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THE SOLUBILITY OF MERCURIC OXIDE IN SODIUM HYDROXIDE SOLUTIONS.

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1. Introduction.

The erratic behavior of some mercuric oxide electrodes towards solutions of sodium hydroxide led to an investigation of the possibility of a compound resulting from the interaction of the oxide and the sodium hydroxide. The method adopted for studying the existence of such a compound is the determination of the solubility of mercuric oxide in sodium hydroxide solutions of various concentrations.

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2. Purification of the Materials.

To prepare the mercuric oxide, mercury purified by 3 distillations *in vacuo* was dissolved in nitric acid, and the solution was evaporated to dryness. The resulting mercuric nitrate was decomposed by heating it in a casserole over a gas burner. This yielded a deep red crystalline oxide. To remove the very finely divided material the oxide was repeatedly shaken with water which was poured off before all the particles had settled.

The sodium hydroxide solutions, which were carbonate free, were made by the electrolytic decomposition of sodium amalgam. The amalgam was prepared by the electrolysis of C. P. sodium hydroxide. The solutions were made from conductivity water collected from the special still in this laboratory.

3. The Experimental Method.

The solubility determinations were carried out by sealing the sodium hydroxide solutions, together with an excess of the red oxide of mercury, in glass tubes of about 150 cc. capacity. One-half of the tubes, containing the alkali at a given concentration, were placed immediately in a rotating device in a thermostat which was kept at 25° ± 0.01°. In order to approach the equilibrium also from the supersaturated side, the other half of the tubes were first agitated for 4 days in a thermostat at 40°. These tubes were then transferred to the thermostat at 25°. All of the tubes were rotated for 4 days at the latter temperature; after which they remained in the thermostat for 24 hours in order to allow the greater part of the oxide to settle. From each of the tubes 100 cc. of the solution was withdrawn through a filter of cotton fiber; and, after acidifying with hydrochloric acid the mercury present was precipitated with hydrogen sulfide. The sulfide precipitate was then transferred to a perforated crucible, dried at 110°, and weighed.

4. The Solubility Values.

The results of the experiments are presented in the following table. The headings are for the most part self-explanatory. The solubility values within parentheses were omitted in taking the mean. Those marked by an asterisk were obtained with 200 cc. of solution taken from two tubes. The significance of the equilibrium constants given in the last column will be described in the next section.

TABLE I.—THE SOLUBILITY OF MERCURIC OXIDE IN SODIUM HYDROXIDE SOLUTIONS.

Mols. per liter of solution.		Milligrams of HgS from 100 cc. of solution.				
NaOH.	OH^-.	From under-saturation.	From super-saturation.	Mean.	Millimols HgO per liter.	Equilibrium constant.
2.09	1.253	7.30	7.10	7.20	30.9	0.0051
1.0758	0.7660	6.50 (6.80)	6.55 6.50	6.52	28.3	0.0050
0.502	0.4257	6.20*	6.25* 6.05	6.17	26.6	0.0049
0.0955	0.0863	6.00 5.90 5.75*	5.55* 5.75*	5.79	24.9	0.0047
0.0503	0.0465	5.75*	....	5.75	24.7	......
0.0096	0.0091	5.60*	5.85 5.75	5.73	24.6	......
0.0000	0.0000	5.50 (5.90) 5.30 5.40*	5.42 5.45*	5.43	23.4	....

5. Discussion of the Results.

In Fig. 1 the lower graph is a plot of the concentrations of mercuric oxide as ordinates against the sodium hydroxide concentrations as abcissas; and the upper graph is a plot of the concentrations of the mercuric oxide against concentrations of hydroxide ion, obtained by multiplying the alkali concentrations by the corresponding equivalent conductance ratios, as given by data from Noyes and Falk.[1]

It will be observed that the value for the solubility in pure water does not fit on either of the graphs. This sudden change of behavior of the oxide, when passing from a neutral solution to one slightly alkaline, can hardly be due to an experimental error; for Schick[2] and Hulett[3] have found values of the solubility in water that agree closely with that (23.4)

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[1] THIS JOURNAL, **34**, 454 (1912).

[2] *Z. physik. Chem.*, **42**, 155 (1903).

