CCCXLI.—*Parallelism between the Effect of Neutral Salts on the Electrical Charge of Hydrated Manganese Oxides and the Concentration of Hydrogen Ions liberated.*

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It is well known that hydrated manganese dioxide develops an acid reaction in contact with neutral solutions of salts (compare Friend, "Text-book of Inorganic Chemistry," VIII, p. 289). A solid of variable composition, depending on the conditions of preparation, is produced which can be represented as $x\mathrm{MnO_2},y\mathrm{MnO},z\mathrm{H_2O}$.* According to classical conceptions, the acid reaction is conditioned by the relative solubilities of the complex acidic solid and its corresponding salts. A parallel case where, instead of an acid, an alkaline reaction is developed is the action of potassium chloride on silver oxide (Noyes and Kohr, *Z. physikal. Chem.*, 1902, **42**, 336).

It has frequently been suggested that the acidic properties of clays or silica depend on the capacity of the substance to adsorb acids. Mukherjee (*Phil. Mag.*, 1922, **44**, 321; *J. Indian Chem. Soc.*, 1925, **2**, 191) has suggested that the liberation of acid is to be attributed to an interchange between cations in solution and hydrogen ions in the double layer, and he has developed a theory of such reactions based on his theory of adsorption of ions (Faraday Society Discussion, October, 1920) and the electrical double layer. He also states that the interaction of silica with electrolytes cannot be accounted for on the basis of our usual conceptions of ionic equilibrium in heterogeneous systems. On the other hand, Joseph (J., 1923, **123**, 2022; 1925, **127**, 2813) considers that the chemical point of view is sufficient to explain this reaction. Evidently, a change in our usual conceptions cannot be made unless there is strong experimental evidence against them. A detailed study was made of the oxides of manganese of variable composition with a view to obtain decisive evidence on the point. The existence of manganites (*e.g.*, $\mathrm{CaO,5MnO_2}$) corresponding to a definite acid or acids is not questioned; moreover, the substance must, broadly

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* The samples obtained in the present work contained traces of potassium.

speaking, behave like an acid, as it contains replaceable hydrogen ions. The question at issue is whether a better explanation of the facts is offered by considerations of solubility or by the conception of an equilibrium between hydrogen ions and cations in the double layer with those in solution. Our observations show that there is a close relationship between the effect of a cation on the electrical charge of the surface and its capacity to liberate hydrogen ions, as postulated by Mukherjee, and that this point of view undoubtedly gives a better explanation of the facts.

EXPERIMENTAL.

Material.—The substance used was obtained by mixing hot solutions of manganous sulphate and potassium permanganate containing a little sulphuric acid; except in one instance, the manganous sulphate was used in slight excess. The composition of the precipitate depends on the conditions of preparation. The approximate compositions of the samples used are :

Sample A, $16MnO_2,3MnO,332H_2O$.
,, B, $7{\cdot}3MnO_2,MnO,114H_2O$.
,, C, $9{\cdot}1MnO_2,0{\cdot}52MnO,92H_2O$.
Sample D, $8{\cdot}2MnO_2,0{\cdot}68MnO$.
,, E, $11MnO_2,1{\cdot}2MnO$.

(Sample C was prepared by using an excess of potassium permanganate solution.)

The first three samples, which were dried in air for 2—4 days, still contained considerable amounts of water; they were kept in stoppered bottles. The last two samples were used for electro-osmotic experiments; they were not dried in air, but were kept in contact with water.

The Stoicheiometric Relationship between the Number of Atoms of Manganese and of Replaceable Hydrogen.—Manganous acid corresponding to MnO_2,H_2O is unstable. The manganites described in the literature correspond to several complex acids, *e.g.*, CaO,MnO_2; $CaO,2MnO_2$; $CaO,5MnO_2$ (compare Friend, *op. cit.*, p. 286). The ratio of the number of acid hydrogen atoms to manganese atoms is therefore variable and depends on the conditions of preparation of the salt. As is well known, in the case of meta- and ortho-acids the potential number of replaceable hydrogen atoms per mol. of the non-metallic oxide is not identical with the actual basicity of the acid. Moreover, in the case of polybasic acids, the extent to which the successive hydrogen ions are replaced by cations depends on the corresponding dissociation constant and the alkalinity of the solution. It was therefore not possible to predict, from the existence of a number of manganites, the basicity of the material employed, especially as the solutions used were not alkaline but acid in reaction (*vide infra*). The number of hydrogen atoms replaceable under the experimental conditions, which is of interest as indicating the stoicheiometrical relations involved, was determined as follows: A mixture of 4 g. of the sample A and 200 c.c. of a saturated solution of barium nitrate (p_H 6·4—6·6) was thoroughly shaken in a resistance-glass (Pyrex) bottle and then left for 24 hours. A definite volume of the clear supernatant liquid was withdrawn, and its p_H determined by comparison with a set of indicator standards (Clark and Lubs). 200 C.c. of fresh barium nitrate solution were added to the bottle and the process was repeated. The results are in Table I, successive withdrawals usually corresponding to intervals of one day.

