

PHASE EQUILIBRIA IN THE SYSTEM NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O

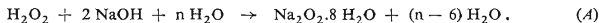
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Received June 17th, 1970

Solubility diagram of the system NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O has been investigated in the concentration region of the formation of solid Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O over the temperature range 0–40°C. According to the measured data, the solubility curves can be interpreted by assuming a dissociation equilibrium of the reaction  $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}_{(s)} + n \text{H}_2\text{O} \rightleftharpoons 2 \text{Na}^+ + \text{O}_2\text{H}^- + \text{OH}^- + (n+7) \text{H}_2\text{O}$ . Apparent equilibrium constant of this reaction (expressed in molalities of the individual components)  $K' = m_{\text{Na}}^2 m_{\text{OH}} m_{\text{O}_2\text{H}^-}$  can, under simplifying assumptions that  $m_{\text{Na}^+} = m_{\text{NaOH}(\text{tot})}$ ,  $m_{\text{O}_2\text{H}^-} = m_{\text{H}_2\text{O}_2(\text{tot})}$ , be described by the relation  $K' = K'_0(1 + Am_{\text{O}_2\text{H}^-} + Bm_{\text{O}_2\text{H}^-}^2)$  where  $K'_0$  means the apparent equilibrium constant, extrapolated to zero concentration of O<sub>2</sub>H<sup>-</sup> ion, and A and B are constants practically independent of temperature between 0–40°C. The relation  $\log K'_0 = 10.225 - 2793.0/T$  was established for the temperature dependence of the apparent equilibrium constant.

Mixing of hydrogen peroxide solution with concentrated sodium hydroxide solutions can result in the formation of solid sodium peroxide octahydrate, Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O, according to the reaction



This reaction which undoubtedly has been known for a long time is also the basis of sodium peroxide preparation, described in some patents<sup>1-3</sup>. In spite of this fact, conditions of the formation of solid sodium peroxide octahydrate from solutions of hydrogen peroxide and sodium hydroxide of various concentrations at different temperatures are not yet known in detail. The first data on the solubility in the system NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O at 0°C were published by Makarov and Grigorjeva<sup>4</sup>. They found that solid sodium peroxide octahydrate is formed in this system from solutions containing higher concentrations of sodium hydroxide and up to 5 weight % of active oxygen (in the form of hydrogen peroxide) whereas higher peroxide concentrations lead to the separation of the compound Na<sub>2</sub>O<sub>2</sub>·2 H<sub>2</sub>O·2 H<sub>2</sub>O. The data, published later by Mironov<sup>5</sup> include the solubility of pure sodium peroxide octahydrate in water over the temperature range -4.3°C (when the eutectic mixture of ice and the mentioned solid peroxide coexists) up to 51.2°C. At higher temperatures an exact solubility determination was impossible

owing to excessive decomposition of peroxide. Further, unpublished partial data on the solubility in this system at 10°C were measured by Divišek, Motlík and Vachuda<sup>6</sup>. Comparison of the results of all the mentioned authors reveal that a fairly good agreement exists between the data of Mironov<sup>5</sup> and those of Divišek, Motlík and Vachuda<sup>6</sup>, while the data of Makarov and Grigorjeva<sup>4</sup> for 0°C are obviously (at least in the region of solid Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O crystallization) incorrect. This can be seen from Fig. 1 in which the data of Makarov and Grigorjeva for 0°C are compared with those of Mironov<sup>5</sup> for 0–40°C.

For this reason we have undertaken a detailed study of the solubility in the mentioned system in the concentration region where the formation of solid sodium peroxide takes place, at 0, 10, 20, 30 and 40°C. The results of these measurements form the subject of the present paper.

## EXPERIMENTAL

*Chemicals:* Saturated solutions of hydrogen peroxide and sodium hydroxide were prepared from c. 80% stabilized solutions of hydrogen peroxide (Chemické závody, Sokolov), c. 50% sodium hydroxide (reagent grade purity) solution in which the content of carbonate was decreased to a negligible amount and from distilled water freed from the dissolved carbon dioxide by boiling. Solid sodium peroxide was formed directly in the reaction medium from the excess initial components according to Eq. (A). For some measurements the product was isolated in pure form by mixing the appropriate initial components at 0°C in stoichiometric ratios, corresponding to Eq. (A) and by filtering off the mother liquors and subsequent careful washing with water.

