

## APPLICATION OF PHASE DIAGRAM OF THE SYSTEM NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O FOR THE PRODUCTION OF HYDROGEN PEROXIDE BY CATHODIC REDUCTION OF OXYGEN IN SODIUM HYDROXIDE SOLUTIONS

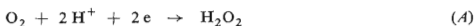
J. BALEJ

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, Prague 6*

Received August 29th, 1971

A general procedure is presented for the determination of the maximum admissible concentration of sodium hydroxide for electrolytic preparation of hydrogen peroxide by cathodic reduction of oxygen in the temperature range 0–40°C at which still no formation of the unwanted solid sodium peroxide occurs in the pores of carbon cathode.

Electrochemical preparation of hydrogen peroxide can be performed in two ways, *viz.* anodic oxidation of water<sup>1,2</sup> or cathodic reduction of oxygen. The first, indirect method *via* peroxydisulphuric acid or peroxydisulphates as intermediates in nowadays replaced by the less expensive autooxidation processes with various organic intermediates<sup>2–4</sup>. The second electrochemical procedure (by cathodic reduction of oxygen) is energetically much more advantageous, since the standard equilibrium potential of cathodic reduction of oxygen according to reaction

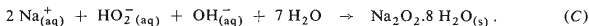


$\varepsilon^0 = 0.682$  V at 25°C (see<sup>5–7</sup>) (literature<sup>2</sup> gives the value 0.693 V) whereas for electrolytic preparation of peroxydisulphates according to reaction



the value of this quantity<sup>5–7</sup> is  $\varepsilon^0 = 2.01$  (according to paper<sup>2</sup> 2.06 V). This was the reason, why attempts have been made to extend the electrolytic preparation of hydrogen peroxide by cathodic reduction of oxygen to industrial scale<sup>1,2</sup>, which, however, remained as yet unsuccessful. The cause is that hitherto no adequate electrode material has been found on which the reaction would proceed with the highest current yields in the region of industrially applied current densities and which, besides, would have a sufficiently long durability. Another drawback is the fact that hydrogen peroxide, as a thermodynamically unstable substance, undergoes easily self-decomposition which, moreover, is very distinctly catalyzed by a number of substances (especially by ions of transition metals which for this reason cannot be used as electrode materials). The results of Berl<sup>8</sup> and Berl<sup>9,10</sup>, obtained in a laboratory-scale electrolyzer with a cathode made of various kinds of activated charcoal, seemed very promising in this respect, as it is demonstrated by further papers<sup>11–14</sup>. Cathodic reduction of oxygen to hydrogen peroxide proceeds both in acidic and in alkaline media. In the former case reaction (A) may be followed by relatively

fast reduction of the primary hydrogen peroxide to water which diminishes the current yield of hydrogen peroxide. Therefore alkaline medium proves more advantageous. Of the currently available electrolytes sodium or potassium hydroxide can be considered. With potassium hydroxide the electrolysis proceeds without difficulties, as the formed hydrogen peroxide, or more correctly the perhydroxyl ions  $\text{HO}_2^-$ , are very well soluble in the technically interesting concentration range of the given system. With sodium hydroxide, however, the solid sodium peroxide octahydrate may be formed under certain concentration conditions, following the reaction



With porous carbon electrodes the highest concentration of perhydroxyl and hydroxyl anions and consequently also the highest probability of formation of solid products is in the electrode pores. This, however, lowers the working surface area of the pores and results in a complete destruction of the electrode. This phenomenon has already been described by Berl<sup>8</sup> who ascribed it erroneously to the deposition of solid sodium hydrogen carbonate. Also Yeager<sup>15</sup> pointed out to the danger of the formation of solid sodium peroxide octahydrate in the pores of carbon electrodes, used for oxygen reduction in fuel cells at high concentrations of sodium hydroxide, even if the electrodes are provided with decomposition catalysts, keeping the concentration of hydrogen peroxide very low.

