CALCULATION OF EQUILIBRIUM COMPOSITION IN MORE CONCENTRATED SYSTEMS H_2O_2–KOH (OR NaOH)–H_2O

Jan BALEJ and Otomar ŠPALEK

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

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From relations for acid–base equilibria in more concentrated systems H_2O_2–KOH (or NaOH)–H_2O equations were derived for the calculation of the concentrations of OH^- and HO_2^- ions and undissociated H_2O_2 during preparation of hydrogen peroxide by cathodic reduction of oxygen in alkali hydroxide solution and during spontaneous decomposition of alkaline hydrogen peroxide solutions. Mass changes of the solutions due to the consumption or evolution of gaseous oxygen were taken into account. The role of various parameters is discussed.

Hydrogen peroxide can be prepared by cathodic reduction of oxygen[1–7] principally either in acidic, neutral, or alkaline medium, if the electrolyte has a good conductivity. In practice, concentrated alkali hydroxide solutions are preferable for low equilibrium voltage of the electrolyser[6] and high energy efficiency attainable. In combination with anodic oxygen evolution, the main cell reaction can be written as

$$\tfrac{1}{2}O_2 + OH^- \rightarrow HO_2^- \qquad (A)$$

with $E^0_{\text{cell}} = 0{\cdot}477$ V. It is seen that an increase in the concentration of HO_2^- ions results in an equivalent drop in the concentration of OH^- ions. The concentrations of the individual components fulfil the following equilibrium:

$$H_2O_2 + OH^- \rightleftarrows HO_2^- + H_2O\,, \qquad (B)$$

which was considered already by Berl[8] in discussing the equilibrium potential of reaction (A) and later by Abel[9] in studying the mechanism of spontaneous decomposition of alkaline hydrogen peroxide solutions. The derived equations[8,9] are, however, valid only for very dilute solutions of hydrogen peroxide, where the consumption or evolution of oxygen does not change appreciably the solution mass. The content of hydrogen peroxide in solutions reached in the electrolyser may be much higher so that the mentioned mass changes are not negligible. In this case the knowledge of their equilibrium composition is necessary for determining the equilibrium potentials and kinetics of reactions in the electroreduction of oxygen to peroxide as well as for determining the kinetics and mechanism of the spontaneous decomposition of alkaline hydrogen peroxide solutions.

The present work deals with the derivation of the dependence of the equilibrium concentration of the components of the studied system on the concentration of alkali hydroxide and on the analytical concentration of hydrogen peroxide; numerical data are also presented.

GENERAL EQUATION FOR m_{OH^-}

Calculation

The equilibrium of reaction (*A*) is characterized by the equilibrium constant

$$K = a_{HO_2^-} \,.\, a_{H_2O}/a_{H_2O_2}a_{OH^-} \,. \tag{1}$$

Its values calculated from the ionization constant of water[10] K_{H_2O} and hydrogen peroxide[11] $K_{H_2O_2}$ as

$$K = K_{H_2O_2}/K_{H_2O} \tag{2}$$

at temperatures 15—35°C are as follows:

t, °C	15	20	25	30	35
K	308·6	261·4	222·2	192·0	169·0

It follows that the equilibrium of reaction (*A*) shifts to the right side with decreasing temperature. The ratio of the concentrations of the ionized and nonionized forms of hydrogen peroxide follows from Eq. (*1*):

$$m_{HO_2^-}/m_{H_2O_2} = K \,.\, K_\gamma \,.\, m_{OH^-} \,. \tag{3}$$

The term

$$K_\gamma = \gamma_{H_2O_2}\gamma_{OH^-}/\gamma_{HO_2^-}a_{H_2O} \tag{4}$$

is the so-called activity quotient, where the activity coefficients of the solutes are expressed in the molal scale and the activity of water in the mole fraction scale. It follows from Eq. (*3*) that the ratio between the ions and molecules of H_2O_2 increases with the molal concentration of hydroxyl ions which changes by reaction (*A*). To evaluate this concentration, we shall consider the mass balances of the individual components in solution:

$$m_{M^+} = b\,, \quad m_{OH^-} + m_{HO_2^-} = b + m_{H^+}\,, \tag{5), (6}$$

$$m_{HO_2^-} + m_{H_2O_2} = a\,, \tag{7}$$

where *a* and *b* denote the analytical concentration of hydrogen peroxide and the total alkality in mol/kg H_2O, respectively. By introducing Eq. (*7*) into (*3*), we obtain the molal concentrations of both forms of H_2O_2 as functions of its analytical concentration and m_{OH^-}:

