CCXCIX.—*The Action of Sodium Hydroxide on Stannic Oxide Sol. Part I.*

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The action of alkali on stannic oxide has been investigated by Frémy, Weber, Rose and others (see Mellor, " Treatise on Inorganic and Theoretical Chemistry," Vol. VII, pp. 414—417), and the existence of simple and complex stannates of types R_2O,SnO_2,nH_2O and $R_2O,5SnO_2,nH_2O$ has been demonstrated. When a solution of α-stannic oxide in dilute aqueous sodium hydroxide is evaporated by heating, it deposits crystals of the composition $Na_2O,SnO_2,3H_2O$, but if it is treated with alcohol in the cold, a precipitate is obtained which varies in composition according to the proportion of alkali to stannic oxide in the solution (Ordway, *Amer. J. Sci.*, 1865, **40**, 173). Van Bemmelen, having observed that at the ordinary temperature and under comparable conditions the amount of a freshly prepared and air-dried hydrogel of stannic oxide which an alkali can dissolve increases continuously with its concentration (" Die Absorption," 1910, 57), believed that stannic oxide passed into colloidal solution under these conditions, and explained the varying composition of the precipitate thrown down by alcohol from this point of view. Zsigmondy and his co-workers (*Z. anorg. Chem.*, 1914, **89**, 210) investigated the peptisation of a 0·5% sol of α-stannic oxide with potassium hydroxide, and found that, as the proportion of the latter was raised, the osmotic pressure and conductivity of the sol increased and the cone of light observed under the ultramicroscope became fainter; hence they concluded that with increasing proportion of alkali the colloidal particles become finer and gradually tend to pass into the crystalloidal condition. No systematic investigation has been made, however, to determine what amount of stannic oxide passes into the crystalloidal state under these conditions, and in order to obtain information on this point measurements have been carried out of (1) membrane equilibria, (2) osmotic pressure, (3) hydroxyl-ion concentration, (4) conductivity, and (5) freezing-point lowering of sols containing various ratios of alkali to stannic oxide. The investigation of the first two points is now described, and that of the other three is recorded in the succeeding paper.

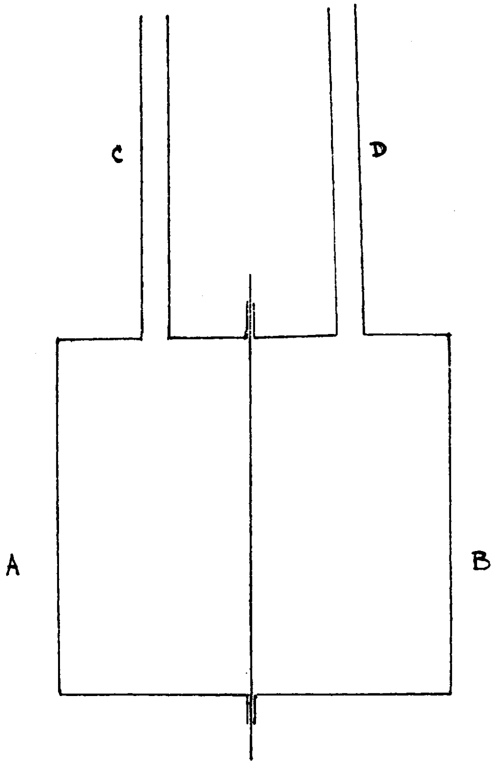
EXPERIMENTAL.

The α-stannic oxide was prepared by slowly adding a solution of pure caustic soda to one of stannic chloride (maintained at about 15°) until the p_H was about 3·6. The precipitate was washed by decantation with cold distilled water until it began to peptise: at this point the supernatant liquid had p_H 5·8 and no chloride could be detected in it. The precipitate was then peptised by addition of a dilute solution of sodium hydroxide free from carbonate. After analysis, the sol was diluted until it contained 16·6 g. of SnO_2 per litre, and then kept in a stoppered Pyrex-glass bottle for about 45 days. The solutions of various ratios of $Na_2O : SnO_2$ were prepared by taking 100 c.c. of the sol and adding to it 10 c.c. of pure sodium hydroxide solution of the requisite strength. The conductivity of the sol changed slowly for about 3 days after the addition of alkali; it was therefore stored in a Pyrex-glass bottle for 7 days before use.

