# CCCCIII.—*Interaction between Hydrated Silica and Neutral Electrolytes in its Relation to the Nature of Hydrolytic Adsorption.*

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The liberation of acids by the action of a neutral solution of a salt on silica is commonly represented as follows (compare Mellor, " Quantitative Inorganic Analysis," London, 1913, p. 172; Joseph and Hancock, J., 1923, **123**, 2022) :

$$2n\text{KCl} + \text{H}_{2n}\text{SiO}_{n+2} \rightleftharpoons 2n\text{HCl} + \text{K}_{2n}\text{SiO}_{n+2} . \quad . \quad (1)$$
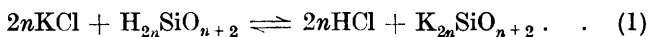
So long as the two pure solid phases coexist at a given temperature, (*a*) the activity of the liberated hydrogen ions in the solution ought to be proportional to that of the potassium ions, and (*b*) if definite concentrations of salts of different cations are compared, the lower the solubility of the corresponding silicate the higher will be the activity of the hydrogen ions necessary to maintain ionic equilibrium with the insoluble acid (Nernst, " Theoretische Chemie," 1921, pp. 615—618; Noyes and Kohr, *Z. physikal. Chem.*, 1902, **42**, 336; Lewis and Randall, " Text Book of Thermodynamics," 1923, p. 482). We now show that the relationship stated in (*a*) does not hold good, and it must be assumed that the solid phase consists of some sort of solid solution of the so-called acid and insoluble salt. Similar cases have been discussed by Küster (*Z. anorg. Chem.*, 1899, **19**, 81).

We consider that the liberation of acids in the present instance is the result of displacement of hydrogen ions in the double layer by cations adsorbed from the solution (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 191; *Phil. Mag.*, 1922, **44**, 321).

Experimental.

As the purity of the silica used in the preliminary portion of this work has been disputed (Joseph and Hancock, *loc. cit.*), hydrated silica obtained from the hydrolysis in transparent silica vessels of doubly distilled silicon tetrachloride was used throughout the present work.* After being washed free from acid the silica was

* The silica could never have come in contact with free alkali, as it was obtained by washing out the acid with pure water until the p_H rose to 6·2—6·4. Unless otherwise stated, the silica was not washed further and it retained a slight amount of acid which could be removed by further washing so that the resistance of the wash water rose to the same value as that of the water used.

air-dried at the ordinary temperature in a place free from fumes. The different samples contained 60—90% of water of hydration.

Resistance glass vessels were used, experiments with transparent fused silica vessels having shown that no extraneous sources of error were thereby introduced. The purity of the water employed was always tested before use. Clark and Lubs's indicators and standards were used. The concentrations of electrolytes added to silica as given below are those of the original solution.

The Equilibrium Concentration of Hydrogen Ions in Contact with a Definite Concentration of Potassium Chloride.

To 14 g. of silica (80% hydration) in a clean transparent silica flask a definite volume of neutral (p_H 6·4—6·6) potassium chloride solution, saturated at room temperature (29—30°), was added, and after a definite interval of time a .measured volume of the clear supernatant liquid was decanted and its p_H tested by indicators. A fresh portion of the potassium chloride solution was added and the process repeated. The results are given in Table I.

TABLE I.

Days.	p_H of KCl extract.	C.c. of sol. ex-tracted.	Days.	p_H of KCl extract.	C.c. of sol. ex-tracted	Days.	p_H of KCl extract.	C.c. of sol. ex-tracted.
—	4·2	50	12	5·2	200	28	6·0	100
1	4·4	50	14	5·4	200	29	6·4	100
2	4·4	25	15	5·4	150	31	6·4	100
2	4·6	50	16	5·5	200	33	6·2	100
5	4·6	25	19	5·7	200	34	6·2	100
5	4·8	75	20	5·7	100	35	6·2	100
6	4·8	50	21	5·8	100	36	6·3	100
8	4·8	100	22	5·8	100	37	6·5	100
8	5·0	100	26	6·0	100	38	6·4	100
9	5·1	300	27	6·0	100	39	6·5	100

From these results, the total amount of acid liberated is calculated to be equivalent to $1·63 \times 10^{-5}$ g.-atom of hydrogen. The composition of the hydrated silica is 13·3 g.-mols. of water per g.-mol. of silicon dioxide. Of these 26·6 g.-atoms of hydrogen, only $3·5 \times 10^{-4}$ g.-atom has been replaced. Table I shows that, instead of a constant equilibrium concentration of hydrogen ions and a sudden fall, there is a gradual diminution until a solid residue is obtained which does not change the p_H of the potassium chloride solution even during 4 days' contact.