Since the solubility diagram of the system  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  was not known in detail nor in the necessary temperature interval, it was not possible to determine in advance the concentration and working conditions for cathodic reduction of oxygen to hydrogen peroxide in sodium hydroxide solution in order to prevent the formation of solid sodium peroxide octahydrate. Only the fundamental data on the solubility in the mentioned system, published in paper<sup>16</sup> have shown that there exists a certain limiting concentration of sodium hydroxide at which no formation of solid sodium peroxide octahydrate takes place, no matter how much the concentration of hydrogen peroxide in the solution is increased. This limiting sodium hydroxide concentration is the higher, the higher is the temperature. This fact can be used to determine the maximum admissible concentration of sodium hydroxide in the starting electrolyte for cathodic reduction of oxygen without formation of solid sodium peroxide octahydrate in the electrode pores. The effort to attain the highest possible concentration of sodium hydroxide was motivated by the aim to use solutions with the highest possible electric conductance, since, according to preliminary estimation, these limiting concentrations always lie on the increasing part of the dependence of electric conductance on concentration, the maximum on the curve at 20°C being at 15 w% NaOH (*i.e.* 4.4 mol/1000 g  $\text{H}_2\text{O}$ )<sup>17</sup>.

The aim of the present work was to investigate these maximum admissible concentrations of initial solution for various reaction conditions of electrolysis (temperature, current and mass yields of the main product), provided that no solid sodium peroxide octahydrate should be formed (especially not in the pores of the carbon cathode).

## THEORETICAL

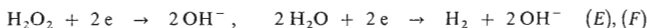
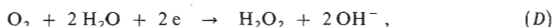
The prerequisites of the procedure are to know both the solubility diagram of the system<sup>16</sup>  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  and the equation of the working line of electrolysis, describing the change of electrolyte composition during electrolysis under the actually existing conditions (*i.e.* expressing not only the course of the main electrode reaction,

yielding hydrogen peroxide, but also the course of further possible reactions on the electrodes as well as chemical reaction in the solution, all of them determining the final composition of the electrolyte and consequently also the possibility of formation of solid sodium peroxide octahydrate).

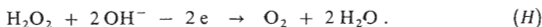
### Equation of the Working Line

The basic assumption is that electrolysis is carried out in a continual-flow electrolyzer with a percolating diaphragm. Fresh electrolyte is fed into the anodic region at a constant flow-rate. Then it passes the filtering diaphragm and enters the cathodic compartment, leaving it as the final solution used either as such or after processing to the final product.

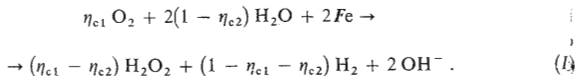
Using sodium hydroxide three cathodic reactions



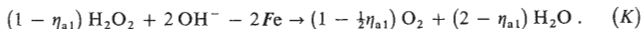
and the following anodic reactions



may take place. The products of cathodic reactions are hydrogen peroxide as the main product and further hydroxyl ions and gaseous hydrogen. Relative amounts of the products or decrease of the initial substances are given by the ratio of current yields of partial cathodic reactions. If we denote the current yield of reaction (D)  $\eta_{c1}$ , that of reaction (E)  $\eta_{c2}$  and the current yield of reaction (F) as  $1 - \eta_{c1} - \eta_{c2}$ , then, after the quantity of electricity corresponding to two Faraday constants has passed, the total course of cathodic process can be expressed by the equation



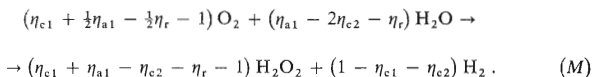
Denoting the current yield of reaction (G)  $\eta_{a1}$  we can describe the total anodic process as



However, hydrogen peroxide formed at the cathode, is lost not only by cathodic reduction ( $E$ ) and by anodic oxidation ( $H$ ) of the part which reaches the anodic region by diffusion and migration (as it must be borne in mind that in alkaline medium hydrogen peroxide exists only in ionized form, as  $O_2H^-$ ), but in part it also undergoes self-decomposition according to equation



If we denote the yield of this reaction under stationary conditions  $\eta_r$ , then the total change of the composition of the system, caused both by electrolysis and chemical decomposition of hydrogen peroxide can be described by the equation