The dialysis was carried out in a Donnan membrane vessel (Fig. 1) consisting of two hard-glass cups, *A* and *B*, each provided with a side tube, and having the membrane stretched between them and firmly clamped in position. A measured volume of the sol was then poured into the cup *A* ("the sol chamber") until it partly filled the attached tube, *C*, and an equal volume of distilled water was poured into the other cup ("the water chamber"). The tubes *C* and *D* were fitted with rubber pressure tubing closed by screw clips. Owing to the presence of colloid and colloidal ions in the sol, there was a tendency for water to enter this chamber and dilute the sol, but this was so nearly counterbalanced by the compression of air in the tube *C* that the dilution of the sol never exceeded 2%. The vessels were shaken twice daily, and 9—10 days were necessary for the attainment of equilibrium, but as a rule 15 days were allowed.

The membrane potential was measured by using two normal calomel electrodes. The jets of the electrode vessels were drawn out so as to be sufficiently long and narrow to be dipped directly into the cups. Two sets of measurements were made by reversing the position of the electrodes, and their mean was taken. The volumes of the solutions in the two chambers were measured and their contents analysed. The total alkali was estimated by titration with hydrochloric acid, methyl-orange being used as indicator, this procedure having been found sufficiently accurate by means of control experiments with stannic oxide sols containing known amounts of sodium hydroxide. The stannic oxide was determined by evaporating a known volume of the sol acidified with nitric acid, washing out the sodium nitrate, and igniting the residue. In the following experiments, membranes of parchment and collodion were used, the latter being prepared in fairly uniform thickness by pouring a definite volume of collodion solution on a dry clean mercury surface of the desired area. The membrane vessels used

FIG. 1.



in the case of collodion were of the same type as those in the case of parchment, but much smaller.

TABLE I.

Original ratio SnO_2:Na_2O, mols.	Final conc. of SnO_2, g./100 c.c. Sol chamber.	Final conc. of SnO_2, g./100 c.c. Water chamber.	Ratio.	Final conc. of Na_2O, g./100 c.c. Sol chamber.	Final conc. of Na_2O, g./100 c.c. Water chamber.	Ratio.	Membrane potential, ϵ (volt).
			Parchment membrane.				
17·2	1·4758	0·0042	351	0·0317	0·0035	9·06	0·022
12·1	1·4720	0·0141	105	0·0451	0·0052	8·7	0·017
9·3	1·4623	0·0197	74·2	0·0545	0·0116	4·7	0·010
6·9	1·4594	0·0304	48	0·0694	0·0198	3·5	0·007
4·5	1·4513	0·0427	34	0·0950	0·0426	2·23	0·004
3·6	1·4139	0·0831	17	0·1104	0·0609	1·81	0·002
2·3	1·4087	0·0903	15·6	0·1640	0·1057	1·55	—
2·0	1·3955	0·1065	13·1	0·1750	0·1352	1·29	—
*1·0	0·6946	0·0556	12·5	0·1672	0·1426	1·17	—
*0·5	0·3952	0·0340	11·6	0·1641	0·1457	1·13	—
			Collodion membrane.				
4	1·4535	0·0338	43	0·1022	0·0478	2·14	
3	1·4385	0·0575	25	0·1332	0·0717	1·86	
2·5	1·4205	0·0782	19·9	0·1534	0·0936	1·64	
2	1·4118	0·0882	16	0·1758	0·1341	1·35	
1	0·7024	0·0312	14	0·1710	0·1390	1·23	

* In these cases the concentration of alkali was kept constant while the amount of SnO_2 was diminished. The concentration of alkali could not be further increased, for it coagulated the colloidal SnO_2.

The data of Table I show that as the ratio $SnO_2 : Na_2O$ is decreased relatively more stannic oxide diffuses into the water compartment, and the ratio of its concentration in the sol chamber to that in the water chamber at first diminishes very rapidly and then slowly. The ratio of alkali in the two chambers also diminishes at first rapidly and then slowly approaches unity. Even when the ratio $SnO_2 : Na_2O$ is 0·5, however, the amount of stannic oxide in the sol chamber is about 12 times as great as that in the water chamber, showing that most of it is in the colloidal condition. Moreover, it does not necessarily follow that the whole of the stannic oxide in the water chamber is in the form of simple stannates, of the type R_2O,SnO_2, or ROH,SnO_2, for the existence of complex stannates is well known, and the experiments with collodion membranes suggest that some of the complex molecules which could pass through parchment are retained by the collodion.