*Working procedure:* For the preparation of saturated solutions coexisting with excess solid phase and for establishing the equilibrium at the desired temperature practically the same apparatus was used that had been found fully convenient in former studies<sup>7</sup>. The reaction vessel was provided by a closure against the air and was filled with purified nitrogen to prevent possible carbonation of the alkaline solution, although it was found by check measurements in the presence of air that the degree of carbonation does not exceed 1% under otherwise identical experimental conditions (time of equilibration, maximum 3 h at all temperatures used) and practically does not affect the measured equilibrium data.

Preparation of saturated solution was performed in the following way: the reaction vessel, fed without interruption with purified nitrogen, was filled with calculated amount of water and c. 50% solution of carbonate free sodium hydroxide. After a thorough mixing and under continuous cooling with ice an adequate amount of hydrogen peroxide solution was added dropwise; thereafter the vessel was transferred into a thermostat. At lower hydrogen peroxide concentrations in the saturated solution no visible decomposition of peroxide took place during the establishing of equilibrium in the thermostat which was maintained at the given temperature within  $\pm 0.05^\circ\text{C}$ . Therefore taking of samples for analysis and particularly pycnometric density determination could be performed quite without difficulties. If the content of hydrogen peroxide in the saturated solution was higher than c. 10 weight %, the decomposition could already be observed, especially at higher temperatures. The composition of saturated solutions did not, however, deviate from the expected course with increasing peroxide decomposition and the reproducibility of the results was quite satisfactory. It can be concluded that the equilibrium is established with a satisfactory rate between the gradually decomposing peroxide in the solution and the solid sodium peroxide octahydrate. The decomposition products being only gaseous oxygen and water, they have no disturbing effect on the results.

**Analytical methods:** Total active oxygen was determined in both saturated solution and the co-existing phase using classical permanganometry in acid medium. Alkalinity was determined by acidimetric titration with methyl red as indicator. When checking the carbonation of the solution by atmospheric carbon dioxide, carbonate was determined in the presence of hydroxide according to Warder<sup>8</sup>. Total alkalinity was expressed as sodium hydroxide. To make possible to express concentrations in volume instead in weight units, the densities of saturated solutions were determined pycnometrically.

## RESULTS AND DISCUSSION

Results of solubility measurements in the system  $\text{NaOH-H}_2\text{O}_2\text{-H}_2\text{O}$  at the temperatures 0, 10, 20, 30 and 40°C are summarized in Table I, giving the compositions of saturated solutions with various contents of active oxygen (expressed as  $\text{H}_2\text{O}_2$ ) and with various alkalinities (expressed as  $\text{NaOH}$ ) both in weight % and in molalities. Densities of the solutions are also presented, as far as their determination was possible. Compositions of saturated solutions at 0°C were determined up to c. 15 weight % of  $\text{H}_2\text{O}_2$ , at higher contents of active oxygen the peroxide decomposition proceeded so fast that a reliable determination of density as well as an accurate determination of the composition was impossible. This limit shifted with increasing temperature towards lower  $\text{H}_2\text{O}_2$  contents in saturated solutions, so that at 40°C the solubility

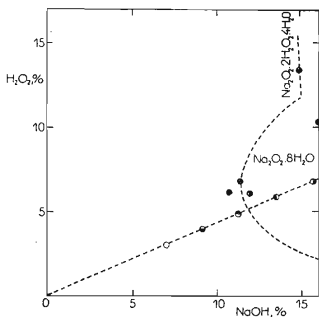


FIG. 1

Comparison of the hitherto Published Solubility Data on the System  $\text{NaOH-H}_2\text{O}_2\text{-H}_2\text{O}$

Makarov, Grigorjeva<sup>4</sup> at 0°C (●), Mironov<sup>5</sup> at 0°C (○) and 10°C (◐) 20°C (◑), 30°C (◒) and 40°C (◔).