From it it follows that sodium hydroxide does not participate in the over-all reaction, its amount remaining unchanged. Only its concentration is different. However, concentration changes caused by migration of ions through diaphragm need not be considered, since under steady conditions of flow, current load and current yields of partial reactions the concentrations of the initial and final solution correspond to each other according to equation ( $M$ ). This equation also indicates that the total amount of the product depends on the current yields of a number of partial electrode and chemical reactions which may be a rather complicated function of actual working conditions. Although we do not know its course we can, as a first approximation, assume that their values are constant at steady working conditions of the flow electrolyzer. For further procedure it is advantageous to choose the main cathodic reaction ( $D$ ) as the basis of next material balance. Denoting the degree of water, transformed electrolytically to peroxide (Eq. ( $B$ ))  $\alpha$ , then the amount of  $H_2O_2$  formed is  $55.5062\alpha/2$  mol  $H_2O_2$ , when both initial and final electrolyte concentrations are expressed in molalities. The simultaneously formed amounts of gaseous hydrogen and of the reduced (Eq. ( $F$ )), oxidized (Eq. ( $H$ )) and chemically decomposed (Eq. ( $L$ )) hydrogen peroxide as well as the total decrease of water are as the follows: gaseous hydrogen  $55.5062\alpha\beta/2$ , cathodically reduced  $H_2O_2$   $55.5062\alpha\gamma/2$ , anodically oxidized  $H_2O_2$   $55.5062\alpha\delta/2$ , chemically decomposed  $H_2O_2$   $55.5062\alpha\epsilon/2$ , total decrease of water (reactions ( $D$ ), ( $F$ ), ( $G$ ), ( $H$ ) and ( $L$ )) is then:

$$\begin{aligned} & 55.5062\alpha(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda), \quad \text{where} \\ & \beta = (1 - \eta_{c1} - \eta_{c2})/\eta_{c1}, \quad \gamma = \eta_{c2}/\eta_{c1}, \quad \delta = (1 - \eta_{a1})/\eta_{c1}, \\ & \epsilon = \eta_r/\eta_{c1}, \quad \lambda = \eta_{a1}/\eta_{c1}, \end{aligned}$$

which denote the so-called relative current yields of partial reactions with respect to the yield of the main production reaction ( $D$ ). To express the concentrations of compounds of the system under study directly in molalities, it is necessary owing to the total decrease of water by the mentioned reactions (decrease of water caused by escape of water vapour in the evolved gaseous hydrogen and oxygen is neglected in view of the low temperature) to divide their amount by the factor  $1 + \alpha(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda)$ . Accordingly, the concentrations of the components of final electrolyte after electrolytical decomposition of  $55 \cdot 5062\alpha$  moles of water (Eq. (D)) have the following values:

$$m_{\text{NaOH}} = m_{\text{NaOH}}^0 / [1 - \alpha(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda)], \quad (1)$$

$$m_{\text{H}_2\text{O}_2} = 27 \cdot 753\alpha(1 - \gamma - \delta - \epsilon) / [1 - \alpha(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda)]. \quad (2)$$

Expressing  $\alpha$  from Eq. (2) as a function of the content of hydrogen peroxide in solution

$$\alpha = m_{\text{H}_2\text{O}_2} / [m_{\text{H}_2\text{O}_2}(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda) + 27 \cdot 753(1 - \gamma - \delta - \epsilon)], \quad (3)$$

and substituting into Eq. (1) we obtain after rearrangement the following expression for the course of the working line of electrolysis in which the concentrations of components are given in molalities

$$m_{\text{NaOH}} = m_{\text{NaOH}}^0 + m_{\text{NaOH}}^0(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda) m_{\text{H}_2\text{O}_2} / [27 \cdot 753(1 - \gamma - \delta - \epsilon)]. \quad (4)$$

Here  $m_{\text{NaOH}}^0$  denotes the concentration of sodium hydroxide, in molality, in the initial electrolyte. From Eq. (4) it follows that under the given conditions and assuming that the relative current yields are constant for given working conditions the working line of electrolysis in the phase diagram of the system  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  is presented as a straight line whose intercept gives the concentration of sodium hydroxide and whose slope,  $k$ , is defined as

$$k = m_{\text{NaOH}}^0(1 + \beta - \delta - \frac{1}{2}\epsilon - \frac{1}{2}\lambda) / [27 \cdot 753(1 - \gamma - \delta - \epsilon)]. \quad (5)$$

$k$  is a function of initial sodium hydroxide concentration and of current yields of partial electrode and chemical reactions.