At the higher ratios of $SnO_2 : Na_2O$ there is a considerable excess of total alkali in the sol chamber over that in the water chamber, showing that some of it is combined with the colloidal stannic oxide. If this colloidal complex (consisting of sodium and stannic oxides) existed in the undissociated condition, then the concentration of the diffusible stannates (simple or complex) would have been the same in both the sol and the water chamber. The conductivity and transport-number determinations of Varga (*Koll.-Chem. Beih.*, 1919, **11**, 25), however, show that the colloidal complex dissociates into a simple kation and a colloidal anion. Assuming that all the diffusible ions are univalent, it can be easily shown from Donnan's principle of membrane equilibria that at equilibrium the following relations must hold between the ions on the two sides of the membrane,

$$[\mathrm{Na}]^{\mathrm{I}}/[\mathrm{Na}]^{\mathrm{II}} = [\mathrm{SnO_3}]^{\mathrm{II}}_n/[\mathrm{SnO_3}]^{\mathrm{I}}_n = [\mathrm{OH}]^{\mathrm{II}}/[\mathrm{OH}]^{\mathrm{I}} \quad . \quad (1)$$

$$RT/F \, . \log_e [\mathrm{Na}]^{\mathrm{I}}/[\mathrm{Na}]^{\mathrm{II}} = \varepsilon \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ε is the membrane potential and $[\mathrm{Na}]^{\mathrm{I}}$, $[\mathrm{SnO_3}]^{\mathrm{I}}_n$, and $[\mathrm{OH}]^{\mathrm{I}}$ represent the activities of the corresponding ions in the sol chamber,* and $[\mathrm{Na}]^{\mathrm{II}}$, $[\mathrm{SnO_3}]^{\mathrm{II}}_n$, and $[\mathrm{OH}]^{\mathrm{II}}$ the analogous quantities in the water chamber. It follows from (1) that

$$[\mathrm{SnO_3}]^{\mathrm{I}}_n \times [\mathrm{Na}]^{\mathrm{I}} = [\mathrm{SnO_3}]^{\mathrm{II}}_n \times [\mathrm{Na}]^{\mathrm{II}}$$

or

$$[\mathrm{SnO_3}]^{\mathrm{I}}_n = [\mathrm{SnO_3}]^{\mathrm{II}}_n \times [\mathrm{Na}]^{\mathrm{II}}/[\mathrm{Na}]^{\mathrm{I}} \quad . \quad . \quad . \quad . \quad (3)$$

Assuming complete dissociation of the electrolytes in the water chamber, $[\mathrm{Na}]^{\mathrm{II}}$ and $[\mathrm{SnO_3}]^{\mathrm{II}}_n$ can be determined by analysis. Therefore, in order to know the value of $[\mathrm{SnO_3}]^{\mathrm{I}}_n$ in the sol chamber a measurement of sodium-ion concentration is necessary. Furthermore, a knowledge of this ionic concentration in the two chambers will enable us to calculate the membrane potential and will also give an idea of the extent of dissociation of the colloidal complex. An attempt was therefore made to measure the sodium-ion activity by using sodium amalgam electrodes. Unfortunately this did not prove successful : the potential of the amalgam electrode fell continuously and after some time the solution turned grey, indicating that the nascent hydrogen evolved by the action of sodium on water reduced the stannic oxide.

The value of $[\mathrm{SnO_3}]^{\mathrm{I}}_n$ can, however, be calculated from the measurement of membrane potential. From (1) and (2) we have at 25°,

$$\varepsilon = 0{\cdot}059 \log [\mathrm{SnO_3}]^{\mathrm{II}}_n/[\mathrm{SnO_3}]^{\mathrm{I}}_n$$

or

$$[\mathrm{SnO_3}]^{\mathrm{I}}_n = [\mathrm{SnO_3}]^{\mathrm{II}}_n \times 10^{-\varepsilon/0{\cdot}059} \quad . \quad . \quad . \quad . \quad (4)$$

At lower ratios of $\mathrm{SnO_2 : Na_2O}$ the membrane potential becomes very small and then the distribution of the diffusible ions becomes the same in both the chambers. The results are given in Table II, the slight dilution in the sol chamber (see p. 2291), which would affect the final results by less than 1·5%, having been ignored.