TABLE I (Sample A).

Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.	Vol. withdrawn (c.c.).	p_H.
150	2·3	200	4·4	200	5·5	200	6·0
200	2·7	200	4·5	200	5·6	200	6·2
200	3·1	200	4·6	200	5·6	200	6·2
200	3·5	200	4·8	200	5·8	200	6·3
200	3·8	200	5·0	200	5·8	200	6·3
200	4·0	200	5·4	200	6·0	200	6·4
200	4·2	200	5·4	200	6·0	200	6·4

The total acid set free as calculated from the above experiment is equivalent to about 1·46 c.c. of *N*-acid. Hence the number of replaceable hydrogen ions per g.-atom of manganese is 0·145. The results of two similar experiments, using different electrolytes and different samples, are given for comparison in Table II, from which it is seen that C contains a much smaller number of replaceable hydrogen ions per atom of manganese than A. Both samples, however, contain manganous oxide molecules, and, on the assumption that they form manganous manganite or the sesquioxide, which may be taken to have no "potential" acidity, the number of replaceable hydrogen ions per mol. of free manganese dioxide has been calculated (Table III, col. 5).

TABLE II.

Sample.	Amount taken.	Electrolyte.	Total acid set free (in c.c. of *N*-acid).	Number of replaceable hydrogen ions per atom of Mn.
A.	10 g.	Sat. potassium nitrate.	3·3	0·132
C.	25 g.	Sat. barium nitrate.	7·1	0·073

The ratio (atoms of quadrivalent manganese) : (replaceable hydrogen ions) is widely different in the two cases. Further, for the same sample the number of replaceable hydrogen ions per atom of

TABLE III.

Sample.	Electrolyte.	Ratio of replaceable hydrogen ions to		
		atoms of Mn.	mols. of MnO_2.	free mols. of MnO_2.
A.	KNO_3	0·132	0·156	0·19
	$Ba(NO_3)_2$	0·145	0·172	0·21
C.	$Ba(NO_3)_2$	0·073	0·077	0·082

manganese is somewhat different according as it is estimated by washing with saturated solutions of potassium nitrate or barium nitrate.

From Table I it appears that successive washings cause a regular fall in the hydrogen-ion concentration. An attempt to explain this fall on the basis of the usual chemical conceptions needs the assumption that a solid solution of the complex salt with the corresponding acid is formed, such that the solubility (or rather, activity) of the complex acid decreases, and the solubility (activity) of the salt increases in the way indicated by the variation in the concentration of hydrogen ions. Nothing is known, however, regarding the solubility of either the complex acid or its salts. The salts of alkali metals are very soluble and it is still more difficult to assume that the solid phase contains insoluble alkali-metal salts in equilibrium with a solution which has an acid reaction. The question is really one of the relative solubilities (activities) of the acid and the alkali-metal salt in a state of solid solution, but, in general, the solubilities of the alkali-metal salts are so great compared with that of the acidic substance that a quantitative consideration of the equilibrium conditions strongly points to the conclusion that the usual chemical conceptions are not likely to be of much service.

Generation of Acids in Contact with Neutral Solutions of Salts.—4 G. of the substance and 100 c.c. of a neutral salt solution were treated exactly as before (p. 2607) but the p_H of the supernatant liquid was now determined by *E.M.F.* measurements, using normal calomel electrodes and a potentiometer reading correctly to 0·5 millivolt. The results are in Tables IV and V. About 4 g. of the substance were also shaken with pure water, and the p_H of the water was changed from 6·2 to 5·4, showing that traces of acid were liberated.

TABLE IV (Sample A).

Conc. of electrolyte.	KCl.			NaCl.			LiCl.		
	E.M.F. (volt).	Temp.	p_H.	*E.M.F.* (volt).	Temp.	p_H.	*E.M.F.* (volt).	Temp.	p_H.
N	0·414	32°	2·16	0·414	34°	2·15	0·415	33°	2·17
N/5	0·420	31	2·28	0·427	33	2·37	—	—	—
N/10	0·425	33	2·34	0·433	33	2·47	0·439	33	2·57
N/100	0·435	33	2·50	0·451	34	2·76	0·470	30	3·11

TABLE V (Sample D).