### *Effect of Relative Yields of Partial Reactions*

To find the real course of the working line of electrolysis it is therefore necessary to know both the initial sodium hydroxide concentration and the actual values of all relative current or chemical yields. However, the latter condition is not met so far, since the dependence of partial yields on the conditions of electrolysis is not

TABLE I  
Values of Quantity  $A$  for Various Values of Yields of Partial Reactions

$\eta_{c1}$	1.0	1.0	1.0	1.0	1.0	1.0	0.8	0.6	0.6	0.7	0.8
$\eta_{c2}$	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.2	0.0	0.1
$\eta_{a1}$	1.0	1.0	1.0	0.9	0.8	0.8	0.8	0.8	0.8	0.9	0.9
$\eta_r$	0.0	0.5	0.9	0.0	0.0	0.1	0.1	0.1	0.2	0.1	0.1
$\beta$	0.0	0.0	0.0	0.0	0.0	0.0	0.125	0.033	0.333	0.429	0.125
$\gamma$	0.0	0.0	0.0	0.0	0.0	0.0	0.125	0.033	0.333	0.00	0.125
$\delta$	0.0	0.0	0.0	0.1	0.2	0.2	0.25	0.333	0.333	0.143	0.125
$\varepsilon$	0.0	0.5	0.9	0.0	0.0	0.1	0.125	0.1674	0.333	0.143	0.125
$\lambda$	1.0	1.0	1.0	0.9	0.8	0.8	1.0	1.333	1.333	1.286	1.125
$A$	0.5	0.5	0.5	0.5	0.5	0.5	0.625	1.5	$\infty$	0.80	0.6

known. Therefore we can investigate only the effect of these quantities on the value of  $k$  in general, by substituting the possible value of relative current and chemical yields into Eq. (5) and in this way to determine the general range of the possible values of  $k$ . For this purpose it is of advantage to transform Eq. (4) into the form of a dependence of relative concentration of sodium hydroxide on the concentration of hydrogen peroxide in solution and on working conditions, expressed in terms of relative yields

$$m_{\text{NaOH}}/m_{\text{NaOH}}^0 = 1 + 0.036032Am_{\text{H}_2\text{O}_2}, \quad (6)$$

where  $A$  is defined as

$$A = (1 + \beta - \delta - \frac{1}{2}\varepsilon - \frac{1}{2}\lambda)/(1 - \gamma - \delta - \varepsilon) \quad (7)$$

and denotes in fact the ratio of the half decrease of water to the increase of hydrogen peroxide during the whole process. In the most favourable case we can presume that the yields of unwanted electrode reactions ( $E$ ), ( $F$ ) and ( $G$ ) as well as of the chemical decomposition ( $L$ ) are zero,  $\beta = \gamma = \delta = \varepsilon = 0$  and  $\eta_{c1} = \eta_{a1} = \lambda = 1.0$ , so that  $A = 0.5$ . In such case

$$m_{\text{NaOH}}/m_{\text{NaOH}}^0 = 1.0 + 0.018016m_{\text{H}_2\text{O}_2}. \quad (8)$$

This, however, can hardly be attained in reality. The values of  $A$  for various possible relative yields  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\varepsilon$ , and  $\lambda$ , and for various possible of  $\eta_{c1}$ ,  $\eta_{c2}$ ,  $\eta_{a1}$ ,  $\eta_r$  are summarized in Table I. It is evident that  $A$  can vary within the limits 0.5 –  $\infty$ . If we take into account only the technically interesting region for which total yields of hydrogen peroxide  $\eta_{\text{tot}} = \eta_{c1} + \eta_{a1} - \eta_{c2} - \eta_r - 1 \geq 0.5$  the value of  $A$  lies within the interval (0.6; 1.0). If we choose, for safety sake, for the least favourable case the maximum technically possible value of  $A = 1.4$ , the working line of electrolysis will be described

by the relation

$$m_{\text{NaOH}} = m_{\text{NaOH}}^0(1 + 0.05m_{\text{H}_2\text{O}_2}). \quad (9)$$

Equation of the working line of electrolysis, determined as described above with the corresponding value of  $A$  can then be used to calculate the maximum admissible concentration of the starting solution,  $m_{\text{NaOH}}^0$  under chosen working conditions at which still no solid sodium peroxide octahydrate could be formed and especially not in the pores of the electrode.