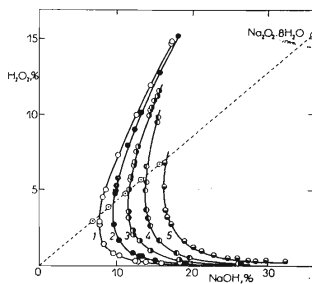


FIG. 2

Solubility Curves in the System  $\text{NaOH-H}_2\text{O}_2\text{-H}_2\text{O}$  according to Our Own Measurements

Temperature: 1 0°C, 2 10°C, 3 20°C, 4 30°C, 5 40°C. ○ Solubility of  $\text{Na}_2\text{O}_2$  according to Mironov<sup>5</sup>.

TABLE I  
Solubility Data in the System NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O at 0, 10, 20, 30 and 40°C  
Coexisting solid phase is in all cases Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O.

NaOH		H <sub>2</sub> O <sub>2</sub>		Density g/cm <sup>3</sup>
weight %	<i>m</i>	weight %	<i>m</i>	
0°C				
26.557	9.0509	0.01307	0.005233	1.2959
26.445	8.9901	0.0160	0.006397	1.2934
23.087	7.5069	0.0271	0.010363	1.2560
19.664	6.1231	0.0500	0.018309	1.2219
13.906	4.0473	0.200	0.068438	1.1581
12.593	3.6145	0.3051	0.10298	1.1438
12.7052	3.6521	0.3231	0.109213	1.1414
11.317	3.2061	0.4363	0.14534	1.1307
11.2441	3.1834	0.4525	0.15066	1.1297
10.428	2.9310	0.628	0.20758	1.1185
9.7283	2.7178	0.786	0.25823	1.1133
8.485	2.3540	1.402	0.45737	1.1003
7.830	2.1898	2.779	0.91392	1.0982
8.265	2.3683	4.487	1.51188	1.1092
8.664	2.5088	5.000	1.70252	1.1148
10.228	3.1003	7.295	2.60022	1.1429
12.705	4.1080	9.976	3.79304	1.1797
14.485	4.9177	11.878	4.74203	1.2036
15.640	5.4586	12.730	5.22475	1.2166
17.260	6.3367	14.646	6.32302	—
17.237	6.3342	14.7315	6.3658	—
10°C				
26.528	9.0303	0.0299	0.0120	1.2901
26.125	8.8447	0.0320	0.0127	1.2878
24.124	7.9473	0.0477	0.01842	1.2635
19.694	6.1397	0.1170	0.0429	1.2170
19.224	5.9618	0.1607	0.0586	1.2023
17.779	5.4171	0.1719	0.0616	1.1982
17.499	5.3144	0.1794	0.06407	1.1971
17.479	5.3074	0.1868	0.0667	1.1935
17.524	5.3239	0.1888	0.06745	1.1952
15.425	4.5759	0.3035	0.1059	1.1714
15.231	4.5101	0.3438	0.1197	1.1675
14.734	4.3385	0.3599	0.1246	1.1655
14.379	4.2198	0.4324	0.1429	1.1714
13.605	3.9619	0.5443	0.1864	1.1500
13.097	3.7931	0.5797	0.1974	1.1480

TABLE I  
 (Continued)

NaOH		H <sub>2</sub> O <sub>2</sub>		Density g/cm <sup>3</sup>
weight %	<i>m</i>	weight %	<i>m</i>	
12.427	3.5774	0.7293	0.24688	1.1402
12.336	3.5482	0.7505	0.25385	1.1397
12.215	3.5107	0.7980	0.2697	1.1372
11.104	3.1671	1.2426	0.4168	1.1266
10.480	2.9806	1.6209	0.5421	1.1194
9.741	2.7801	2.6621	0.8934	1.1151
9.841	2.8769	4.6453	1.5970	1.1233
9.9546	2.9273	5.0296	1.7392	1.1254
10.038	2.9591	5.1577	1.7880	1.1273
10.323	3.0760	5.7768	2.0241	1.1325
11.623	3.6110	7.9065	2.8884	1.1560
12.474	3.9682	8.9422	3.3452	1.1675
13.349	4.3624	10.1499	3.9004	1.1816
18.124	6.5419	15.1659	6.6833	—
20°C				
27.309	9.3991	0.05477	0.02187	1.2964
24.431	8.0925	0.095	0.0370	1.2631
21.808	6.9858	0.1494	0.05627	1.2393
19.843	6.2068	0.2319	0.0853	1.2149
18.696	5.7697	0.2949	0.10703	1.2025
17.064	5.1710	0.4379	0.15605	1.1860
15.958	4.7796	0.5724	0.2016	1.1746
15.280	4.5475	0.7188	0.25155	1.1673
15.073	4.4791	0.8013	0.2800	1.1640
12.438	3.6638	1.9858	0.68219	1.1409
11.767	3.4626	3.2741	1.13292	1.1367
11.661	3.4365	3.5058	1.21490	1.1366
11.679 <sup>a</sup>	3.5014	4.9642	1.7507	1.1425
11.859	3.59113	5.5859	1.98914	1.1460
12.013	3.65592	5.8433	2.09119	1.1478
12.301	3.79866	6.7459	2.44975	1.1560
12.609	3.94548	7.4944	2.75757	1.1623
12.848	4.04538	7.755	2.87139	1.1660
14.324	4.7264	9.9122	3.84612	1.1884
14.677	4.8898	10.2829	4.02848	1.1920
14.718	4.9121	10.378	4.07304	1.1952
14.624	4.8794	10.4485	4.09949	1.1950
15.063	5.0869	10.9106	4.33288	1.2002
15.602	5.3568	11.5829	4.67643	—