$$m_{HO_2^-} = aKK_\gamma m_{OH^-}/(1 + KK_\gamma m_{OH^-})\,, \tag{8}$$

$$m_{H_2O_2} = a/(1 + KK_\gamma m_{OH^-})\,. \tag{9}$$

It can be shown that the value of m_{H^+} is in alkali hydroxide solutions even at high peroxide concentrations negligible against m_{OH^-} and thus also against the cation concentration m_{M^+}. With this simplification, Eqs (*6*) and (*7*) give

$$m_{HO_2^-} = b - m_{OH^-}\,, \qquad (10)$$

$$m_{H_2O_2} = a - b + m_{OH^-}\,. \qquad (11)$$

By introducing these relations into (*3*) and rearranging we obtain the actual concentration of OH^- ions in the ternary system H_2O_2–KOH (or NaOH)–H_2O in the form:

$$m_{OH^-} = \tfrac{1}{2}[b - a - 1/KK_\gamma + \sqrt{((a - b + 1/KK_\gamma)^2 + 4b/KK_\gamma)}]\,. \qquad (12)$$

This equation, in contrast to that given by Abel[9], applies for any ratio of a/b.

When Eq. (*12*) is applied for the case of preparation or decomposition of concentrated peroxide solutions, it is necessary, as already mentioned, to consider the mass changes of the solution caused by consumption or evolution of oxygen. Therefore the quantities a and b must be expressed as functions of their initial values, a_0 and b_0, as will be shown below.

Preparation of Hydrogen Peroxide by Cathodic Reduction of Oxygen

The dependence of the total alkality, b, on the analytical concentration of hydrogen peroxide, a, in the stationary state in the catholyte flowing out from a flow-through electrolyser with a filtering diaphragm, where cathodic reaction of oxygen to peroxide and anodic oxygen evolution are the prevailing reactions, can be expressed as[7]

$$b = b_0(1 + 0{\cdot}036032\,.\,A\,.\,a)\,. \qquad (13)$$

The constant, A, involves the influence of other possible reactions (cathodic reduction of peroxide to water and its anodic oxidation to oxygen, cathodic evolution of hydrogen, and spontaneous chemical decomposition of peroxide) on the peroxide concentration in the outflowing electrolyte. If no cathodic hydrogen evolution takes place, then $A = 0{\cdot}5$. In the opposite case, the value of A becomes higher. In practice, it can be expected that the conditions of the electrolysis will be chosen so as to prevent the cathodic evolution of hydrogen, hence the value of $A = 0{\cdot}5$ will be considered in further calculations.

From Eqs (*12*) and (*13*) we obtain the final concentration of hydroxyl ions as function of the analytical concentration of the peroxide:

$$m_{OH^-} = \tfrac{1}{2}\{b_0(1 + 0{\cdot}03603Aa) - a - K^{-1}K_\gamma^{-1} +$$
$$+ \sqrt{[(a - b_0(1 + 0{\cdot}03603Aa) + K^{-1}K_\gamma^{-1})^2 + 4b_0(1 + 0{\cdot}03603Aa)/KK_\gamma]}\}\,. \qquad (14)$$

By introducing this result into Eqs (*8*), (*9*) and (*3*) the equilibrium concentrations of both forms of hydrogen peroxide and their ratio can be calculated. It is, of course, necessary to estimate the value of the activity quotient K_γ, which can be considerably different from unity since the solution is rather concentrated. In both cases under discussion (preparation and decomposition of the peroxide), however, the ionic strength of the solution does not change when reaction (*A*) proceeds in either direction and the mass changes are neglected. Accordingly, the activity coefficients of both anions do not change either and their ratio in Eq. (*4*) can be set equal to one. Hence, the value of K_γ will be controlled by the ratio of $\gamma_{H_2O_2}/a_{H_2O}$ whose value, however, for the ternary system considered is not known. The activity of water in more concentrated alkali hydroxide solutions[12] decreases approximately linearly with the concentration of the hydroxide. In the H_2O_2–H_2O system, the activity coefficient $\gamma_{H_2O_2}$ increases with the peroxide concentration[13]. In the numerical model calculations, we set therefore the quotient K_γ alternatively equal to 0·1, 1·0, and 10.