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* $[\mathrm{SnO_3}]^{\mathrm{I}}_n$ represents the total concentration of the simple and complex stannates.

TABLE II.

Parchment membrane.

Ratio $SnO_2 : Na_2O$, mols.	SnO_2 in water chamber, g./100 c.c.	ϵ, volt.	Diffusible SnO_2 in sol chamber, g./100 c.c., calc.	Total diffusible SnO_2, g./100 c.c.	$2 \times SnO_2$ in water chamber, g./100 c.c.
17·2	0·0042	0·022	0·0018	0·0060	0·0084
12·1	0·0141	0·017	0·0073	0·0214	0·0282
9·3	0·0197	0·010	0·0133	0·0330	0·0394
6·9	0·0304	0·007	0·0230	0·0534	0·0608
4·5	0·0427	0·004	0·0365	0·0792	0·0854
3·6	0·0831	0·002	0·0769	0·1600	0·1662
2·3	0·0903	—	—	—	0·1806
2·0	0·1065	—	—	—	0·2130
*1·0	0·0556	—	—	—	0·1112
*0·5	0·0340	—	—	—	0·0680

* For molar ratios 1 and 0·5 there were 7·5 g. and 3·79 g. respectively of SnO_2 per litre.

The above table shows that at higher ratios of $SnO_2 : Na_2O$ the amount of diffusible stannic oxide per 100 c.c. in the sol chamber is much less than that in the water chamber. This difference, however, diminishes as the proportion of alkali increases, and for the ratio 3·6 the deficiency is only 7%. In the last column are given the values obtained by doubling the amount of stannic oxide per 100 c.c. in the water chamber. For the ratio 3·6, the values in cols. 5 and 6 differ by only 3·7%; at lower ratios the difference would be still less, and hence the total amount of diffusible stannic oxide per 100 c.c. of the sol is double that present in 100 c.c. of the water chamber. It can therefore be concluded that, even for the ratio 0·5, only 19% of the total stannic oxide is diffusible and the remaining 81% is in the colloidal condition.

It is seen from Table I that when the ratio $SnO_2 : Na_2O$ is 12·1, the ratio of distribution of Na_2O in the two chambers is 8·7, whereas the ratio of the sodium ions calculated from the membrane potential is only 1·94. This shows that the greater proportion of the colloidal complex containing Na_2O is undissociated, and only a small portion dissociates into a colloidal anion and the $Na^{\cdot}$ kation.

One of the assumptions on which relations (1) and (2) are based is that all the diffusible ions are univalent (see p. 2294); this can be verified by determining $[OH]^{I}$ and $[OH]^{II}$ by the *E.M.F.* method and comparing the observed membrane potential with that calculated from the expression

$$RT/F \,.\, \log_\epsilon [OH]^{II}/[OH]^{I} = \varepsilon \quad . \quad . \quad . \quad . \quad (5)$$

The results given on the next page show sufficiently good agreement to justify the above assumption.

$SnO_2 : Na_2O$, mols.	$[OH]^{II} \times 10^4$.	$[OH]^{I} \times 10^4$.	ϵ, calc. (volt).	ϵ, obs. (volt).
12·1	9·5	4·9	0·017	0·017
9·3	27·6	19·0	0·009	0·010
6·9	48·0	37·3	0·0065	0·007

Zsigmondy and his co-workers (*loc. cit.*) measured the osmotic pressure of stannic oxide sols, in which the ratio $SnO_2 : K_2O$ varied from 200 to 50, against their respective dialysed solutions. With increasing proportion of alkali an increase in the osmotic pressure was observed. This was interpreted as being due to an increase in the number of colloidal particles as a result of disintegration of the bigger ones. Similar measurements of osmotic pressure were undertaken in the present case, in the hope that they might give some idea of the average molecular weight of the colloidal aggregates, but the pressure showed a continuous diminution with increase in the proportion of alkali. The turbidity of the sol at first diminished as increasing quantities of alkali were added until the ratio 4 was reached, after which it began to increase again, the sol in which the ratio was 2 being very turbid. This seems to show that there is probably no relation between the number of colloidal particles and the observed osmotic pressure, the latter being mainly due to the excess concentration of the diffusible ions inside the sol chamber as a consequence of the Donnan equilibrium. This conclusion can be tested by calculating the osmotic pressure from this excess concentration and comparing the calculated values with the observed.

