrogen cell and the hydrogen overvoltage on graphite in sodium hydroxide solutions were discussed in our earlier work^{1,2}. We derived³ under simplifying assumptions also theoretical relations for the dependence of the decomposition rate on technically important parameters. The kinetics of the amalgam decomposition in a short-circuited amalgam-hydrogen cell with a graphite cathode has been studied experimentally by many authors⁴⁻¹⁰. In the usual experimental arrangement, the graphite cathode was dipped in a solution of sodium hydroxide and connected with the amalgam by an outer current lead⁴⁻⁹. The decomposition rate was proportional to the measured current in the short circuit. Burian and coworkers¹⁰ determined the decomposition rate by measuring the rate of hydrogen evolution in the reaction (B).

The measurements were in the cited works carried out with a stationary (not flowing) amalgam and the geometry of the decomposition cell was in some cases different from that in horizontal decomposers.

Our aim was to obtain kinetic data for the reaction (B) under the conditions corresponding to the industrial decomposition process. We therefore used a flow-through horizontal decomposer in which the arrangement of the electrodes and the hydrodynamics of the reacting liquids were such as in an industrial decomposer and which enabled long-term measurements in a stationary state. The obtained data were correlated with our theoretical equations³.

EXPERIMENTAL

Apparatus. The individual parts of the measuring apparatus (Fig. 1) were assembled into two circuits for circulation of the amalgam and the soda lye. The circulation of the amalgam was

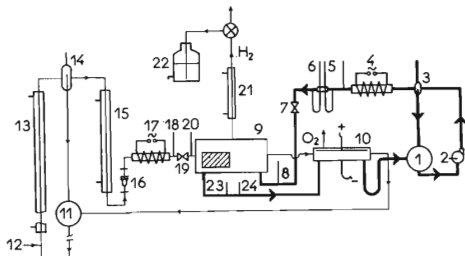


FIG. 1

Scheme of Apparatus for Measurement of Decomposition Rates

1 Amalgam reservoir, 2 screw pump for amalgam, 3, 14 overflow vessels, 4, 17 resistance heating, 5, 18 contact thermometers, 6 amalgam flow meter, 7, 19 clamps, 8, 20 thermometers, 9 decomposer, 10 electrolyser, 11 soda lye reservoir, 12 hydrogen lift pump for soda lye, 13, 15 heating mantles, 16 rotameter, 21 hydrogen cooler, 22 Mariotte bottle, 23 electric lead for potential measurement, 24 soda lye bridge to Hg/HgO reference electrode.

achieved by a screw pump 2 made of teflon and organic glass. The amalgam was expelled from reservoir 1 into overflow vessel 3, passed through heating 4 and contact thermometer 5 to a capillary flow meter 6 and over thermometer 8 into decomposer 9. The rate of flow was regulated by clamp 7.

The decomposer of the filter press type (Fig. 2) was made of organic glass. The frame, *a*, was joined by screws with two thick plates, *b*, into which a plate, *c*, of the Elektrokohle Lichtenberg graphite (GDR) of dimensions $100 \times 90 \times 6$ mm was cemented in such a way that the graphite surface and the surface of the organic glass formed a single plane. Platinum wires, *d*, were introduced into the graphite to enable measurement of the voltage drop on the contact resistance between the amalgam and the graphite. A silicon rubber gasket, *e*, was between the supporting plates and the frame; the plate distance, 5 mm, was delimited by distance strips $f_1 - f_4$. The plates and the frame formed a rectangular channel of width 0.5 cm, height 7 cm and length 40 cm whose portion of length 10 cm had side walls of graphite. This portion of the channel was a 1 : 1 model of an industrial decomposer channel of a common construction.

The amalgam entering the decomposer passed first through a 25 cm long stabilizing section, came between the graphite plates where the decomposition took place, and went to the outlet. The distance strips f_1 and f_2 were shaped so that they enabled an undisturbed flow of the amalgam along the graphite and at the same time the contact resistance between the amalgam and the graphite was kept low. The rate of the amalgam decomposition was determined from the rate of hydrogen evolution. The hydrogen was led through cooler 21 into Mariotte bottle 22.

The amalgam flowed from the decomposer over sensing device 23, 24 (for potentiometric measurement of the sodium concentration) into a glass electrolyser 10. There the amalgam served as a cathode, and oxygen was evolved on the platinum counter-electrodes. The electric current was controlled so as to compensate the decomposition of the amalgam in the decomposer. The net result of the reactions both in the decomposer and electrolyser was the decomposition of water to hydrogen and oxygen. With respect to a considerable holding capacity of the apparatus (5 dm^3), the changes in the soda lye concentration were very slow.

