

CCCXCVII.—*The Interaction of Acids and Neutral Salts with Stannic Oxide and its Relation to Electrical Charge.*

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IN a previous paper (J., 1926, 2605) the inadequacy of the chemical theory to account for the development of an acid reaction when hydrated oxides of manganese are treated with solutions of neutral salts has been pointed out. It has also been shown how Mukherjee's theory of exchange adsorption (*Phil. Mag.*, 1922, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 191) satisfactorily explains the facts.

According to this theory, the liberation of hydrogen ions is to be attributed to their displacement from the double layer by the kations in solution. Like the oxides of manganese, hydrated stannic oxide is also known to liberate acids when brought in contact with solutions of neutral salts. As early as 1812, from his investigations on the properties of stannic oxide prepared by various methods, Berzelius concluded that the substance is acidic in nature and exists in two forms—the  $\alpha$ - and  $\beta$ -stannic acids. There is, however, considerable controversy over the actual existence of these different forms. The so-called  $\alpha$ -acid may be prepared by the hydrolysis of stannic chloride or sulphate solution, or by the action of alkalis on them in the cold; the  $\beta$ -acid may be obtained by the action of concentrated nitric acid on metallic tin. The existence of definite hydrates of the two acids has also been reported by different investigators (compare Weiser, *J. Physical Chem.*, 1922, 26, 654). Van Bemmelen ("Die Absorption," 1910, 59, 66) studied the dehydration of stannic oxide prepared by different methods, but his results do not confirm the existence of any definite hydrate of either acid. Mecklenburg (*Z. anorg. Chem.*, 1912, 74, 207) measured the adsorption of phosphoric acid by stannic oxide prepared at different temperatures, and showed that by suitable variation of temperature it is possible to obtain samples having all grades of properties intermediate between the  $\alpha$ - and the  $\beta$ -acid. Hence he concluded that both acids are colloidal in nature and that the difference in their properties is mainly due to the difference in the size of their particles, the  $\alpha$ -acid being the more finely divided. Recently the question of the formation of stable hydrates of stannic oxides has again been raised by Willstätter and his collaborators (*Ber.*, 1924, 57, 63). Their views have, however, been adversely criticised by Posnjak (*J. Physical Chem.*, 1926, 30, 1073), who investigated the X-ray spectra of both the  $\alpha$ - and the  $\beta$ -oxide. His results seem strongly to support the views of Mecklenburg, for the lines from the  $\alpha$ -acid are wider than those from the  $\beta$ -acid, showing that the former possesses particles of finer size than the latter. In view of these controversies, the interaction of the  $\alpha$ - and  $\beta$ -stannic oxides with electrolytes was investigated.

#### EXPERIMENTAL.

$\beta$ -Stannic acid, prepared by the action of concentrated nitric acid on pure metallic tin, was washed by decantation with boiling water, and then with boiling conductivity water. The final washing was done under suction on a Buchner funnel until the  $p_H$  of the wash liquid rose to 6.0. When 5 g. of this sample were shaken with 100 c.c. of water its  $p_H$  changed from 6.4 to 5.8.

The  $\alpha$ -acid was obtained by adding dilute ammonia to a solution of stannic chloride at 5°. The precipitate was washed several times with cold water, then with dilute nitric acid to remove the last traces of ammonia, and finally with conductivity water until the  $p_H$  of water in contact with it was 6.0.

*Estimation of the Total Amount of Hydrogen Ions replaceable by the Kation of a Neutral Salt.*—The  $\alpha$ - and the  $\beta$ -oxide are known to form alkali salts of the form  $R_2O, SnO_2$  and  $R_2O, 5SnO_2$ , respectively (compare J. N. Friend, "Text Book of Inorganic Chemistry," Vol. V, p. 533). Since the samples that we are dealing with liberate hydrogen ions in contact with neutral salts, the question naturally arises as to what will be the final composition of the substances when all the hydrogen ions are removed by washing with the solution of a salt such as barium chloride. A definite weight of hydrated stannic oxide was therefore shaken with a known volume of saturated barium chloride solution ( $p_H$  6.6) in a Pyrex-glass bottle for 15 minutes. After 24 hours as much as possible of the clear upper liquid was withdrawn and its  $p_H$  determined by either the *E.M.F.* or the indicator method. A measured volume of fresh barium chloride solution was added and the whole process repeated many times. With the progress of washing the  $p_H$  of the solution rose continuously as shown by the following data for 3 g. of the  $\beta$ -oxide (water content, 55%) :