#### *Determination of Maximum Admissible Concentrations of the Starting Solution*

From the shape of solubility curves<sup>16</sup> in the system  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  it is evident that this problem has a solution in the case when the working line is a tangent to the corresponding solubility curve of sodium peroxide octahydrate at the temperature of electrolysis. This is a difference from the problem solved earlier<sup>18,19</sup> when the question was to find the intersection of the working line of electrolysis with the region of crystallization of the product as the least soluble component of the system. The present task can be solved either analytically by calculating the equation of the tangent with the known slope (Eq. (5)) to the solubility curve of sodium peroxide octahydrate in the mentioned system and at a certain temperature. This solubility curve is also described by the analytic expression (Eq. (6) and (7) of paper<sup>16</sup>). The alternative solution is a graphical one, by constructing a tangent with a defined slope to the solubility curve. The slope of the tangent is a function of sodium hydroxide concentration in the initial solution and therefore its value must be determined so that we find its value for an *a priori* chosen  $m_{\text{NaOH}}^{0'}$  lying in the close vicinity to the presumed real  $m_{\text{NaOH}}^0$  and to this estimated working straight line we construct a parallel straight line, touching the solubility curve of sodium peroxide. The intercept on this tangent represents the corresponding value of  $m_{\text{NaOH}}^0$ .

Fig. 1 shows the found working straight lines of electrolytical preparation of hydrogen peroxide by cathodic reduction of oxygen in sodium hydroxide solution. The straight lines are tangents to the solubility curves of sodium peroxide at  $0-40^\circ\text{C}$ , comprising quite safely the whole technically possible range of temperatures. The corresponding values of maximum admissible concentrations of initial solutions are presented in Table II. Because the real values of current and chemical yields of the partial reactions are not known, the tangents and the corresponding values of  $m_{\text{NaOH}}^0$  are given both in Fig. 1 and in Table I for the most and the least favourable cases of  $A$  ( $A = 0.5$  and  $A = 1.4$ , respectively). The results indicate that for  $A = 0.5$  the maximum admissible concentration of sodium hydroxide in the initial solution is slightly higher than for  $A = 1.4$ , since in the former case electrolytic decomposition of water does not reach such high degree and thus the concentration of the solution does not increase. Relative differences in the concentration of initial electrolyte vary within  $3-6.6$  rel. %.

The above described procedure was performed till now for the case that the solubility of sodium peroxide octahydrate should not be exceeded in the main phase of

catholyte in the cathodic compartment of a continuously working electrolyzer with a percolating diaphragm. For this reason, when determining the working line of electrolysis the course of all partial electrode and chemical reactions was taken into account, disregarding any concentration gradient between the bulk of the solution and the working surface of the electrodes. This simplification was fairly appropriate in solving the earlier problems<sup>18,19</sup>.

However, the present question of electrolytic preparation of hydrogen peroxide cannot be solved in general without taking into account the concentration gradients, arising between the bulk of the electrolyte and the working surface of the electrode, as the cathodic reaction of peroxide formation takes place in porous diffusion carbon electrodes where the main portion of the current is used for the reaction

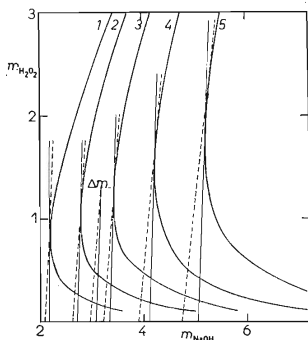


FIG. 1

Course of the Electrolysis Working Lines as Tangents to the Solubility Curves of  $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$  in the System  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$   
 ———  $A = 0.5$ , - - - -  $A = 1.4$ . Temperature: 1 0, 2 10, 3 20, 4 30, 5 40°C. The intersection of the straight lines with the horizontal axis represents the sought  $m_{\text{NaOH}}^0$  for the given temperature.