Conc. of electrolyte.	$BaCl_2$.			$SrCl_2$.			$MgCl_2$.		
	E.M.F. (volt).	Temp.	p_H.	*E.M.F.* (volt).	Temp.	p_H.	*E.M.F.* (volt).	Temp.	p_H.
N/5	0·407	30°	2·06	0·414	30°	2·18	0·425	30°	2·36
N/10	0·410	30	2·11	0·417	30	2·23	0·427	30	2·40
N/50	0·417	30	2·23	0·424	30	2·35	0·435	33	2·50
N/100	0·422	30	2·31	0·431	33	2·44	0·439	33	2·59
N/200	0·437	30	2·56	0·440	33	2·59	—	—	—

The above tables show that the capacity of the cations to liberate hydrogen ions is in the order Ba > Sr > Mg > K > Na > Li. According to the chemical point of view, these results signify that the solubility (activity) of the corresponding complex salts in the solid solution should decrease in the above order for ions of equal valency. From this point of view it is not possible to predict *a priori* that the above order should represent the order of solubilities (activities) of the molecules. On the other hand, Mukherjee's theory predicts this order on theoretical grounds.

Table IV also shows that at high concentrations (about *N*) the p_H tends to the same limit for all the three univalent cations. (It was not possible to use higher concentrations of electrolytes because of the oxidation of the liberated hydrochloric acid by the manganese dioxide.) From the chemical point of view the p_H values at *N* concentrations show that the solubilities of the three alkali salts are identical. This conclusion contradicts the assumption of a difference in solubility which it is necessary to make in order to explain the behaviour of these electrolytes at lower concentrations. Within the range of concentrations examined, no manganese could be detected in solution.

With the bivalent cations the higher acidity developed precluded the use of higher concentrations, but probably here also practically the same p_H would have been observed for all of them.

The Adsorbability of Cations as determined from Electro-osmotic Experiments.—In contrast to the chemical point of view, the other theory attributes the liberation of hydrogen ions to the adsorption of cations. This theory also postulates that the adsorbability of a cation determines its capacity to diminish the negative charge of the surface. Electro-osmotic experiments were therefore carried out to determine the order of adsorption of the cations. The apparatus was a modified form of that used by Briggs (*J. Physical Chem.*, 1918, **22**, 256), the straight tube being replaced by a **U**-tube which was always filled with the precipitate between two marks symmetrically situated one on each limb. The electrodes were connected to the main (220 volts) circuit and the distance between them was maintained constant. The results are reproducible within 5%; those given in any one table were carried out under identical conditions and with the same apparatus. A different U-tube was used for the observations recorded in Table VIII. The rates of movement of the air bubbles are expressed in cm. per 3 minutes, but they only qualitatively represent the variation in the charge per unit area of the surface.

TABLE VI (Sample D).

	Electrolyte.			
Conc.	LiCl.	NaCl.	KCl.	$BaCl_2$.
0	—	− 9·8	−9·8	− 9·8
N/10000	—	—	—	− 8·3
N/5000	—	—	—	− 5·4
N/3000	−17·7	−16	−7·4	—
N/1000	−16·5	−16·3	−5·4	+ 8
N/500	−14·3	−13·1	−3·8	+13
N/250	−13·4	−11·7	−3·0	+16·7
N/125	—	—	—	+14·5

TABLE VII (Sample E).

	Electrolyte.			
Conc.	$BaCl_2$.	$SrCl_2$.	$MgCl_2$.	KCl.
0	−10·8	−10·8	−10·8	−10·8
N/10000	—	−10·5	−11·0	—
N/5000	—	− 9·2	−10·0	—
N/3000	—	—	—	—
N/1000	+ 3·6	− 0·6	− 7·7	—
N/500	+11·0	+ 3·0	− 4·0	—
N/250	—	+ 7·1	− 0·2	− 1·8
N/125	—	+ 9·6	+ 1·1	—

TABLE VIII (Sample E).