Vol. of solution added, c.c.	Vol. of solution withdrawn, c.c.	Final $p_H$ of solution.
200	160	3.1
200	160	3.2
200	200	3.3

Towards the end, however, the hydrogen-ion concentration changed very slowly, and a small quantity of 0.2*N*-barium hydroxide was therefore added to bring the  $p_H$  of the solution to 6.6. In this way it is found that for every 6.6 g.-mols. of the  $\beta$ -oxide there is 1 g.-atom of replaceable hydrogen.

The total amount of replaceable hydrogen ions was also estimated by a different method. To a large volume of saturated barium chloride solution in contact with stannic oxide barium hydroxide solution was added in small quantities at a time, each addition being followed by a vigorous shaking. Here also, with both the  $\alpha$ - and the  $\beta$ -oxide, the  $p_H$  of the solution was found to increase regularly with increasing amounts of alkali added. The addition of alkali was continued until the  $p_H$  of the barium chloride solution had risen to about 6.7. By this method it is found that every 6.3 g.-mols. of the  $\beta$ -oxide contain 1 g.-ion of replaceable hydrogen, which agrees fairly closely with the value obtained by the previous method.

In the case of the  $\alpha$ -oxide, it is found that for every 4.9 g.-mols. of  $\text{SnO}_2$  there is 1 g.-ion of replaceable hydrogen. This shows that for every molecule of  $\text{SnO}_2$  the  $\alpha$ -oxide contains more replaceable hydrogen ions than the  $\beta$ -oxide. In both cases, however, the stoichiometric ratio  $\text{SnO}_2 : \text{H}$  is fractional. Further, the increase in  $p_{\text{H}}$  observed with repeated washing by barium chloride solution or with successive additions of small quantities of alkali cannot be satisfactorily explained from the chemical point of view of insoluble salt formation. This has been discussed in detail in the previous paper (*loc. cit.*).

*Electrical Adsorbability of the Kations and their Capacity to liberate Hydrogen Ions.*—20 G. of the  $\beta$ -oxide were shaken with 200 c.c. of the electrolyte solution as before. After 24 hours the clear supernatant solution was withdrawn, and its  $p_{\text{H}}$  measured by the *E.M.F.* method. In this way the concentration of hydrogen ions liberated by different salts at the same gram-molecular concentration was determined. The electrical charge of the substance was measured by the electro-endosmotic method. The arrangement used is an improvement of that previously described by the author (*loc. cit.*). The electro-endosmotic flow of a liquid through a porous diaphragm depends, among other factors, directly on the potential across the latter. In the present arrangement a definite potential as indicated by a voltmeter was applied between the electrodes, and could be maintained constant within  $\pm 1$  volt by means of an adjustable resistance. The potential across the diaphragm was determined in the following way. The total resistance, consisting of that of the diaphragm and the electrolyte, was measured by the conductivity method. The electrodes were then lowered so as just to touch the ends of the diaphragm and the resistance was measured again. If  $T$  and  $D$  be the total and the diaphragm resistances, respectively, then the potential across the diaphragm is given by the expression  $DV/T$ , where  $V$  is the potential indicated by the voltmeter when the electrodes were in their original position (*i.e.*, when the resistance between them was  $T$ ). In order that the potential across the diaphragm should remain constant during the electro-endosmotic experiment it is necessary that  $D/T$  should remain constant: the maximum variation in this ratio before and after the experiment was always within 3%, and the mean was used in calculating the potential. The value of  $D/T$  was, however, found to increase with increasing concentration of the electrolytes, even when the other factors, such as the length of the diaphragm or the distance between the electrodes, were constant; for the same concentration of different electrolytes, however, it was almost the same, as seen from the following results:

Concentration of electrolyte.	Values of $D/T$ for		
	KCl.	LiCl.	NaCl.
0.0002N	0.53	0.54	0.53
0.001	0.55	0.55	0.54
0.002	0.56	0.57	0.56
0.004	0.57	0.57	0.56

This increase in the ratio of  $D/T$  is probably to be attributed to the relatively high value of the surface conduction in the capillaries, especially when the concentration of the electrolyte inside them is very low (compare Smoluchowski, *Physikal. Z.*, 1905, 6, 529; Freundlich, "Kapillarchemie," 2nd edtn., p. 249).