That all the replaceable hydrogen ions have not yet been removed is evident from the following experiments : 10 g. of silica (hydration 70%) were washed repeatedly as above with N-barium chloride solution (p_H 6·4) until the p_H of the extract showed no change. The clear supernatant solution was removed as far as possible by means

of a pipette and 50 c.c. of saturated barium chloride solution were added. The p_H of the supernatant solution fell to 5·8. The solution was removed once more and 50 c.c. of sodium nitrate solution, saturated at room temperature (p_H 6·4), were added. The p_H now fell to 4·8. In Table II are shown the total amounts of acid liberated by different cations until no more hydrogen ions are set free. It is seen that the capacity of the cations to liberate acids on continued washing is in the order $K^{\cdot} > Na^{\cdot} > Ba^{\cdot\cdot}$ in molar solution; also that the total amount of acid liberated depends on the concentration of the cation.

TABLE II.

	N-KCl.	N-NaCl.	N-BaCl₂.	2N-BaCl₂.	Sat. BaCl₂.*	Sat. NaNO₃.*
G.-ions of H· liberated ($\times 10^4$)	0·3	0·2	0·15	0·15	0·34	0·56
G.-ions of H· per g.-mol. of SiO₂ ($\times 10^4$)	6	4	3	3	6	10

* A different sample, with 66·15% water of hydration, was used in these experiments.

The solubility relationships which should be satisfied if our usual conceptions of such equilibria are valid for this case must now be considered.

Let S_A be the solubility of the " pure " acid (uncontaminated by its salts) in g.-mols. per litre, and S_K that of the corresponding " pure " potassium salt. In view of the weak character of silicic acid and its probable solubility, we shall assume that only the first-stage dissociation need be taken into account, especially as we are dealing with acidic solutions. The solubility in water of the acid or of the salt is a function of the composition of the solid solution, i.e., the product of the respective molar fraction (expressed in terms of simple molecular weights of the acid and of the salt *) multiplied by the solubility of the pure substance. For the acid the ionic product must be a constant depending on the temperature and composition of the solid solution and will be given by

$$C_{H^{\cdot}} \times C_{A'} = \{f(1-x) \cdot S_A \alpha(1-x)\}^2 \quad . \quad . \quad (2) \dagger$$

where $C_{H^{\cdot}}$ and $C_{A'}$ denote respectively the gram-ionic concentrations (or rather activities) of the hydrogen ion and the anion of the silicic acid in the solution; $(1-x)$ is equal to the fraction of the acid remaining unchanged; $f(1-x) \cdot S_A$ is the solubility of the acid under these conditions; α is the theoretical degree of dissociation of the acid in a solution saturated with reference to the acid only in the solid

* For the barium salt the molar fraction will be $(1-x/2)$ for the acid and $x/2$ for the salt, assuming x to be small.

† The validity of this and the following equations is considered in the " Discussion."

solution, *i.e.*, assuming that the silicate is not passing into the solution, so that $C_{\text{H}\cdot} = C_{\text{A}'}$. Actually $C_{\text{H}\cdot} > C_{\text{A}'}$, but for equilibrium the ionic product $C_{\text{H}\cdot} \times C_{\text{A}'}$, which in these dilute solutions measures the activity, must have a constant value determined by the above expression.

Similarly, putting $\alpha = 1$ for the salts, we have

$$C_{\text{K}\cdot} \times C_{\text{A}'} = \{f(x) . S_{\text{K}}\}^2 \quad . \quad . \quad . \quad . \quad (3)$$

$$C_{\text{Ba}\cdot\cdot} \times C^2_{\text{A}'} = 4\{f(x/2) . S_{\text{Ba}}\}^3 \quad . \quad . \quad . \quad (4)$$

whence

$$C_{\text{H}\cdot} = C_{\text{K}\cdot}\{f(1 - x) . S_{\text{A}}\alpha(1 - x)\}^2/\{f(x) . S_{\text{K}}\}^2 \quad . \quad . \quad (5)$$

and

$$C_{\text{H}\cdot} = C_{\text{Ba}\cdot\cdot}^{1/2}\{f(1 - x/2) . S_{\text{A}}\alpha(1 - x/2)\}^2/2\{f(x/2) . S_{\text{Ba}}\}^{3/2} \quad (6)$$

The decrease in the concentration of hydrogen ions is to be explained by a gradual increase in the value of x.