TABLE I  
(Continued)

NaOH		H <sub>2</sub> O <sub>2</sub>		Density g/cm <sup>3</sup>
weight %	<i>m</i>	weight %	<i>m</i>	
30°C				
27.373	9.43922	0.1304	0.05289	1.2934
26.229	8.90848	0.1642	0.06558	1.2730
23.889	7.86991	0.2174	0.08423	1.2529
22.633	7.33987	0.2791	0.10643	1.2410
20.611	6.52554	0.4251	0.15824	1.2191
19.491	6.09502	0.5655	0.20796	1.2073
19.696	6.17595	0.5733	0.21139	1.2065
17.746	5.81640	0.6802	0.24816	1.1997
18.064	5.56830	0.8363	0.30315	1.1907
15.625	4.71888	1.5939	0.56604	1.1711
14.512	4.37819	2.6220	0.93023	1.1622
14.208	4.29633	3.1175	1.10854	1.1604
14.223	4.30317	3.1461	1.11931	1.1601
14.007	4.25302	3.6573	1.30584	1.1573
14.012	4.25503	3.6612	1.30732	1.1595
13.991	4.24847	3.6821	1.31483	1.1594
13.835	4.25576	4.8900	1.76877	1.1616
14.058	4.44260	6.5360	2.41978	1.1706
15.432	5.13824	9.4827	3.71216	1.1985
15.528	5.19428	9.7389	3.91430	1.2011
40°C				
32.398	12.01764	0.2059	0.08980	1.2970
29.912	10.70515	0.2331	0.09810	1.2805
28.510	10.00876	0.2760	0.11394	1.2704
27.507	9.52367	0.2879	0.11721	1.2651
26.049	8.85249	0.3866	0.15447	1.2523
24.740	8.27036	0.4749	0.18668	1.2431
23.041	7.54548	0.6143	0.23658	1.2267
21.264	6.82990	0.9022	0.34076	1.2155
20.097	6.38634	1.2319	0.46034	1.2063
19.012	5.98718	1.6022	0.59332	1.2022
17.278	5.39897	2.7149	0.99757	1.1935
16.882	5.29193	3.3634	1.23977	1.1910
16.702	5.24030	3.6163	1.33421	1.1903
16.343	5.23357	5.5883	2.10436	1.1920
16.426	5.34492	6.7423	2.57980	1.1959

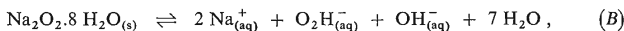
<sup>a</sup> Measured directly by dissolving pure Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O in water.

could be measured only up to 6.7%  $\text{H}_2\text{O}_2$  in the solution. By analysis of the co-existing solid phase it was found that in all cases an equilibrium exists between the saturated solutions and the solid sodium peroxide octahydrate as the stable solid phase.