Owing to this surface conduction the resistance of the diaphragm does not diminish proportionately as the electrolyte concentration increases. The total resistance  $T$ , on the other hand, is determined mainly by that of the electrolyte, and hence it diminishes almost in proportion to the increase in the electrolyte concentration. The consequence is that the ratio  $D/T$  increases with the increasing concentration of the electrolyte. The variation of  $D/T$  brings about a corresponding change in the value of the potential across the diaphragm. It is therefore evident that a strict comparison of the results at different concentrations of the electrolytes is only possible when the necessary correction due to this variation has been introduced. In Table I the distance moved by the air bubble corresponds to a potential of 100 volts across the diaphragm. The plus and the minus signs indicate the charge of the diaphragm.

TABLE I.

$\beta$ -Stannic oxide (water content, 55%).

Concentration of electrolyte (g.-mols.).	$p_H$ values for					
	MgCl <sub>2</sub> .	BaCl <sub>2</sub> .	SrCl <sub>2</sub> .	LiCl.	NaCl.	KCl.
2.00	—	—	—	3.70	4.00	4.16
1.00	3.28	3.34	3.37	3.84	4.09	4.20
0.75	3.36	3.40	3.44	—	—	—
0.50	3.45	3.47	3.50	3.98	4.16	—
0.25	3.56	3.59	3.61	—	—	—
0.20	—	—	—	4.13	—	—
0.10	3.65	3.68	3.70	—	—	—
0.05	3.68	—	—	—	—	—
0.04	—	—	—	4.22	4.26	4.30
0.002	3.78	3.81	3.82	—	—	—

  

Concentration of electrolyte (g.-mols.).	Distance moved by the air bubble (cm. in 2 mins.).					
	MgCl <sub>2</sub> .	BaCl <sub>2</sub> .	SrCl <sub>2</sub> .	LiCl.	NaCl.	KCl.
0.0	-0.43	-0.43	-0.43	-0.43	-0.44	-0.44
0.0003	+0.70	+0.35	+0.30	-1.03	-1.20	-1.35
0.001	+1.20	+1.0	+0.90	-0.82	-0.93	-0.95
0.002	+1.30	+1.1	+1.0	-0.48	-0.54	-0.65
0.004	+1.37	+1.35	+1.1	-0.32	-0.30	-0.47
0.008	+1.40	+1.35	—	-0.16	-0.22	—

It will be seen from the above data that the capacity of the kations to liberate hydrogen ions is in the order  $Mg^{++} > Ba^{++} > Sr^{++} > Li^+ > Na^+ > K^+$ . The electro-endosmotic experiments show that hydrated stannic oxide is charged negatively in contact with water, and that the capacity of the kations to diminish the negative charge of the surface, as indicated by the movement of the air bubble, is in the same order. In the case of the alkali-metal chlorides at low concentrations the negative charge of the surface is greater than with pure water. The bivalent kations reverse the negative charge of the surface at as low a concentration as 0.0003M. The concentration of the liberated hydrogen ions, however, increases continuously up to a concentration of 1M of the bivalent kations. This shows that hydrogen ions continue to be liberated even after the surface has become positively charged.

*The Adsorption Theory and the Liberation of Hydrogen Ions by Kations.*—As stannic oxide is negatively charged, it follows from Mukherjee's theory (*loc. cit.*) that the hydrogen ions are held in the neighbourhood of the surface by electrostatic attraction. Hence, the greater the capacity of a kation to diminish the negative charge the greater should be its effect on the liberation of hydrogen ions, and that is what has been observed. The observed reversal of electrical charge of stannic oxide by bivalent kations, and the change in  $p_H$  on repeated washing with barium chloride solution can be explained in exactly the same way as before (Ghosh, *loc. cit.*, p. 2611). The rise in  $p_H$  with successive additions of alkali also admits of a simple explanation. The addition of alkali in small amounts simply removes the liberated hydrogen ions, and therefore produces the same effect as that of withdrawing the original acidic barium chloride solution and replacing it by a fresh one of  $p_H$  6.6. That the  $\alpha$ -oxide contains more replaceable hydrogen ions, mol. for mol., than the  $\beta$ -oxide, only shows that the former consists of finer particles and hence possesses greater active surface than the latter.