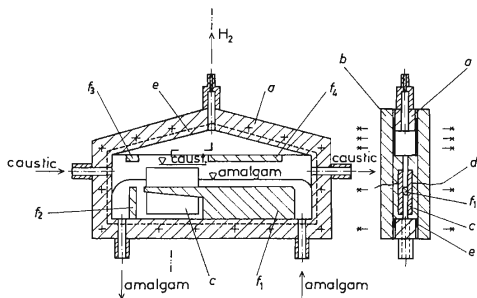


FIG. 2

Scheme of Amalgam Decomposer

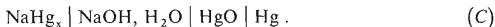
a Frame, *b* side plate, *c* graphite plate, *d* platinum lead for potential measurement, *e* silicon rubber gasket, $f_1 - f_4$ distance strips.

The circulation of the soda lye was maintained by a hydrogen lift pump 12 fed with electrolytic hydrogen purified with a saturated solution of KMnO_4 and with a 40% solution of NaOH . From the reservoir 11 the solution was pumped through heat exchanger 13 into overflow vessel 14, flowed through another heat exchanger 15, rotameter 16, supplementary heating 17, contact thermometer 18, clamp 19 (regulation of the rate of flow), and thermometer 20. The soda lye then passed through the decomposer (in a counter-current with respect to the amalgam) and through the electrolyser into the reservoir.

The rate of flow of the soda lye was adjusted to $6-8 \text{ cm}^3/\text{s}$. As long as the decomposer operated as a differential reactor, the decomposition rate was not influenced by the rate of flow of the soda lye. The character of the soda lye flow in the decomposer was in a decisive manner influenced by the amalgam flow and stirring of the solution by the evolved hydrogen.

Prior to filling, the apparatus was 3-4 times washed by circulating 10% NaOH at 70°C for 1 hour. The apparatus was then filled with 1 dm^3 of pure mercury and 5 dm^3 of the soda lye of a chosen concentration. The rates of flow of both liquids were adjusted and the amalgam was generated electrolytically. A steady rate of the decomposition (measured with the aid of a Mariotte bottle) was attained after 1-2 h of measurement. Samples of the amalgam and the soda lye were taken near to decomposer inlets. The decomposition rate (A/cm) is referred to a unit length of the amalgam-graphite-soda lye three-phase boundary.

Chemicals and analytical methods. Mercury was washed with 7% HNO_3 and distilled water, dried and distilled in vacuum prior to filling the apparatus. The sodium concentration in the amalgam was determined potentiometrically by measuring the electromotive force of the cell



The calibration curve was determined by titration with 0.1M-HCl. The mean deviation of the calibration points was 0.5 mV so that according to the Nernst equation the average relative error of the potentiometric determination was $\pm 1.3\%$.

Solutions of NaOH were prepared from the soda lye obtained from the plant Spolana Neratovice. The concentration of NaOH was determined titrimetrically with 0.1M-HCl, that of Na_2CO_3 by the Winkler method. The molar ratio of NaOH to Na_2CO_3 was always larger than 90 so that the specific resistance and activity of NaOH and H_2O were only slightly influenced by the carbonate.

RESULTS AND DISCUSSION

The decomposition rate was measured as a function of the temperature ($70-90^\circ\text{C}$), amalgam concentration (0.01-0.6 wt.% Na), soda lye concentration (10-41 wt.% NaOH), and rate of amalgam flow ($12-43 \text{ cm}^3/\text{cm s}$). The tabulated experimental data (in total 101 values of the decomposition rate) are available on request by the authors. On this basis, the empirical constants k_A and k_B were evaluated on a computer as 0.579 and $8850 \text{ cm}^2/\text{A}$, respectively; these constants are involved in the equations for the decomposition rate derived in our preceding work³. In calculating the theoretical decomposition rates for the individual experimental points, we used the Tafel constants a'_K and b'_K determined for each temperature and soda lye concentration by a linear interpolation (or extrapolation in the case of 10 wt.% NaOH) from the values measured for the employed Elektrokohle Lichtenberg graphite².

The product $|I| \varrho_{AG}$ representing the voltage drop on the amalgam-graphite contact resistance was set equal to its measured value. The height of the wetted portion of the graphite was $b = 2.5$ cm so that $Y_R = b/a = 10$ and the dimensionless parameter F_1 could be calculated from Eq. (30) of ref.³. The electromotive force of the decomposer element was calculated according to ref.¹. For the constants $k_A = 0.579$ and $k_B = 8850$ cm²/A determined by iterations for the whole set of data, the mean deviation between the theoretical and experimental decomposition rates was $\pm 13.3\%$.