From the course of the solubility curves (Fig. 2) it follows that the lower is the concentration of sodium hydroxide at a given temperature, the higher must be the content of hydrogen peroxide for exceeding the solubility limit of sodium hydroxide octahydrate; consequently, in solutions containing 30% or more of NaOH crystallisation of solid peroxide octahydrate takes place at very low hydrogen peroxide concentrations. This finding supports the earlier found phenomenon that in cathodic reduction of oxygen in rather concentrated solutions of sodium hydroxide porous carbon cathodes are attacked by the solid phase separating in their pores<sup>9,10</sup>. This phenomenon was erroneously ascribed by Berl<sup>9</sup> to the separation of solid sodium hydrogen carbonate. Therefore in the currently used low-temperature fuel cells with oxygen cathode and alkaline electrolyte potassium hydroxide solution is employed, though more expensive, since in this case at the same hydrogen peroxide concentrations no separation of the solid phase can occur in the pores of electrode and thus the danger of electrode destruction is avoided.

However, with decreasing concentration of sodium hydroxide the limiting concentration of hydrogen peroxide, causing the separation of solid sodium peroxide octahydrate, increases up to a certain value, over which a further increase of hydrogen peroxide concentration does not bring about any separation of solid sodium peroxide. Minimum value of hydroxide concentration in solution is attained, when the molar ratio of both components,  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2}$  is about 2, *i.e.*, when the composition of the solution corresponds roughly to saturated sodium peroxide solution. The mentioned facts and the hyperbolic form of the solubility curves at all examined temperatures prove that equilibrium conditions in the system  $\text{NaOH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$  are determined by the law of chemical equilibrium between the starting substances and the products.

It is evident from the measured data (see Fig. 2) that the composition of saturated solutions stayed within the concentration limits characterized by molar ratio  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2} \geq 1.0$ . It must be taken into account that under these conditions hydrogen peroxide is present in the solution not as an undissociated particle, but mainly as perhydroxyl anion  $\text{O}_2\text{H}^-$ . For this reason it is more convenient to express the solubility equilibrium in the studied system not in terms of Eq. (A) but by the relation



where the amount of  $\text{O}_2\text{H}^-$  and  $\text{OH}^-$  ions is determined by hydrolytic equilibrium



Equilibrium constant of reaction (B) is then defined by the expression

$$K = a_{\text{Na}^+}^2 a_{\text{O}_2\text{H}^-} a_{\text{OH}^-} a_{\text{H}_2\text{O}}^{-7}, \quad (1)$$

which, on expressing the activities as products of molalities and the corresponding activity coefficients, can be written in the form

$$K = m_{\text{Na}^+}^2 m_{\text{O}_2\text{H}^-} m_{\text{OH}^-} \gamma_{\text{Na}^+}^2 \gamma_{\text{O}_2\text{H}^-} \gamma_{\text{OH}^-} a_{\text{H}_2\text{O}}^{-7}. \quad (2)$$

For an exact evaluation of the true equilibrium constant  $K$  it is necessary, according to Eq. (2), to know both the real molalities of the determining ions in saturated solutions of different compositions and the corresponding values of activity coefficients in solutions of the given composition and at the given temperature. These values, owing to rather variable composition of saturated solutions, cannot be *a priori* taken as constant and consequently they cannot be included into the equilibrium constant.

A similar example of equilibrium was solved by Berl<sup>11</sup> who tried to elucidate the dependence of the measured equilibrium potential of the electrode reaction  $\text{O}_2 + \text{H}_2\text{O} + 2e = \text{O}_2\text{H}^- + \text{OH}^-$  on the composition of the solution in the system KOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O. By applying analogous relations to the system, containing sodium hydroxide, we have found that the dissociation degree of hydrogen peroxide, defined as

$$m_{\text{O}_2\text{H}^-} / m_{\text{H}_2\text{O}_2(\text{tot})} = K'_a / (m_{\text{H}^+} + K'_a) \quad (3)$$

is for nearly all measured solutions and at all temperatures very close to unity (in all cases  $\alpha > 0.992$ ). The calculation was carried out using the values of hydrogen peroxide dissociation constant,  $K'_a$  measured in the temperature interval 10–30°C by Evans and Uri<sup>12</sup> which were extrapolated to the temperature interval 0–40°C, assuming the independence of the dissociation heat of temperature. With the above consideration it can be reasonably expected that  $m_{\text{O}_2\text{H}^-} = m_{\text{H}_2\text{O}_2(\text{tot})}$ . Provided a total dissociation of sodium hydroxide takes place it holds that  $m_{\text{Na}^+} = m_{\text{NaOH}(\text{tot})}$ . Hence it follows that  $m_{\text{OH}^-} = m_{\text{NaOH}(\text{tot})} - m_{\text{H}_2\text{O}_2(\text{tot})}$ . By the above relation the real molalities of individual ions, determining the resulting equilibrium of reaction (B), are defined with sufficient accuracy.