#### *The Adsorption of Anions.*

Reference to the electro-endosmotic data shows that at low concentrations of the chlorides of the univalent kations the negative charge of hydrated stannic oxide increases. This may be due either (1) to the primary adsorption of the anion, or (2) to a redistribution of the kations in the "double layer" leading to an increase in the number of "uncovered" primarily adsorbed anions (which in this case may be the  $SnO_3H^-$  ion) (compare Mukherjee and Iyer, *J. Indian Chem. Soc.*, 1926, **3**, 321). Among the kations, potassium has been found to be least effective in diminishing the negative charge of the surface. A measurement of adsorption of

potassium salts may therefore give some idea of the adsorption of anions, since any adsorption of the salt can in this case be attributed to this cause. For this purpose 10 g. of the substance were shaken in a Pyrex-glass bottle with 100 c.c. of a solution of potassium salt, and after 24 hours the solution was analysed. The results given below (for  $\beta$ -oxide of 54.4% water content) show that there is hardly any primary adsorption of anions :

## Weights of salt per 10 c.c.

Initially after correcting for hydration.	After adsorption.	Amount adsorbed.
	$\text{KNO}_3$ .	
0.9757 g.	0.9748 g.	+0.0009 g.
0.2442 ,,	0.2450 ,,	-0.0008 ,,
0.0490 ,,	0.0488 ,,	+0.0002 ,,
	$\text{K}_2\text{SO}_4$ .	
0.1820 g.	0.1809 g.	+0.0011 g.
0.0462 ,,	0.0458 ,,	+0.0004 ,,

*Adsorption of Acids and its Relation to Electrical Charge.*

A weighed quantity of hydrated stannic oxide was shaken as before (p. 3029) with a measured volume of an acid solution of known strength, and after 24 hours the acid concentration in the supernatant liquid was determined, the *E.M.F.* method being used for low concentrations, and alkali titration for others. As the hydrated oxide contained a large amount of water, a correction had to be introduced for its diluting effect. The amount of adsorption was calculated by multiplying the difference between the corrected initial concentration of the acid and its concentration after adsorption by the total volume of the solution. Tin was not present in the acid solutions within the range of concentrations investigated; the observed adsorption was therefore not due to the formation of any soluble tin salt. The electrical charge was measured by the electro-endosmotic method as previously described. The sample used in Table II is different from that used in the other table. In the following tables  $\alpha$  denotes the number of g.-ions of hydrogen adsorbed, and  $d$  the distance (in mm.) moved by the air bubble in 2 minutes. In each case 200 c.c. of acid solution were used, together with 20 g. of  $\beta$ -oxide of 54.5% water content.

The electro-endosmotic results show that all the acids, except phosphoric, reverse the initial negative charge of the surface. This indicates that hydrogen ions are primarily adsorbed by the surface. In the case of sulphuric acid, it will be noticed that with increasing concentration the positive charge at first increases, reaches a maximum, and then diminishes again, whereas for nitric

TABLE II.

Initial conc. (corr.).	Final conc.	$\alpha \times 10^4$ (obs.).	$\alpha \times 10^4$ (calc.).	Initial conc. (corr.).	Final conc.	$\alpha \times 10^4$ (obs.).	$\alpha \times 10^4$ (calc.).
Sulphuric acid ( $K_0 = 1.66$ , $K_1 = 188^*$ ).				Nitric acid ( $K_0 = 0.121$ , $K_1 = 28$ ).			
0.124	0.0835	85	83	0.189	0.172	(35.8)	35.8
0.0935	0.0550	(80.8)	80.8	0.143	0.126	34.6	33.6
0.0720	0.0370	73.5	77	0.096	0.082	29.4	30.0
0.0475	0.0170	64	67	0.063	0.052	25.8	25.7
0.0318	0.0082	49.6	53	0.019	0.0134	(11.8)	11.8
0.0186	0.0031	(32.6)	32.6	0.0091	0.006	6.4	6.2
0.0119	0.0015	21.8	19.8	0.0052	0.0036	3.4	3.9
0.0056	0.0007	10.4	10.3	0.00114	0.00075	0.8	0.89
0.0028	0.00037	5.2	5.7				