If C denotes this excess, then

$$C = [Na]^{I} + [SnO_3]^{I}_n + [OH]^{I} - [Na]^{II} - [SnO_3]^{II}_n - [OH]^{II} \quad (6)$$

In the water chamber, for the maintenance of electrical neutrality we have

$$[Na]^{II} = [SnO_3]^{II}_n + [OH]^{II},$$

and from (1) and (2)

$$\frac{[Na]^{I}}{[Na]^{II}} = \frac{[SnO_3]^{II}_n}{[SnO_3]^{I}_n} = \frac{[OH]^{II}}{[OH]^{I}} = e^{\epsilon F/RT} = K \text{ (say)} \quad . \quad . \quad (7)$$

Substituting these values of $[Na]^{I}$,$[SnO_3]^{I}_n$, and $[OH]^{I}$ in (6), we get

$$\begin{aligned} C &= K[Na]^{II} + ([SnO_3]^{II}_n + [OH]^{II})/K - 2[Na]^{II} \\ &= K[Na]^{II} + [Na]^{II}/K - 2[Na]^{II} \\ &= [Na]^{II}\{K + 1/K - 2\} \quad . \quad . \quad . \quad . \quad . \quad (8) \end{aligned}$$

If the osmotic pressure of the colloidal particles be negligible, then the observed pressure should be equal to $RTC = RT[Na]^{II}/(K + 1/K - 2)$. The osmotic pressure was measured by using collodion thimbles cemented on to glass tubes of suitable diameter by collodion. The arrangement was such as to preclude contamination of the solutions by carbon dioxide from the air. In Table III the osmotic pressure (P) is given in cm. of water.

TABLE III.

Parchment membrane.

$SnO_2 : Na_2O$, mols.	ϵ, volt.	K.	$[Na]^{II}$.	P, calc.	P, obs.
17·2	0·022	2·37	0·00116	23·2	21·5
12·1	0·017	1·94	0·00168	19·2	17·3
9·3	0·010	1·48	0·00374	14·8	13·2
6·9	0·007	1·32	0·00639	12·6	11·0
4·5	0·004	1·17	0·01374	8·7	9·8
3·6	0·002	1·08	0·01964	3·0	6·6
2·3	0	1·00	0·03410	0	5·0

In view of the fact that a small error in K will introduce a relatively large error in the calculated values of P, the agreement is not unsatisfactory as far as the molar ratio 4·5. It will, however, be noticed that for ratios of 6·9 and above the calculated values of osmotic pressure are higher than the observed; below this they are lower and rapidly approach zero, whereas the observed pressure diminishes slowly. Two alternative explanations might be suggested for this discrepancy: (1) that the assumption that all the diffusible ions are univalent no longer holds for ratios lower than 4·5, or (2) that the colloidal particles exert a small but appreciable osmotic pressure.

Summary.

1. The action of sodium hydroxide on stannic oxide sols in which the ratio $SnO_2 : Na_2O$ varied from 17·2 to 0·5 has been investigated at ordinary temperature. The results show that even at the lowest value of this ratio the amount of diffusible stannic oxide does not exceed 19%, the remaining 81% being in the colloidal condition.

2. Within the range investigated, the membrane potential calculated on the assumption that the diffusible ions are all univalent agrees with the observed value.

3. The ratio of the activity of the sodium ions in the sol to that in the water chamber, deduced from the membrane potential, is much less than the ratio of total Na_2O in the two chambers as determined by titration. This indicates that the dissociation of the colloidal complex, consisting of Na_2O and SnO_2, is small.

4. For ratios of 4·5 and above, the observed osmotic pressure can be accounted for as being due to the excess concentration of diffusible ions in the sol chamber as a result of the Donnan equilibrium, but at lower ratios the calculated values are much too small.

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