However, in order to determine accurately the true equilibrium constant of reaction (B) it is inevitable to know the corresponding activity coefficients in solutions of the given real composition. These data are not available so far. However, when using the values of  $\gamma_{\pm\text{NaOH}}$  and  $a_{\text{H}_2\text{O}}$  found for the binary system NaOH-H<sub>2</sub>O (see<sup>13</sup>) for solutions with the same ionic strength and using the values  $\gamma_{\text{O}_2\text{H}^-}$  determined under the simplifying assumption that  $\gamma_{\text{O}_2\text{H}^-} = \gamma_{\text{H}_2\text{O}_2}$ , whereby  $\gamma_{\text{H}_2\text{O}_2}$  were calculated from the dependence of  $p_{\text{H}_2\text{O}_2}$  on the composition of aqueous hydrogen peroxide



solutions at different temperatures (infinite dilution was chosen as standard state: for  $m_{\text{H}_2\text{O}_2} \rightarrow 0$ ,  $\gamma_{\text{H}_2\text{O}_2} = 1.0$ ) the values of the equilibrium constant  $K$  of reaction (B) were found to be dependent on the composition of the solution (see Fig. 3). The found values of the equilibrium constant  $K$  showed two differing shapes of the dependence on  $m_{\text{H}_2\text{O}_2}$  for concentration regions with  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2} > 2$  and  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2} < 2$  having a transient region for  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2} \sim 2$ . This means that the presumptions made when applying the activity coefficients measured for binary systems to a ternary system are not quite justified.

Therefore we have calculated the values of the apparent equilibrium constant

$$K' = m_{\text{Na}^+}^2 \cdot m_{\text{O}_2\text{H}^-} \cdot m_{\text{OH}^-} = K/\gamma_{\pm\text{NaOH}}^3 \gamma_{\text{O}_2\text{H}^-} a_{\text{H}_2\text{O}}^7 = \\ = m_{\text{NaOH}(\text{tot})}^2 m_{\text{H}_2\text{O}_2(\text{tot})} [m_{\text{NaOH}(\text{tot})} - m_{\text{H}_2\text{O}(\text{tot})}] \quad (4)$$

This constant, evaluated in the above way was found to have a more plausible dependence on hydrogen peroxide concentration (or on its anion  $\text{O}_2\text{H}^-$ ). As can be seen from Fig. 4, with decreasing concentration of perhydroxyl anion the values of  $K'$  approach at a given temperature to a certain limiting value,  $K'_0$ . Up to perhydroxyl ion concentrations  $m_{\text{O}_2\text{H}^-} \leq 0.1$  the value of  $K'_0$  practically equals  $K'_0$  and with further

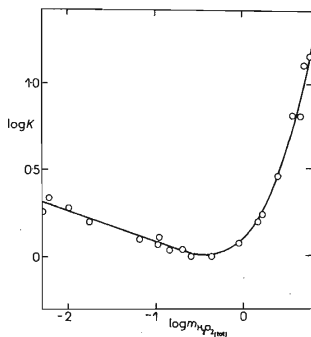


FIG. 3

Dependence of the Equilibrium Constant,  $K$ , of Reaction (B) on the Molality of  $\text{H}_2\text{O}_2$ ,  $m_{\text{H}_2\text{O}_2(\text{tot})}$  on Applying Activity Coefficients of the Components, determined in Binary Aqueous Systems

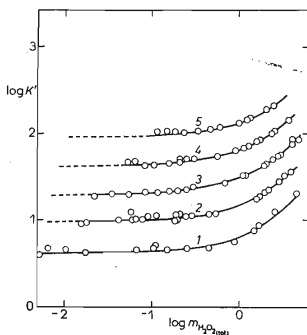


FIG. 4

Dependence of the Apparent Equilibrium Constant,  $K'$ , on the Molality  $m_{\text{H}_2\text{O}_2(\text{tot})}$

Temperature: 1 0°C, 2 10°C, 3 20°C, 4 30°C, 5 40°C.