The results of the model calculations of m_{OH^-} and other quantities as functions of the analytical concentration of peroxide, a, for different values of b_0, K, K_γ, and A are shown in Figs 1–3. Dimensionless ratios were used to obtain more representative values.

Spontaneous Decomposition of Alkaline Solutions of Hydrogen Peroxide

The dependence of the overall alkality, b, determined by acidimetric titration, on the analytical concentration of the peroxide, a, in any stage of the decomposition follows from balance equations in the form

$$b = b_0(1 + 0{\cdot}01802a)/[1 + 0{\cdot}01802(a_0 - a)]\,, \tag{15}$$

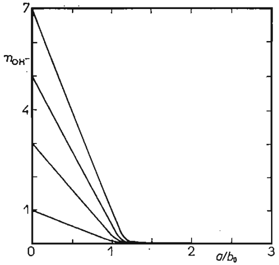

FIG. 1

Dependence of m_{OH^-} on a/b_0 for Different Values of b_0 in the Preparation of Hydrogen Peroxide by Cathodic Reduction of Oxygen
$K = 222{\cdot}22$ (25°C), $K_\gamma = 1{\cdot}0$, $A = 0{\cdot}5$.

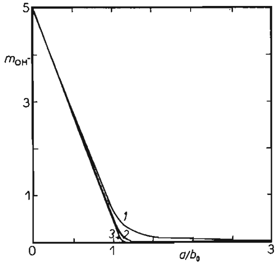

FIG. 2

Dependence of m_{OH^-} on a/b_0 for Preparation of Hydrogen Peroxide by Cathodic Reduction of Oxygen
Values of K_γ: *1* 0·1; *2* 1·0; *3* 10. $K = 222{\cdot}2$, $b_0 = 5$, $A = 0{\cdot}5$.

where a_0 denotes, as above, the initial total molal concentration of hydrogen peroxide. By introducing this relation into (*12*) we obtain the actual concentration of OH^- ions as function of a_0, a and b_0:

$$m_{OH^-} = \frac{1}{2}\left(\frac{b_0(1 + 0{\cdot}01802a)}{1 + 0{\cdot}01802(a_0 - a)} - a - \frac{1}{KK_\gamma}\right) + \\ + \frac{1}{2}\sqrt{\left[\left(a - \frac{b_0(1 + 0{\cdot}01802a)}{1 + 0{\cdot}01802(a_0 - a)} + \frac{1}{KK_\gamma}\right)^2 + \frac{4b_0(1 + 0{\cdot}01802a)}{KK_\gamma(1 + 0{\cdot}01802(a_0 - a))}\right]} . \quad (16)$$

In studying the kinetics of the peroxide decomposition, it is preferable to express the concentrations on the molar rather than on the molal scale as the kinetic constants are related to the molar concentrations of reacting species. In such case, Eq. (*12*) can be used in the same form where the concentrations and activity coefficients are expressed on the molar scale. When the mass changes due to the evolution of oxygen are considered, it is necessary to know the dependence of the density of the solution on its composition; our measurements[14], however, revealed that the density does not change appreciably, hence it will be set equal to the density, ϱ, of the solution after complete decomposition of the peroxide. In such a case we arrive at the equation

$$b' = b'_0[1 - 0{\cdot}016(a'_0 - a')/\varrho] , \quad (17)$$

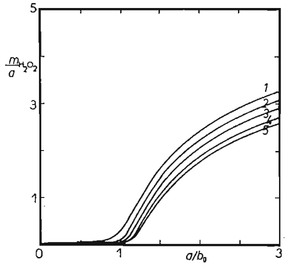

FIG. 3

Dependence of $m_{H_2O_2}/a$ on a/b_0 for Preparation of Hydrogen Peroxide by Cathodic Reduction of Oxygen

Values of b_0: *1* 1; *2* 3; *3* 5; *4* 7; *5* 3. Curves *1*–*4*: $A = 0{\cdot}5$; curve *5*: $A = 1{\cdot}4$. $K = 222{\cdot}2$, $K_\gamma = 1{\cdot}0$.