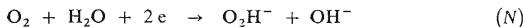
TABLE II

Maximum Admissible Concentrations of NaOH in the Initial Electrolyte at Various Temperatures in the Case that no Separation of Solid  $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$  would take place in the Bulk of the Electrolyte

°C	$A = 0.5$		$A = 1.4$	
	molality	weight %	molality	weight %
0	2.15	6.83	2.09	6.64
10	2.71	8.44	2.62	8.18
20	3.34	10.22	3.21	9.86
30	4.11	12.28	3.90	11.71
40	5.03	14.62	4.72	13.85



inside the electrode pores. In alkaline medium the actual reduction of oxygen to hydrogen peroxide follows the equation



and not the over-all schematic equation (D) (which was quite satisfactory for determining the equation of total change during electrolysis and to find the working line of electrolysis, expressing final concentration changes in the bulk of the resulting electrolyte) and thus it is evident that the maximum concentrations of both perhydroxyl and hydroxyl ions, determining the solubility of sodium peroxide according to Eq. (C), are situated just on the working surface of porous cathode. The formed perhydroxyl and hydroxyl anions are transported from the place of their origin on the cathode both by migration and by convective diffusion flow. The final concentration gradient results from the equilibrium between the rate of formation of these ions by oxygen reduction and the rate of their transport. The transport rate of the ions formed in porous electrodes cannot be taken as sufficient and consequently neither the concentration gradient between the inside of the pores and the main bulk phase of catholyte can be neglected in our case. This means, that the corresponding concentration gradient,  $\Delta m_{\text{NaOH}}$ , must be subtracted from the value,  $m_{\text{NaOH}}^0$ , as determined in the above described way.

Assuming that the total rate of formation of both anions on cathode is affected in addition to the main production reaction also by two consumption reactions (E) and (F) with corresponding current yields and assuming further self-decomposition of hydrogen peroxide (L) in the near-to-electrode layer, with the relative yield  $\varepsilon_{r,d}$ , differing from  $\varepsilon_r$  as calculated for total volume of the electrolyte, then under stationary conditions the total amount of both ions formed on 1 cm<sup>2</sup> of the surface area of electrode per 1 s must be removed from the electrode working surface by migration and convective diffusion. This condition is expressed for hydroxyl ions in the following general form

$$(i_c/2F + km_{\text{O}_2\text{H}^-} \cdot v_p)(1 - t_{\text{OH}^-}) = f(D, \vartheta, \Delta m_{\text{OH}^-}), \quad (10)$$

where  $i_c$  denotes the cathodic current density,  $k$  is the rate constant of reaction (M),  $m_{\text{O}_2\text{H}^-}$  denotes the mean molality of perhydroxyl ions inside the porous electrode,  $v_p$  stands for the volume of pores filled with electrolyte per 1 cm<sup>2</sup> of the geometric area of electrode,  $t_{\text{OH}^-}$  and  $D$  are transference number and diffusion coefficient of OH<sup>-</sup> ion, respectively, and  $\vartheta$  is the thickness of the diffusion layer. The right-hand side of the equation is a general form of the dependence of diffusion rate of hydroxyl ions from the surface of the inside of pores into the bulk of catholyte. The term  $\vartheta$  comprises all factors which might affect its value with porous electrodes. Evidently, the actual course of this dependence is governed by physical properties as well as by the structure of porous electrode and also by the function of oxy-

gen electrode. Up to now, no real dependences are known for the case studied in this work so that the definite solution of the maximum admissible concentrations of sodium hydroxide for electrolytic preparation of hydrogen peroxide remains open and only a general calculation procedure is given in the present paper. For tentative estimation we shall further consider a case of steady diffusion at an infinite plane electrode with a constant thickness of diffusion layer. In this case, assuming in approximation no self-decomposition of hydrogen peroxide in the pores taking place, the equilibrium concentration gradient  $\Delta m_{\text{OH}^-}$  equals

$$\Delta m_{\text{OH}^-} = i_c(1 - t_{\text{OH}^-}) \vartheta / 2FD. \quad (11)$$

Taking  $\vartheta$  e.g. 0.05 cm (which corresponds to natural convection)  $D_{\text{OH}^-} = 5 \cdot 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ , and  $t_{\text{OH}^-} = 0.5$ , then for  $i_c = 0.1 \text{ A/cm}^2$  the value of  $\Delta m_{\text{OH}^-} \approx 2.5 \cdot 10^{-4}$   $\text{mol/cm}^3$ , i.e. 0.25 mol/l. This value would have to be subtracted from the originally calculated concentration  $m_{\text{NaOH}}^0$  to avoid the separation of solid sodium peroxide octahydrate in the pores of carbon electrode (Fig. 1).