\*  $K_0$  and  $K_1$  are constants (see below), and the values of  $\alpha$  which are enclosed in parentheses in each case were used in calculating the corresponding values of the constants.

acid it continues to increase within the range investigated. The ratio of the total change in electrical charge (as indicated by the movement of the air bubble) to the amount of hydrogen ions adsorbed, however, diminishes continuously from the start, showing that with increasing concentration of the acids the electrical adsorption of the anions is preponderating more and more over the primary adsorption of the hydrogen ions. In the above table the calculated values of  $\alpha$  were obtained from the expression  $K_0C/(1 + K_1C)$  (compare Langmuir), where  $K_0$  and  $K_1$  are constants. It can be easily shown that  $K_0/K_1$  is a measure of the active surface.

The agreement between the observed and calculated values is fair. A comparison of the adsorption of the acids with their effect on the electrical charge shows that the adsorption is greater the less the positive charge of the surface. The order of adsorption of the acids is  $H_3PO_4 > H_2SO_4 > HCl > HNO_3, CCl_3 \cdot CO_2H, C_6H_5 \cdot SO_3H$ . The magnitude of adsorption of the monobasic acids is very nearly the same, that of hydrochloric acid, however, being slightly the greatest. The capacity of the different acids to increase the positive charge of the surface is in the order  $HNO_3, etc. > HCl > H_2SO_4 > H_3PO_4$ . The above results therefore lead to the conclusion that there exists a sort of inverse proportionality between the adsorption of acids and their effect on the positive charge of the surface. This is to be expected also on theoretical grounds: the other factors remaining constant, the chance of a hydrogen ion reaching the surface is the less the greater the positive charge of the surface, owing to increasing electrostatic repulsion.

(1) When an acid with a multivalent anion is used, the anion because of its high electrical adsorbability diminishes the positive charge of the surface, and hence favours the further primary adsorp-



TABLE III.

[100 C.c. of solution and 10 g. of hydrated  $\beta$ -stannic acid (water content, 54.5%) were used throughout the experiments here recorded.]

Initial conc. (corr.)	Final conc.	$\alpha \times 10^4$ (obs.)	$\alpha \times 10^4$ (calc.)	Initial conc. (corr.)	Final conc.	$\alpha \times 10^4$ (obs.)	$\alpha \times 10^4$ (calc.)
Phosphoric acid ( $K_0 = 6.1$ , $K_1 = 570$ ).				Hydrochloric acid ( $K_0 = 0.161$ , $K_1 = 55$ ).			
0.177	0.074	108	105	0.0492	0.0316	(18.5)	18.5
0.131	0.038	(97.6)	98	0.0354	0.0206	15.5	15.3
0.097	0.016	85	87	0.0192	0.0102	9.5	10.6
0.0646	0.005	(62.6)	62	0.0118	0.0054	(6.7)	6.7
0.0165	0.0006	16.6	13.4	0.00495	0.0031	4.1	4.3
Trichloroacetic acid ( $K_0 = 0.073$ , $K_1 = 22.8$ ).				Benzenesulphonic acid ( $K_0 = 0.064$ , $K_1 = 23.4$ ).			
0.093	0.074	(20.0)	20.0	0.096	0.079	(17.8)	17.8
0.0705	0.054	17.3	17.7	0.076	0.061	15.8	16.2
0.0475	0.034	14.2	13.9	0.0481	0.0366	12.1	12.5
0.024	0.0161	8.2	8.5	0.0244	0.0170	7.8	7.8
0.0121	0.0076	(4.7)	4.7	0.0124	0.0082	(4.4)	4.4
0.0011	0.0038	2.3	2.5	0.0062	0.0043	2.0	2.5
Nitric acid.				Sulphuric acid.			
0.091	0.072	20.0	—	0.071	0.0328	40.0	—
0.0467	0.033	14.3	—	0.0475	0.0146	34.6	—