The Concentration of Hydrogen Ions in Contact with Different Salts.

To 40 c.c. of each of a number of salt solutions contained in resistance-glass bottles were added 5 g. of silica. The hydrogen-ion concentration of the clear upper liquid as shown in Table III was determined after 24 hours from *E.M.F.* measurements, using normal calomel electrodes; the measurements were correct to ± 0.5 millivolt.

TABLE III.

Conc. (g.-mol. per litre).	(SiO$_2$, 41·1%; H$_2$O, 58·9%.) KCl.		(SiO$_2$, 39·0%; H$_2$O, 61·0%.) NaCl.		BaCl$_2$.	
	$p_{\text{H}\cdot}$	$C_{\text{H}\cdot} \times 10^6$.	$p_{\text{H}\cdot}$	$C_{\text{H}\cdot} \times 10^6$.	$p_{\text{H}\cdot}$	$C_{\text{H}\cdot} \times 10^6$.
1	4·54	28·8	4·6	25	—	—
0·5	—	—	—	—	4·56	27·6
0·04	4·71	19·5	4·76	17·4	—	—
0·02	4·72	19·0	5·20	6·31	4·76	17·4
0·01	5·03	9·33	5·42	3·80	5·06	8·71
0·004	5·17	6·76	5·75	1·78	—	—
0·002	5·52	3·02	6·05	0·89	—	—
0·001	5·57	2·69	—	—	—	—

The relative effects of barium, calcium, potassium, and sodium chlorides were determined in strictly comparable experiments with a different sample of silica (hydration 62%). The results are given below. As before, the hydrogen-ion concentrations were determined from *E.M.F.* measurements.

TABLE III (*a*).

Electrolyte and concentration.	M.		0·01M.		0·002M.	
	$C_{\text{H}\cdot} \times 10^6$.	$p_{\text{H}\cdot}$	$C_{\text{H}\cdot} \times 10^6$.	$p_{\text{H}\cdot}$	$C_{\text{H}\cdot} \times 10^6$.	$p_{\text{H}\cdot}$
BaCl$_2$	56·2	4·25	15·1	4·82	3·09	5·51
CaCl$_2$	49·9	4·31	8·91	5·05	1·74	5·76
KCl	39·8	4·40	5·62	5·25	1·22	5·95
NaCl	35·5	4·45	4·73	5·39	0·725	6·14

The relative effects of calcium and barium chlorides, being of special interest, were studied simultaneously and the data are given in Table IV. The silica contained 89·7% of water.

TABLE IV.

Concentration of electrolyte.

	0·05M.	0·01M.	0·005M.	0·002M.	0·001M.	0·0005M.
BaCl₂ $\begin{cases} C_{H^\cdot} \times 10^6 \\ p_H \end{cases}$	28·8	7·18	5·62	4·20	3·12	2·45
	4·54	5·144	5·25	5·377	5·506	5·615
CaCl₂ $\begin{cases} C_{H^\cdot} \times 10^6 \\ p_H \end{cases}$	22·0	4·41	3·49	2·44	1·66	1·10
	4·657	5·356	5·457	5·613	5·779	5·94

From the chemical point of view, the above results signify that the solubilities of the sodium and calcium salts are respectively greater than those of the potassium and barium salts, whereas actually calcium silicate is less soluble than the barium salt (Joseph and Oakley, J., 1925, **127**, 2816). On comparing the relative effects of these cations we find that at the higher concentrations individual differences tend to disappear. The only way to surmount this difficulty would be to assume, either that a calcium salt of some complex acid is formed which is more soluble than the corresponding barium salt, or that the relative solubilities of the calcium and barium salts in a state of solid solution have no relation to their relative solubilities in the pure state.

Moreover, in the experiment on the determination of the total quantity of acid liberated by repeated washing, potassium and barium solutions at a molar concentration had practically the same hydrogen-ion concentration initially (p_H 4·2 and 4·6, respectively) as determined with indicators. At the close of the washing, the p_H was 6·4 for both. Reference to the equations shows that this can only be explained by assuming that the solubility of the barium salt in a state of solid solution increases relatively much more rapidly with its percentage composition than that of the potassium salt. The same remark applies to the sodium salt. Thus at each stage we have to introduce *ad hoc* assumptions of changes in solubility.

The Effect of Electrolytes on the Electrical Charge of the Surface.