The maximum admissible concentrations of sodium hydroxide in the initial electrolyte, determined in the described way, are of course valid in the case that solid sodium peroxide is formed without any necessary oversaturation. Actual conditions of solid phase formation will of course be given by oversaturation threshold and by the temperature in the working layer of the electrode. This temperature is slightly higher (owing to the heat produced by electrode reactions proceeding at a limited rate) than it is in the bulk of catholyte. This would decrease the danger of exceeding the solubility product of the least soluble component at the mentioned temperature of electrolysis. This advantage of necessary oversaturation is in our case very small since the number of active centers in a diffusion porous electrode with a large active surface area is very high thus making the oversaturation limit very low. Also the solubility measurements in this system have shown<sup>16</sup> that the equilibrium is attained relatively quickly.

## CONCLUSION

In spite of the unknown transport rate of the formed hydroxyl and perhydroxyl ions from the inside of a porous carbon electrode it was possible, on the basis of a general calculation procedure, to estimate the maximum admissible sodium hydroxide concentration in the initial electrolyte for the preparation of hydrogen peroxide by cathodic reduction of oxygen in the given medium<sup>20</sup>. The described treatment is also suitable for analogous electrolytic processes working with porous electrodes, provided the corresponding solubility diagrams of the used systems and the course of all electrode and chemical reactions are known which define the equation of the working line of electrolysis.

## REFERENCES

1. Machu W.: *Das Wasserstoffperoxid und die Perverbindungen*, 2. Ed. Springer, Wien 1951.
2. Schumb W. C., Satterfield C. H., Wentworth R. L.: *Hydrogen Peroxide*. Reinhold, New York 1955.
3. Regner A.: *Technická elektrochemie*, Vol. *Elektrochemie anorganických látek*, p. 560. Academia, Prague 1967.
4. Powell R.: *Hydrogen Peroxide Manufacture*. Chem. Proc. Review No 20. Noyes Development Corp., Park Ridge 1968.
5. Latimer W. M.: *Oxidation Potentials*, 2nd Ed. Prentice Hall, Englewood Cliffs 1952.
6. Pourbaix M.: *Atlas d'Equilibres Electrochimiques à 25°C*, p. 542. Gauthier-Villars, Paris 1963.
7. de Béthune A. J. in the book: *Encyclopedia of Electrochemistry* (C. A. Hampel, Ed.), p. 414. Reinhold, New York 1964.
8. Berl E.: *Trans. Electrochem. Soc.* 76, 359 (1939).
9. Berl W. G.: *Trans. Electrochem. Soc.* 83, 253 (1943).
10. Berl E.: US Pat. 2 000 815 (1935), 2 091 129, 2 093 989 (1937).
11. Mizuno S.: *J. Electrochem. Soc. Japan* 17, 262, 288 (1949); 18, 48, 80 (1950).
12. Mizuno S., Yamada D., Yasikawa S.: *J. Electrochem. Soc. Japan* 18, 116, 167 (1950).
13. Voronin N. N., Ignatenko E. Ch., Barmašenko I. B.: *Ž. Prikl. Chim.* 34, 2043 (1961).
14. Ignatenko E. Ch., Barmašenko I. B.: *Ž. Prikl. Chim.* 37, 2415 (1964).
15. Yeager E. in the book: *Fuel Cells* (W. Mitchel, Ed.). p. 299. Academic Press, New York 1963.
16. Balej J.: *This Journal* 36, 426 (1971).
17. *Gmelins Handbuch der Anorganischen Chemie*, 8. Aufl. *Natrium*, p. 229. Verlag Chemie, Berlin 1928.
18. Balej J.: *This Journal* 30, 2663 (1965); 35, 1954 (1970).
19. Regner A., Balej J., Roušar I.: *Chem. průmysl* 12, 8 (1962).
20. Balej J.: *Czechoslov. Pat. PV* 823—71.

Translated by V. Čermáková.