increasing of  $m_{\text{O}_2\text{H}^-}$  it also increases. The course of the  $\log K'$  *vers.*  $\log m_{\text{O}_2\text{H}^-}$  dependence is in this concentration range ( $m_{\text{O}_2\text{H}^-} > 0.1$ ) analogous for all measured temperatures. This finding enables us to express in a relatively simple way the dependence of  $K'$  on the composition of saturated solution in the form of a relatively simple empirical equation

$$K' = K'_0 [1 + Am_{\text{H}_2\text{O}_2(\text{tot})} + Bm_{\text{H}_2\text{O}_2(\text{tot})}^2], \quad (5)$$

which after evaluation of the experimental data has the form

$$K' = K'_0 [1 + 0.492m_{\text{H}_2\text{O}_2(\text{tot})} + 0.0532m_{\text{H}_2\text{O}_2(\text{tot})}^2]. \quad (6)$$

Values of the equilibrium constant,  $K'_0$ , for different temperatures are presented in Table II. Their temperature dependence can be expressed in the usual form

$$\log K'_0 = 10.225 - 2793.0/T. \quad (7)$$

As can be seen, the solubility data of the studied system NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O in the region of formation of solid sodium peroxide octahydrate N<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O are fully described by Eqs (6) and (7). The agreement of the equilibrium data calculated in this way, with those determined experimentally is demonstrated in Fig. 5 in which full lines denote the course of the solubility isotherms calculated according to Eqs (6) and (7), whereas points denote experimentally determined values (see also Table I). The mean quadratic errors of experimental data from the results of correlation equations lie within the limits of 1.0% rel.

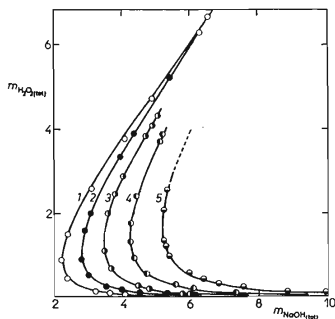


FIG. 5

Comparison of the Solubility Curves in the System NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O Calculated according to Eqs (6) and (7) with those Measured at 1 0°C, 2 10°C, 3 20°C, 4 30°C and 5 40°C (see Table I)

Although Eq. (5), resp. (6) were established only empirically, their course can be fairly well explained on the ground of the hitherto knowledge of the dependence of activity coefficients on composition in more concentrated solutions of stronger electrolytes. It follows from Eq. (4) that the apparent equilibrium constant,  $K'_0$ , implies already the values of the activity coefficients of both  $\text{Na}^+$  and  $\text{OH}^-$  ions and of water. From the course of the solubility data of the studied system at the same temperature it further follows (see also Table I) that in the measured concentration range the contents of the mentioned substances vary only within one order of magnitude so that the effect of the differences in activity coefficients will not be appreciable. On the contrary, the concentration of perhydroxyl ion varies in the studied concentration range by three orders of magnitude and consequently the relative change of the activity coefficient of the respective substance will manifest itself much more distinctly than it is with other components of the studied system. The expression of the right-hand side of Eq. (5) or (6) can therefore be considered as a correction term, expressing the dependence of the relative activity coefficients of this system on the most variable content of perhydroxyl ion. The form of this correction term corresponds to correlation equation serving for expressing the dependence of relative activity coefficients on the composition of multi-component systems<sup>15</sup>.

From the results of our measurements also the solubility of pure sodium peroxide in water in the studied temperature range 0–40°C can be derived. The respective data, read from the solubility diagram for molar ratio  $m_{\text{NaOH}}/m_{\text{H}_2\text{O}_2} = 2$ , are summarized in Table III. They agree with the data obtained according to Eq. (6) (after substituting the appropriate relation between total peroxide content and total alkalinity of the solution) within 1% rel. From these data also the solubility product of this substance can be determined according to Eq. (B), under the above mentioned assumption of total dissociation. As in this case  $m_{\text{Na}^+} = 2m_{\text{O}_2\text{H}^-} = 2m_{\text{OH}^-}$ , the solubility product is given by

TABLE II

Values of Apparent Equilibrium Constant  $K'_0$  of Reaction (B) and Values of the Solubility Product of  $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$  in Water in the Temperature Range between 0–40°C

°C	$K'_0$	$S_{\text{exp}}$	$S_{\text{calc}}$
0	4.00	6.294	6.493
10	9.36	16.04	17.00
20	20.00	38.82	41.02
30	40.10	91.17	93.87
40	80.90	211.0	221.5

TABLE III

Solubility of Na<sub>2</sub>O<sub>2</sub> in Water, Determined from the Experimentally Found Solubility Data in the System NaOH-H<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O in the Temperature Range 0-40°C  
Coexisting Solid Phase is Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O.