	Electrolyte.				
Conc.	KCl.	KNO_3.	K_2SO_4.	K_2HPO_4.	KOH.
0	−8·2	−8·2	−8·2	− 8·2	− 8·2
N/1000	−6·5	−7·5	−8·8	− 8·9	− 9·3
N/500	−5·7	−6·8	−8·7	−10·3	−11·4

From these tables certain conclusions may be drawn: (1) Hydrated manganese oxides carry a negative charge in contact with water. (2) Hydroxyl ions increase the negative charge markedly. (3) The capacity of the cations to decrease the negative charge of the surface is in the order Ba>Sr>Mg>K>Na>Li, which is the same as the order of their capacity to liberate hydrogen ions. (4) In the case of lithium and sodium chlorides, at low concentration the negative charge increases. (5) The bivalent cations reverse the charge of the surface. In the case of magnesium chloride, there is evidence of a slight increase in the negative charge at very low concentrations; in that of barium chloride (Table VI), after the reversal of the initial sign in the charge of the surface, the positive charge reaches a maximum and then falls again. (6) The reversal of charge with bivalent cations for the two samples examined occurs between concentrations N/3000 and N/125. It has already been observed that the concentration of the liberated hydrogen ions continues to increase up to a concentration of 0·2N of the bivalent electrolytes, *i.e.*, hydrogen ions continue to be liberated even after the surface has become positively charged. (7) From the experiments with potassium salts of various acids it is seen that the negative charge of the surface depends on the nature of the anions, thus showing that some of the anions are adsorbed.

The Adsorption Theory and the Liberation of Hydrogen Ions by Cations.—It follows from the theory of electrical adsorption (Mukherjee, *loc. cit.*) that the adsorbability of cations by a negatively-charged surface is determined by their valency, mobility, and hydration, provided that the atoms on the surface do not react chemically with the cations, either through primary, secondary, or residual valencies. It is at once possible to deduce from this theory that the adsorbability of the cations used should be in the order Ba > Sr > Mg > K > Na > Li, which agrees notably with that observed in the electro-osmotic experiments and in the liberation of hydrogen ions.

It has been remarked already that the bivalent cations reverse the electrical charge of the surface. On Mukherjee's theory, one must assume that the point-charges which constitute the negatively-charged primary sheet of the double layer must be univalent ions. When a barium ion is fixed on any of these point-charges, its corresponding hydrogen ion will be displaced. The surface at this point will have a net positive charge consisting of the original primarily-adsorbed univalent negative ion and the electrically-adsorbed bivalent cation. In the mobile sheet of the double layer one of the partner chlorine ions of the barium ion will take the place of the hydrogen ion which has passed into the bulk of the solution. The displaced hydrogen ion will have as its partner in the solution the other chlorine ion of the barium chloride molecule. One adsorbed bivalent cation thus displaces one hydrogen ion. Also, when the negative charge of the surface becomes zero and the surface begins to get positively charged, only half of the initial "uncovered" primarily-adsorbed negative ions are covered with bivalent cations and in the mobile sheet there will be cations (including hydrogen ions) and anions in equivalent quantities. A further increase in the concentration of bivalent cations will liberate fresh quantities of hydrogen ions. On the other hand, from purely chemical considerations one would expect that one barium ion would combine with two univalent negative ions on the surface and thus displace two hydrogen ions. The concentration of liberated hydrogen ions for the same molar concentration of a salt thus represents the amounts of cations adsorbed, and the order of adsorption of these cations is the same as their capacity to liberate hydrogen ions, *viz.*, Ba > Sr > Mg > K > Na > Li.

The fact that at higher concentrations potassium, sodium, and lithium ions set free hydrogen ions at identical concentrations can also be easily explained by this theory. If it is assumed that the number and the nature of the univalent anions primarily adsorbed per unit surface do not change on the addition of an electrolyte, then the main interaction between the ions in the double layer and those in solution will be a replacement of the hydrogen ions in the double layer by cations in solution. Hydrogen ions may be displaced by a cation through its penetration into the mobile sheet of the double layer or through its electrical adsorption. It has just been seen that one cation fixed on the surface by electrical adsorption displaces, irrespective of its valency, one hydrogen ion from the double layer. Besides these electrically-adsorbed cations there may be present in the double layer a number of cations simply as a result of their osmotic pressure in the bulk of the solution. The double layer as a whole is electrically neutral, and, since the cations must carry a charge equivalent to that of the primarily adsorbed anions, the total amount of charge carried by cations of all sorts in the double layer (under the above assumption) must remain constant. As the proportion of metallic cations to hydrogen ions in the double layer increases, a slight further replacement will increase the ratio more and more rapidly. Consequently the rate of increase of the concentration of hydrogen ions diminishes rapidly with increasing concentration of salts, and at high concentrations a limiting value of the hydrogen-ion concentration is reached which, as has been observed, is practically the same for the three alkali-metal cations.

Similarly, the decrease in the hydrogen-ion concentration in the successive washings recorded in Table I should be referred to the same cause. As the washing progresses, a further small replacement of hydrogen ions in the double layer by metallic ions changes at an increasing rate the ratio of the metallic ions to hydrogen ions.