*Electro-endosmotic measurements.*

Initial conc. (corr.)	Final conc.	$\alpha \times 10^4$ .	$d$ .	$\Delta d$ .	$\Delta d/\alpha \times 10^3$ .
Amount of substance = 16 g.					
Sulphuric acid. Volume of solution = 200 c.c.					
0.0311	0.0082	49	+ 2.2	6.2	1.3
0.0184	0.0031	32	+ 2.8	6.8	2.1
0.0119	0.0015	20	+ 3.8	7.8	3.9
0.0057	0.0007	10	+ 2.7	6.7	6.7
0.0028	0.00037	5	+ 1.4	5.4	10.8
0	0	0	- 4.0	—	—
Nitric acid. Volume of solution = 200 c.c.					
0.019	0.0134	12	+13.0	17.0	14
0.009	0.006	6.4	+11.0	15.0	23
0.0052	0.00036	3.4	+ 9.7	13.7	40
0.00114	0.00075	0.8	+ 7.2	11.2	140
0	0	0.0	- 4.0	—	—

Potential across the diaphragm = 80 volts.  
Amount of substance = 15 g.

Distance (mm.) moved by the air bubble in 2 mins.

Initial conc. of acid.	$H_3PO_4$ .	$H_2SO_4$ .	HCl.	$HNO_3$ .	$CCl_3 \cdot CO_2H$ .	$C_6H_5 \cdot SO_3H$ .
0.02	- 2.0	+ 2.8	—	—	—	—
0.01	- 2.6	+ 3.4	—	—	—	—
0.008	- 2.8	—	+ 12.8	+ 13.0	+ 14.0	+ 14.4
0.004	—	+ 1.8	+ 11.0	+ 12.0	+ 12.3	+ 12.3

tion of hydrogen ions; moreover, multivalent anions may bring about increase in adsorption of hydrogen ions in another way. (2) When a multivalent anion is electrically adsorbed (or bound) opposite to one of the primarily adsorbed hydrogen ions, all its valencies except one are free, and hence a number of hydrogen ions corresponding to the number of the free valencies of the anion will be drawn near the surface. This will produce the same effect as an increase in the number of primarily adsorbed hydrogen ions. (3) There is yet another factor which may influence the adsorption of hydrogen ions. If the surface be positively charged, there will be an equivalent number of anions surrounding it. Some of these will be free and their number will increase with increasing electrical charge. If these free ions exist in the form of a diffuse layer of thickness, say,  $\delta$  round the surface, then within this layer the average concentration of hydrogen ions will be much less than in the bulk of the solution. If the electrical charge is reduced to zero or brought to a very low value by increasing the anion concentration, then the value of  $\delta$  becomes negligibly small and hence a volume of liquid  $S\delta$  (where  $S$  is the total solid-liquid interfacial area) which was formerly only partly accessible to the hydrogen ions now becomes completely so. This will also produce an apparent increase in the adsorption of hydrogen ions.

*Effect of Neutral Salts on the Adsorption of Hydrogen Ions.*

The effect of electrical charge on the adsorption of acids can also be tested in the following way. If the concentration of the hydrogen ions be maintained constant and that of the anion is increased by adding a neutral salt with an inactive kation, the positive charge of the surface will be diminished, and hence the adsorption of hydrogen ions will be greater in presence of a neutral salt than in its absence. It will be seen from the previous experiments that of all the kations the potassium ion is the least active; potassium salts were therefore used in the following experiments. The adsorption of acid was measured as previously described.

It will be observed that the adsorption of nitric acid is considerably greater in presence of potassium nitrate than in its absence. When the concentration of the salt is kept constant and that of the acid varied, the percentage rise in adsorption increases with the decreasing concentration of the acid. Again, keeping the concentration of nitric acid constant and increasing that of the salt, the adsorption of the acid is found to increase. Here we are not dealing with any multivalent anion, and hence increase in adsorption is to be attributed to the diminution of the positive charge of the surface and also of the thickness of the diffuse layer  $\delta$ .

TABLE IV.

Amount of substance taken, 10 g. (water content, 54.5%); volume of solution = 100 c.c.