Electro-osmotic experiments were carried out in a modified form of the apparatus used by Briggs (*Nature*, 1922, **109**, Dec. 2). As there are inherent defects in this method of measurement, the results are only comparative. The electrodes were always connected to the main (220 volts) circuit, and their relative positions were fixed. The measurements were made at room temperature (29—30°), and are reproducible to within 6%. The figures given in Tables V, VI, and VII indicate the movement of the bubble in cm. per 3 minutes.

TABLE V.

Concentration (g.-mols. per 1000 litres).

Electro-lyte.	0.	0·1.	0·16.	0·2.	0·25.	0·33.	0·5.	1·0.	2·0.	8·0.
NaCl	3·2	—	—	5·7	—	6·0	—	3·5	3·1	—
KCl	3·2	—	—	5·6	5·3	5·1	4·0	2·8	2·2	1·0
BaCl₂	3·2	4·0	3·9	—	—	—	3·0	2·6	—	—
HCl	3·2	—	—	1·4	—	0·9	—	0·6	—	—

TABLE VI.

Electro-lyte.	Concentration.			Electro-lyte.	Concentration.		
	0.	0·0002N.	0·001N.		0.	0·0002N.	0·001N.
(COOK)₂	3·5	7·2	6·3	KBr	3·5	5·7	2·5
K₂SO₄	3·5	6·4	3·7	KNO₃	3·5	5·4	2·5
KCl	3·5	5·6	2·8				

TABLE VII.

10^3 × Concentration of electrolyte.

Electrolyte.	0.	0·2N.	0·33N.	0·5N.	1N.	2N.
LiNO₃	3·5	6·1	6·5	6·0	4·5	3·3
KNO₃	3·5	5·4	5·0	—	2·6	2·5
RbNO₃	3·5	4·3	3·5	—	2·9	2·2

From Tables V—VII we find that (1) chemically pure hydrated silica has a negative charge in contact with pure water; (2) the capacity of these univalent cations of decreasing the negative charge at higher concentrations shows that their order of adsorption is H˙>Rb˙>K˙>Na˙ (compare *J. Indian Chem. Soc.*, 1925, **2**, 204); (3) it appears that, taking into consideration its valency, the barium ion is weakly adsorbed; (4) the experiments with potassium salts of different acids (Table VI) leave no doubt that anions are primarily adsorbed, since different anions have different effects.

The weak adsorbability of barium may be referred, on the basis of electrical adsorption, to a large value of x in the equation $W = N_1 N_2 E^2 / Dx$ [Faraday Society Discussion, October, 1920; equation (10)]; on this theory barium will still have a greater effect than calcium.

Adsorbability of the Cation and its Capacity to Liberate Hydrogen Ions.

In comparing the effect of a cation on the electrical charge of the surface of a solid with its capacity to set free hydrogen ions from the surface layer, we have to remember that, whereas the variation in the electrical charge depends on the relative amounts of cations and anions " fixed " on the surface, the liberated hydrogen ions may come either from the mobile sheet of the double layer or from the primary layer. On theoretical grounds, in considering the equilibrium concentration of hydrogen ions in the present instance,

we are mainly concerned with the displacement by cations of hydrogen ions from the mobile sheet of the double layer. If we compare the relative effects of these cations we find that the concentrations of hydrogen ions decrease in the order $Ba^{..} > Ca^{..} > K^. > Na^.$. In complete agreement with our theory, the order is the same as that indicated by mobility (K, $\frac{1}{2}$Ba, Na) and valency which should determine the number of g.-ions of hydrogen liberated by the cation. At high concentrations, as hydrogen ions in the double layer are increasingly replaced by cations, and as the number of anions *primarily* adsorbed does not change to any large extent at these concentrations, the effect of the adsorption of a further amount of the cation will produce a much greater change in the ratio between the cation and hydrogen ions present in the double layer than when a smaller number of cations are present in it. Since the equilibrium is between the ions in the double layer and those in the bulk of the solution, the ratio between the two ions must also increase rapidly in the latter. The rate at which the concentration of the hydrogen ions increases with the concentration of the cation will therefore rapidly decrease and individual differences between the different cations will also diminish, because at high concentrations the adsorption will tend to a limit, namely, that corresponding to the state when all the primarily adsorbed anions are " covered " by cations. It is evident that at higher concentrations the different cations will be in equilibrium with practically the same concentration of hydrogen ions. It is thus unnecessary to introduce assumptions regarding changes in solubility, especially as we might doubt whether a solid solution of silica is really formed under the conditions of the experiments. The total quantities of acid liberated also show a similar effect of the concentration and adsorbability of the cation.