°C	0	10	20	30	40
$m_{\text{Na}_2\text{O}_2}$ , mol/kg H <sub>2</sub> O	1.121	1.415	1.765	2.186	2.697
weight % Na <sub>2</sub> O <sub>2</sub>	8.039	9.938	12.098	14.596	17.377

$$S = m_{\text{Na}}^2 + m_{\text{O}_2\text{H}} - m_{\text{OH}^-} = 4m_{\text{H}_2\text{O}_2(\text{tot})}^4 \quad (8)$$

The values of the solubility product of sodium peroxide, obtained in this way from the experimentally found solubility data are listed in Table II for temperatures 0-40°C. The temperature dependence of this quantity was found to have the following form

$$\log S = 12.741 - 3262.2/T. \quad (9)$$

From the correlation equation describing the dependence of the apparent equilibrium constant  $K'_0$  on the composition of the solution the value of the solubility product can be obtained, if the condition  $m_{\text{NaOH}(\text{tot})} = 2m_{\text{H}_2\text{O}_2(\text{tot})}$  is substituted. The respective values of the solubility product,  $S_{\text{calc}}$ , are also presented in Table II.

Comparing the up to now published data with our own experimental results we can conclude that the data of Makarov and Grigorjeva<sup>6</sup>, referred to for 0°C, are for the region of coexistence of solid Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O erroneous, as they would correspond to temperatures higher than 20°C. Also the scattering of the values exceed the admissible limits of reliability. The values of solubility of pure sodium peroxide in water, found by Mironov, are somewhat lower than the our ones (cf. Fig. 2 and Table III). The reason of this discrepancy can be lower accuracy in maintaining constant temperature in the mentioned work ( $\pm 0.5^\circ\text{C}$ ) and lower purity of the used sodium peroxide (impurities of 1% Na<sub>2</sub>CO<sub>3</sub> and 0.6% NaOH) together with the fact that the measured solubilities were not corrected for the presence of these admixtures.

*The author wishes to express his gratitude to the late Professor A. Regner for his interest in this work. Thanks are also due to Mrs A. Vosyková for efficient experimental help and to Dr J. Hostomský, Institute of Chemicals Technology, Prague, for carrying out some computations.*

## REFERENCES

1. Farbenfabriken, vorm. Bayer u. Co: DRP 219790 (1980).
2. Moyer J. R., Bon C. K., Schechter D. L. (Dow Chemical Co.): US pat. 3 156 528 (1964).
3. Bon C. K., Neipert M. P., Schechter D. L.: *Electrochem. Technology* 6, 287 (1968).
4. Makarov S. Z., Grigorjeva N. K.: *Izv. Akad. Nauk SSSR, Otdel. Chim. Nauk* 1955, 176.
5. Mironov K. E.: *Ž. Neorg. Chim.* 10, 531 (1955).
6. Divíšek J., Motlík K., Vachuda J.: Private communication.
7. Balej J., Regner A.: *This Journal* 25, 1685 (1960).
8. Čůta F.: *Analytická chemie odměrná*, p. 272. Published by NČSAV, Prague 1956.
9. Berl E.: *Trans. Electrochem. Soc.* 76, 359 (1939).
10. Yeager E. in the book: *Fuel Cells* (W. Mitchell, Ed.), p. 299. Academic Press, New York 1963.
11. Berl W. G.: *Trans. Electrochem. Soc.* 83, 253 (1943).
12. Evans M. G., Uri N.: *Trans. Faraday Soc.* 45, 224 (1949).
13. Akerlöf G., Kegeles G.: *J. Am. Chem. Soc.* 62, 620 (1940).
14. Schumb W. C., Satterfield C. N., Wentworth R. L.: *Hydrogen Peroxide*, p. 227. Reinhold, New York 1955.
15. Erdős E.: *Chem. listy* 51, 1632 (1957).

Translated by V. Čermáková.