Initial concs. (corr.).	Final conc. of acid.		Amount of acid adsorbed (as c.c. of 0.2N).
Mixtures of HNO <sub>3</sub> + KNO <sub>3</sub> .			
HNO <sub>3</sub> .	KNO <sub>3</sub> .		
0.091	0	0.072	10.0
0.093	0.25	0.069	12.5
0.0467	0	0.0334	7.0
0.0475	0.25	0.0296	9.4
0.024	0	0.0154	4.5
0.024	0.25	0.0092	7.8
0.0244	0.1	0.0110	7.1
0.0244	0.05	0.0124	6.3
Mixtures of HNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> .			
HNO <sub>3</sub> .	K <sub>2</sub> SO <sub>4</sub> .		
0.0910	0	0.0720	10.0
0.0940	0.2	0.0490	23.7
0.0467	0	0.0334	7.0
0.0467	0.2	0.0129	17.7
Mixtures of H <sub>2</sub> SO <sub>4</sub> + K <sub>2</sub> SO <sub>4</sub> .			
H <sub>2</sub> SO <sub>4</sub> .	K <sub>2</sub> SO <sub>4</sub> .		
0.0495	0	0.0154	18.0
0.0481	0.2	0.0158	17.0
0.0491	0.05	0.0156	17.6

The adsorption of hydrogen ions is much greater in the nitric acid-potassium sulphate mixture than in nitric acid and potassium nitrate. In this case, in addition to the two factors mentioned above, the effect of the multivalent anions makes itself felt. In the sulphuric acid-potassium sulphate mixture the adsorption of acid is not at all increased: on the contrary, a slight decrease in adsorption is observed. This is not surprising, for in presence of 0.015N-sulphuric acid the charge of the surface is very small (nearly zero), and hence an increase in the number of SO<sub>4</sub><sup>''</sup> ions is not likely to favour any further adsorption. The K<sup>+</sup> ions on the other hand can displace from the mobile layer some of the hydrogen ions associated with the electrically adsorbed SO<sub>4</sub><sup>''</sup> ions, and thus slightly decrease the adsorption.

*The Variation of Active Surface with the Amount of Substance taken.*—It has been emphasised that in the interaction of stannic oxide with electrolytes it is the solid-liquid interface that is directly taking part in the reaction. The question arises as to how the active surface increases with the amount of substance taken. It has already been mentioned that  $K_0/K_1$  is a measure of the active surface. Therefore, by taking different quantities of stannic oxide and determining the values of  $K_0$  and  $K_1$  for each quantity, it is possible to find how the active surface varies with the amount of substance. The adsorption of acid was measured as before. 100 C.c.

of a sulphuric acid solution were used, with 10 g. of the  $\beta$ -oxide (water content, 54.5%) in the first case and 5 g. in the second.

	Initial conc. (corr.).	Final conc.	$\alpha \times 10^3$ .	$K_0$ .	$K_1$ .	$K_0/K_1$ .
(1)	0.071	0.0328	4.0	1.03	228	0.0045
	0.0475	0.0146	3.46			
(2)	0.073	0.052	2.14	0.44	186	0.0024
	0.049	0.0295	1.99			

It will thus be seen that the active surface increases in the ratio 1 : 1.9 as the amount of substance is doubled.

### Summary.

1. A study of the interaction of hydrated stannic oxides with electrolytes shows that the adsorption theory offers a much better explanation of the observed facts than the chemical theory of insoluble salt formation.

2. In accordance with Mecklenburg's views, the  $\alpha$ -oxide has been found to possess greater active surface per unit weight, and hence finer particles, than the  $\beta$ -oxide.

3. The capacity of the kations to liberate hydrogen ions is in the order  $Mg^{++} > Ba^{++} > Sr^{++} > Li^+ > Na^+ > K^+$ , and, in satisfactory agreement with Mukherjee's theory, the same order has been observed in their effect on the negative charge of the surface.

4. The electro-endosmotic results indicate that the hydrogen ions are primarily adsorbed, and the adsorption of an acid is greater the less the positive charge of the surface. The order of adsorption of the acids is  $H_3PO_4 > H_2SO_4 > HCl > HNO_3, C_6H_5 \cdot SO_3H, CCl_3 \cdot CO_2H$ . The capacity of the acids to increase the positive charge of the surface is in the order  $HNO_3, etc. > HCl > H_2SO_4 > H_3PO_4$ . This leads to the conclusion that the greater the capacity of the anion to diminish the positive charge of the surface the greater is the adsorption of the hydrogen ions. The adsorptions of the kations and anions are thus not independent of each other.

5. In presence of salts with inactive kations, the adsorption of hydrogen ions is increased. In this respect, salts with multivalent anions are more effective than those with univalent anions.

6. The active surface has been found to vary nearly proportionately with the amount of substance.

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