[3] *Ibid.*, **37**, 401 (1901).

given in Table I; their determinations leading to 23.8 and 23.0 millimols per liter, respectively. The most probable explanation of this sudden change of solubility is that the oxide undergoes a dispersion into much finer particles when it is introduced into an alkaline solution. Red and yellow forms of the oxide are known; but it is generally considered that the only difference between them is that the latter is in a finer state of division. Cohen[1] has found that there is a difference of 0.685 millivolt when the two forms of the oxide are made into electrodes of the form Hg + HgO, KOH. This is to be expected since finely divided substances have greater solubilities than coarsely crystalline ones. On the other hand, Schick[2] found that the two oxides have, within the experimental error, the same solubility in water; but it seemes probable that in the prolonged agitation with water during his investigation the yellow substance was transformed into the red one. In this laboratory the reverse of this process, the change from red to yellow, has been observed to take place when the oxide is shaken with a solution of an alkali for a few hours. Evidently the disintegration of the red substance occurs even in very dilute alkali solution. This being the case, the finely divided form might be expected to be more soluble than the red variety. And, in fact, the extension of the lines of Fig. 1 to the zero ordinate doubtless gives the solubility in pure water of the yellow substance that was present in these experiments. The value of this solubility is 24.5 millimols per liter.

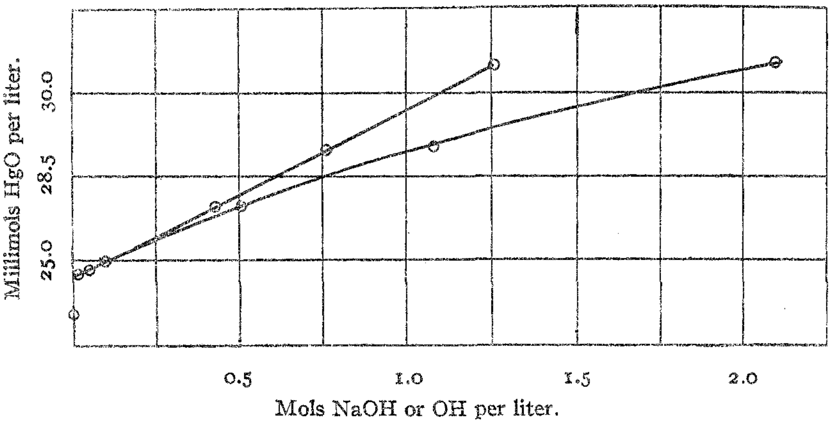

Fig. 1.

The steady increase of the solubility of mercuric oxide as the concentration of sodium hydroxide is increased indicates that the hydrated oxide functions as a very weak acid. Since the increase in solubility is pro-

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[1] *Z. physik. Chem.* 34, 69 (1900).

[2] *Loc. cit.*

portional to the first power of the hydroxide ion concentration, the equilibrium is doubtless represented by the following equation:

$$\mathrm{Na^+ + OH^- + HgO(s) = Na^+ + HHgO_2^-}$$

The equilibrium constant K of this reaction is evidently given by the expression $K = (\mathrm{HHgO_2^-})/(\mathrm{OH^-})$. Now the concentration of the anion $\mathrm{HHgO_2^-}$ at each concentration of sodium hydroxide is equal to the observed solubility s of mercuric oxide in the solution less its solubility s_o in water, multiplied by the degree of ionization γ' of the sodium mercurate; that is $(\mathrm{HHgO_2^-}) = (s - s_o)\gamma'$. Owing to the slight solubility of the mercuric oxide the concentration of the sodium hydroxide is not appreciably affected by its presence, and the hydroxyl ion concentration becomes $c\gamma$, where c is the total concentration of the sodium hydroxide and γ its ionization. The expression for the equilibrium constant then becomes $K = (s - s_o)\gamma'/c\gamma$.

The values of this equilibrium constant are given in the last column of Table I. They were computed under the assumption that the ionizations of the sodium mercurate and sodium hydroxide in the presence of each other are equal (that $\gamma' = \gamma$), and by using for the solubility in water s_o the extrapolated value (0.0245) instead of the observed one.

An estimate of the ionization constant of the mercuric acid $\mathrm{H^+\,HHgO_2^-}$ may also be made. If the acid is represented by HA, the ionization-constant $K_A = (\mathrm{H^+})(\mathrm{A^-})/(\mathrm{HA})$. Substituting for $(\mathrm{H^+})$ its value from $K_w = (H^+)(\mathrm{OH^-})$ and for the ratio $(\mathrm{A^-})/(\mathrm{OH^-})$ the constant K just described, we obtain $K_A = K_wK/(\mathrm{HA})$. For the value of (HA) the (extrapolated) solubility of mercuric oxide may be used. This expression involves the additional equilibrium, $\mathrm{HgO + H_2O = H_2HgO_2}$; but the equilibriumc onstant of this hydration reaction is included in the ionization constant, as in the analogous cases of the ionization constants of ammonium hydroxide and carbonic acids.

By substituting in this equation for K_w the value[1] 0.81×10^{-14}, for K the value 5.0×10^{-3} (the mean of the first 3 values given in Table I, and for (HA) the value 24.5×10^{-3}, we find for the ionization constant of the first hydrogen of mercuric acid $(\mathrm{H_2HgO_2})$ the value 1.7×10^{-15}.

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[1] Lewis and Randall, THIS JOURNAL, 36, 1979 (1914).