The Dependence of the Concentration of Hydrogen Ions on the Amount of Silica used.

If one changes the ratio of the weight of silica to the volume of solution—the amount of potassium chloride remaining constant—it is obvious that the extent of interchange between the hydrogen and potassium ions will be different. Consequently the ratio of the concentration of potassium to hydrogen ions should also vary. One of us (Mukherjee, Faraday Society Discussion, *loc. cit.*), in discussing the effect of a cation on the negative charge of the surface, considered the simplest case in which the following conditions were satisfied : (a) The number of primarily adsorbed ions per unit surface and their nature do not change; (b) there is only one kind of cation in the solution and in the double layer.

Apparently these conditions do not hold good in the present

instance, where two kinds of cation and more than one type of adsorbable anion are present. Experiments with different quantities of silica (see Table VIII) illustrate the relationship existing between the ratios of the cations in the double layer and in the solution.

TABLE VIII.

(Electrolyte, 50 c.c. of N-KCl. Hydration of silica, 89·7%.)

Wt. of silica.	$C_{H^.} \times 10^5$.	G.-atoms of K adsorbed per 10^5 g. of hydrated SiO_2.	G.-atoms of K adsorbed per 10^5 mol. of SiO_2.	$C_K./C_H.$ (corrected for H_2O of hydration).
1 g.	3·1	0·158	92·1	0·32 $\times 10^5$
2 ,,	3·59	0·092	27·1	0·27 $\times 10^5$
4 ,,	4·82	0·062	9·3	0·19 $\times 10^5$
8 ,,	8·32	0·059	4·3	0·106 $\times 10^5$

It will be seen from col. 3 that the amount of potassium per g. of silica diminishes with increasing quantities of silica; also that the amount of potassium taken up by the solid is not proportional to the weight of the solid used (compare Joseph and Oakley, *loc. cit.*). As the amount of potassium adsorbed is very small compared with the total amount present, the concentration of the potassium ions is not materially altered by adsorption. Col. 5 gives the ratio of concentration of potassium to hydrogen ions in the solution, showing that a decrease in the ratio of potassium to hydrogen ions in the double layer is attended by a simultaneous although smaller decrease in the ratio in the solution. The higher concentration of hydrogen ions in the solution requires for equilibrium a relative increase in the number of hydrogen ions per unit surface of the double layer.

In conjunction with equation (5), these results signify that a decrease in the value of x increases the value of $C_{H^.}$. Assuming x to be small, $C_{H^.}$ should vary inversely as x^2 [putting $f(x) = x$]. Col. 2 shows that the rate of increase is much smaller than is required by this relationship. If x is not very small, then the divergence becomes still greater. As nothing is known regarding the manner in which the solubilities of the components of the solid solution change with the composition, a discussion of these results from the chemical point of view is unprofitable. From our point of view, it is easy to understand that a greater number of hydrogen ions in the double layer can only be in equilibrium with a higher concentration in solution.

The Adsorption of Acids by Silica.

The total amount of acid liberated on continued washing gives a rough indication of the amount of hydroxyl ions (covered or uncovered) adsorbed per g. of the 'substance. As the primary adsorption is attributed to chemical forces, other anions may also

be adsorbed. We have already seen from electro-osmotic experiments that anions are primarily adsorbed. The adsorption of anions is closely related to the adsorption of acids. A quantitative determination of the latter is of interest in relation to the acidity of clays. On chemical grounds, one would expect that the primary adsorption of hydroxyl ions would be very strong compared with that of other anions. The adsorption of acids should therefore be lower than that indicated by the total amount of acid liberated on continued washing. The adsorption of hydrochloric acid has been determined both by conductivity and by $E.M.F.$ methods, corrections being applied for the diluting effect of the water of hydration. (It can also be demonstrated by the use of indicators.) In view of the method of preparation of the silica (p. 3023), the only possible extraneous source of alkali is ammonia from the air, but this was shown to be absent throughout. Great care was taken to shelter the samples from dust and fumes. The extremely low conductivity of the water in contact with silica shows that there are no electrolytic impurities.

TABLE IX.

Experiment A (Wt. of silica, 40 g.; hydration, 84·4%; vol. of solution, 100 c.c.).