The equilibrium is thus between the ions in the double layer and those in solution. A change in the ratio of the ions in one produces a change of the ratio in the other.

Analytical Measurement of the Adsorption of Anions and Cations.— The development of acidity has been referred to the adsorption of cations. It has also been seen from electro-osmotic experiments that anions are adsorbed. The adsorption theory assumes that anions are primarily adsorbed on the surface. Electro-osmotic experiments have shown that marked adsorption of hydroxyl ions takes place. It is likely that other anions are also adsorbed. Analytical measurements were undertaken to determine the magnitude of the adsorption of cations and anions. In calculating the adsorption of anions, correction has been made for the diluting effect of the water of hydration (compare Wo. Ostwald and Izagguire, *Kolloid Z.*, 1919, **30**, 279; Mukherjee, *J. Indian Chem. Soc.*, *loc. cit.*).

4 G. of the substance and 100 c.c. of a salt solution were shaken

as before, and the concentration of the alkali metal in the solution was estimated as sulphate. The amount adsorbed (corrected for hydration) is given in Table IX, col. 3, and the acidity of the solution in col. 4; it follows from these that, within the limits of experimental error, the number of cations adsorbed is equal to the number of hydrogen ions liberated, *i.e.*, the adsorption of cations is mostly the result of an exchange with hydrogen ions. This does not exclude the possibility of anions being adsorbed in much smaller but appreciable amounts. It has already been concluded from the electro-osmotic experiments that anions are adsorbed.

TABLE IX (Sample A).

Electrolyte.	Concentration.	Cation adsorbed (g.-atom × 10^3).	Hydrogen liberated (g.-atom × 10^3).
KCl	*N*	0·82	0·69
"	*N*/5	0·51	0·53
"	*N*/10	0·44	0·46
NaCl	*N*	0·69	0·67
"	*N*/5	0·39	0·42
"	*N*/10	0·29	0·33
LiCl	*N*	0·52	0·68
"	*N*/10	0·28	0·26

It will be seen from Table X that the adsorption of anions can be demonstrated when acids are used, for in this case there is no question of exchange of cations and the decrease in hydrogen-ion concentration should be attributed to the adsorption of both anions and cations. The potassium, which is present in traces in the samples (p. 2605), is set free in contact with acid, but not with pure water, and is the result of exchange with hydrogen ions; in the case of sulphuric acid solutions, it was estimated as sulphate, and in the case of other acids it was assumed that the potassium was exchanged for its equivalent of hydrogen ions in the solution. 5 G. of the sample were shaken with 50 c.c. of acid solution and left undisturbed for 24 hours; a definite volume of the clear supernatant liquid was withdrawn and titrated with standard alkali.

TABLE X (Sample C).

Acid.	Initial conc. (g.-mol. per litre).	Conc. corrected for dilution by water.	Final conc. after adsorption.	Potassium exchanged (g.-atoms) × 10^5.	Acid adsorbed (g.-equivs.) × 10^5.
HNO_3	0·2	0·188	0·184	9	11
"	0·1	0·094	0·092	8·2	1·8
H_2SO_4	0·1	0·094	0·089	9	41
"	0·05	0·047	0·043	8·2	31·8
H_3PO_4.*	0·1	0·094	0·079	9	141
"	0·05	0·047	0·039	8·2	71·8

* In the above calculations, this acid has been regarded as dibasic.

Even when allowance is made for the disappearance of the hydrogen ions through exchange with potassium ions, it is seen that the adsorption of the acid, although much smaller than the amount of acid set free in the other experiments, is quite noticeable. The adsorption of different acids from g.-molar concentrations is in the order $H_3PO_4 > H_2SO_4 > HNO_3$. The same order has been noticed for the effect of potassium salts of these acids on the negative charge of the surface. Both these effects being considered, the adsorption of these anions seems to be proved beyond doubt.

Summary.

(1) The interaction of manganese oxides with neutral salts can be satisfactorily accounted for by the adsorption theory of Mukherjee.

(2) In agreement with this theory, the capacity of the different cations to liberate hydrogen ions is in the order Ba > Sr > Mg > K > Na > Li, which is the same as that obtained from electro-osmotic experiments and represents their capacity to neutralise the negative charge of the surface.

(3) The bivalent cations reverse the sign of the charge of the surface, showing that the primarily adsorbed ions are univalent. The electrical adsorption of one bivalent cation will therefore liberate one hydrogen ion. In addition, hydrogen ions are probably replaced by cations penetrating into the mobile sheet of the double layer on account of their osmotic pressure.

(4) The adsorption of acids and the primary adsorption of anions have been demonstrated.

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