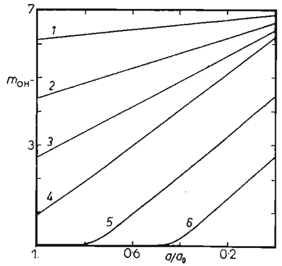

FIG. 4

Dependence of m_{OH^-} on a/a_0 for Spontaneous Decomposition of Hydrogen Peroxide in Alkaline Solution

1 $a_0 = 1$, $b_0 = 7$; *2* $a_0 = 3$, $b_0 = 7$; *3* $a_0 = 5$, $b_0 = 7$; *4* $a_0 = 7$, $b_0 = 7$; *5* $a_0 = 7$, $b_0 = 5$; *6* $a_0 = 7$, $b_0 = 3$. $K = 222{\cdot}2$, $K_\gamma = 1{\cdot}0$.

where the concentrations are in mol/dm^3. From this and Eq. (*12*) the molar concentration of OH^- ions (c_{OH^-}) follows as function of the analytical concentration of hydrogen peroxide (a'_0 and a') and OH^- ions (b'_0):

$$c_{OH^-} = \tfrac{1}{2}\{b'_0[1 - 0{\cdot}016(a'_0 - a')/\varrho] - a' - K^{-1}K_\gamma^{-1} + \\ + \sqrt{[(a' - b'_0(1 - 0{\cdot}016(a'_0 - a')/\varrho) + 1/KK_\gamma)^2 + 4b'_0K^{-1}K_\gamma^{-1}} \, . \\ . \, (1 - 0{\cdot}016(a'_0 - a')/\varrho)]\} \, . \qquad (18)$$

The results of model calculations of m_{OH^-} are shown in Figs 4 and 5 in dimensionless variables. The results in terms of molar concentrations are analogous.

As the analysis of the solutions during decomposition of the peroxide is based on weighing rather than on measuring the volume of the solution containing oxygen bubbles, it is more convenient to express the overall alkality instead of Eq. (*12*) or (*17*) in mass per cent NaOH or KOH, b'', as function of the per cent H_2O_2, a'':

$$b'' = b''_0(1 - 0{\cdot}00471a'')/(1 - 0{\cdot}00471a''_0) \, . \qquad (19)$$

DISCUSSION

It is seen from Fig. 1 that during preparation of hydrogen peroxide by cathodic reduction of oxygen the concentration of OH^- ions decreases practically linearly until the ratio of a/b_0 becomes close to one and then the decrease of m_{OH^-} slows down since the further formed peroxide remains in the molecular form. The decrease of m_{OH^-} is somewhat influenced also by the activity quotient K_γ (Fig. 2). Since this quantity is in all equations multiplied by the equilibrium constant, Fig. 2 shows qualitatively also the influence of the temperature, by which the equilibrium constant becomes smaller.

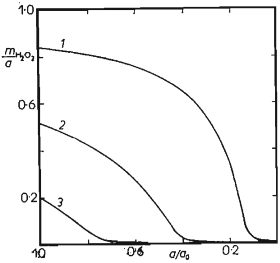

FIG. 5

Dependence of $m_{H_2O_2}/a$ on a/a_0 for Spontaneous Decomposition of Hydrogen Peroxide in Alkaline Solution

Values of b_0: *1* 1; *2* 3; *3* 5. $a_0 = 7$, $K = 222{\cdot}2$, $K_\gamma = 1{\cdot}0$.

The ratio of the undissociated peroxide to its total content as function of a/b_0 is shown in Fig. 3. It is seen that for smaller values of a/b_0 (up to about 0·7) the fraction of molecular peroxide is small, but it increases significantly when a/b_0 becomes close to one; this increase is influenced also by the initial hydroxide concentration, b_0, and the value of A.

Analogous but quantitatively not the same conclusions follow from Fig. 4 and 5 depicting the spontaneous decomposition of alkaline solutions of hydrogen peroxide.

The significance of the correction for the mass changes as given above is illustrated by a practical example. We shall consider the spontaneous decomposition of a solution of the initial composition $a''_0 = 19{\cdot}60\%\ H_2O_2$, $b'' = 15{\cdot}41\%$ KOH. After complete decomposition at 20°C, analysis revealed $b'' = 16{\cdot}99\%$ KOH and this means that the solution mass dropped by 10·23% relatively. Eq. (*19*) leads to $b'' = 16{\cdot}98\%$ in full agreement with the analysis, although the loss of water vapour carried away by the gaseous oxygen was neglected. The cathodic reduction of oxygen in alkaline medium enables to obtain solutions of 10% and more peroxide at a high current yield, hence the given example is not far from reality and the correction for the mass changes of the solution is justified.

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