Method.	Conc. of acid ($\times 10^4$).		Conc. of original acid (corrected for dilution by hydration) $\times 10^4$.	Change in conc. due to adsorption $\times 10^4$.	Amount adsorbed per g.-mol. of silicon dioxide $\times 10^4$.
	Before adsorption.	After adsorption.			
Conductivity.*	9·6	6·85	7·22	0·37	0·47
$E.M.F.$	9·43	6·38	7·05	0·67	0·65

Experiment B (Wt. of silica, 20 g.; hydration, 59·6%; vol. of solution, 30 c.c.).

$E.M.F.$	2·82	0·43	2	1·97	0·62

Experiment C (Wt. of silica, 100 g.; hydration, 86·6%; vol. of solution, 100 c.c.).

Conductivity	3·05	1·46	1·93	0·47	0·5
$E.M.F.$	2·93	1	1·86	0·86	0·91

* For hydrochloric acid Λ_∞ has been taken as 455 at 30°.

We have found a difference in the amount adsorbed as calculated from $E.M.F.$ and from conductivity measurements. The difference cannot be accounted for on the basis of replacement of hydrogen ion by another cation and, as no free alkali could possibly come in contact with the samples, we believe the $E.M.F.$ to be less accurate than the conductivity measurements, especially as the hydrogen electrodes often lost their reproducibility. The liquid is never free from suspended particles, although in presence of neutral salt the upper liquid becomes perfectly clear after 24 hours.

The only impurity that could possibly be present in our silica is titanium oxide : the silicon tetrachloride employed (Merck or Kahlbaum) contained titanium chloride, but two distillations from a water-bath rendered it free from titanium as shown by the following analytical data, for which we are indebted to Mr. P. R. Ray, M.A. : (1) 8·8009 g. of hydrated silica were heated with hydrofluoric and sulphuric acids in a platinum basin. The latter gained 0·3 mg. in weight, of which 0·1 mg. was due to impurities in the acids, as shown by a control. The difference of 0·2 mg. is within the limits of experimental error. (2) 6 G. of ignited silica were fused with potassium bisulphate and extracted with water. Colorimetric comparisons, after the addition of hydrogen peroxide, showed this solution to contain less titanium than 0·04 c.c. of a solution containing 1 mg. of titanium per c.c., i.e., the titanium, if any, is therefore less than 8×10^{-5} g.-atom per mol. of silicon dioxide, too little to account for the observed adsorption.

The results given above leave no doubt as to the adsorption of acid by silica, and the amount adsorbed, although small, is comparable with the acidity to be attributed to the silica itself.

Discussion.

We shall now briefly discuss some further difficulties in the way of applying our usual chemical conceptions to this reaction. It is well known that in the presence of an electrolyte with or without a common ion the solubility of the so-called undissociated molecules does not remain constant. The product of the ionic activities, however, is constant and independent of the concentration and nature of the ions present. Considerations based on the solubility of pure phases give no clue as to the activity of the hydrogen ion liberated in presence of different cations. Thus in equations (2) to (6) it is not sufficient to know the values of S_A, S_{Ba}, etc. : we must also know how the solubility (or activity) changes with the nature and concentration of the added electrolyte; i.e., the function $f(1 - x)$ or $f(x)$ may vary from one electrolyte to another. As these equations in reality deal with thermodynamic quantities and not with solubilities, we have always to assume that the solubilities are such as would satisfy the thermodynamic relationships. Moreover, it is not at present possible to predict on theoretical grounds the solubilities of the different salts in such cases. On the contrary, from our point of view the capacity of a cation to liberate hydrogen ions depends upon its mobility and valency when the cation is not primarily adsorbed by the surface, and electrical forces alone are responsible for the adsorption.

Lastly, if we consider that at the same molar concentration the

activity coefficient of the bivalent cations is less than that of the univalent cations (Lewis and Randall, *loc. cit.*), it appears that the activity of the liberated hydrogen ions would be still greater for the bivalent cations than for univalent ions when their effects are compared at concentrations such that both have the same actual activity. The order $K^{.}>Ba^{..}>Na^{.}$ is, however, theoretically possible if mobility alone determines the electrical adsorbability.

Summary.

(1) It is shown that the usual conceptions of chemical equilibrium fail to account for the interaction between silica and neutral salt solutions.

(2) In agreement with Mukherjee's theory, there is a close relationship between the valency and mobility of the cation and its effect on the liberation of hydrogen ions.

(3) The adsorption of acids by silica has been definitely demonstrated.

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