The constant k_A corresponds at a rate of the amalgam flow of 35 cm³/cm s to the mass transfer coefficient $i_{A,lim}/Fc_{Na} = 0.121$ cm/s ($i_{A,lim}$ denotes limiting anodic current density, c_{Na} amalgam concentration in mol/cm³). This coefficient was determined for a stationary amalgam⁹, where convection is due only to gradients of the interfacial tension formed during the reaction, as 0.048 cm/s, *i.e.*, smaller by a factor of 2.5. In our case, a more intense forced convection of the amalgam during the measurement increases the mass transfer above the limit given by the surface motion of the stationary amalgam. The value of $k_B = 8850$ cm²/A leads to acceptable values of the volume fraction of hydrogen in the emulsion, namely 0.12–0.5.

The differences between experimental and theoretical decomposition rates are due partly to the limited reproducibility of the measurements, partly to differences between the model and real systems. The reproducibility is probably influenced mainly by slow changes of the hydrogen overvoltage on graphite (in the course of several days). For example, it follows from the theoretical equations that a change of the Tafel constant a_K by 30 mV, which is possible in our case, leads to a change of the decomposition rate by up to 10%.

The differences between the real and model systems are due mainly to neglecting the curvature of the amalgam surface (the 6th assumption in ref.³). In reality, the graphite is practically not wetted by the amalgam, so that the latter forms a meniscus. The real mean length of the lines of current in the electrolyte at the three-phase boundary is smaller than in a rectangular model element of the decomposer. Therefore, in the real case the influence of the electrical resistance of the soda lye on the decomposition rate is smaller than in the model. Also our other assumptions³ introduced in the theory represent a certain idealization. However, the principal agreement between calculated and experimental decomposition rates (only two adjustable constants are involved in the equations) suggests that the model describes the properties of the real system which are important for the calculation of the decomposition rate.

The influence of the amalgam concentration on the decomposition rate is manifested in a triple way: With increasing amalgam concentration the electromotive force of the amalgam-hydrogen cell increases, while the anodic overvoltage due to the limited rate of the diffusion of sodium in the amalgam and the Reynolds number

for the amalgam flow decrease. As long as the amalgam concentration is higher than a certain limit which depends on its rate of flow (*e.g.*, it is 0.03 wt.% Na at a rate of flow of $34 \text{ cm}^3/\text{cm s}$), the anodic overvoltage is negligible and the dependence of the decomposition rate on the amalgam concentration is given only by the concentration dependence of the electromotive force and kinematic viscosity of the amalgam. Then the following empirical equation holds:

$$I_{\text{exp}} = \text{const. } N_{\text{Na}}^n, \quad (1)$$

where $n = 0.2$ on the average. If the amalgam concentration drops below the mentioned limit, the exponent n rises up to $n = 1$ indicating that the decomposition rate is governed by the rate of sodium transport in the amalgam.

The dependence of the decomposition rate on the soda lye concentration is due to the concentration dependence of the electromotive force of the decomposer cell, the Tafel constant a_K for hydrogen evolution on graphite, and the specific resistance of the soda lye. The first two quantities decrease with increasing concentration of the soda lye whereas the third one attains a minimum¹¹ at 23 wt. % NaOH (70°C) or 28 wt.% NaOH (90°C). This is in accord with both the theoretical and experimental dependences of the decomposition rate on the soda lye concentration, which show a flat maximum at 18–22 wt.% NaOH.

The dependence of the decomposition rate on the rate of flow of the amalgam is given by the transport of sodium from the bulk to the interface (important at low amalgam concentrations) and by the dependence of the mean specific resistance of the hydrogen-electrolyte emulsion on the rate of flow of the amalgam (Eq. (13) in ref.³). Experimentally, the decomposition rate is proportional to the rate of amalgam flow raised to the power of 0.5–0.8.

The apparent activation energy was calculated as

$$W = -R \partial \ln |I_{\text{exp}}| / \partial (1/T). \quad (2)$$

The activation energy values at 70–90°C, 0.1 wt.% Na and soda lye concentrations 10, 20 and 40 wt.% were 1, 2, and 4 kcal/mol, respectively. The low activation energy is related to the low activation energy of the individual rate-controlling processes, namely passage of electric current through the electrolyte, transport of sodium to the interface, and evolution of hydrogen on graphite².

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