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Contrasting effects of chlorides and sulphates on the hydrogen ion concentration of acid solutions.

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In the course of an investigation upon the effect of neutral salts upon hydrogen ion concentration we have noted a striking contrast in the effect of chlorides, sulphates and magnesium salts on the apparent hydrogen ion concentration of solutions of hydrochloric and of sulphuric acids.

The results of our measurements are given below. In all cases a solution of acid was mixed with a solution of a given salt and diluted to 100 c.c. The concentration of this solution of the mixture was always 0.1 normal with respect to the acid and that particular concentration of the salt whose effect upon the hydrogen ion concentration was to be studied. The hydrogen ion concentrations were measured two days after the solutions were made up.

The effect of chlorides in increasing the hydrogen ion concentration of hydrochloric acid solutions is not new. This has previously been shown by Harned[1] and by Fales and Nelson[2]. Arrhenius[3] found that the hydrogen ion activities of acetic and of hydrochloric acids were increased by neutral salts which he thought was due to the salts increasing the dissociation of the acids. It is possible that recent work on the hydration of ions in aqueous solution will offer a more plausible explanation.

When the chlorides are arranged in order of their ability to increase the hydrogen ion activity, we get the following series: $MgCl_2 > BaCl_2 > LiCl > NaCl > NH_4Cl = KCl$ which, with the exception of magnesium and barium is in inverse order to a series of these cations arranged in order of their equivalent conductivities.

In the above series the salts are arranged in order of the increasing hydration (*i.e.*, number of molecules of water combined

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[1] *J. Am. Chem. Soc.*, *37*, 2460 (1915).

[2] *J. Am. Chem. Soc.*, *37*, 2769 (1915).

[3] *Z. physik. Chem.*, *31*, 197 (1899).

with the ions at infinite dilution) of their cations—K^+, 9.6; NH_4^+, 10.7; Na^+, 16.9; Li^+, 24.0;[1] Ba^{++}, relatively higher;[2] Mg^{++}, higher than Ba^{++}.[3]

The contrast in the effect of sodium and ammonium sulphates in decreasing the hydrogen ion concentration as compared with the increasing action of the chlorides is noteworthy.

The peculiar effect of magnesium salts is interesting, especially in that the concentrations for bend in the curves is in each case between 0.5 and 1 molar. We have tried to find an explanation for these peculiarities in Jones' "Hydrates in Aqueous Solutions."[3] Jones states, "Magnesium sulphate, like all the other sulphates studied, gives abnormal results. It appears to form no hydrates in aqueous solution, notwithstanding the fact that it crystallized with seven molecules of water of crystallization. It is almost

TABLE I.

EFFECT OF SALTS UPON THE CONCENTRATION OF HYDROGEN ION OF 0.1 NORMAL SULPHURIC ACID.

Conc. Salt.	Log. C_{H+}.	Conc. Salt.	Log. C_{H+}.
Sodium Chloride		*Ammonium Chloride.*	
0	− 1.21	0	− 1.21
1 Molar........	− 0.99	1 Molar	− 1.08
2 "	− 0.78	2 "	− 0.98
3 "	− 0.57	3 "	− 0.84
4 "	− 0.36	4 "	− 0.72
Magnesium Chloride.		*Sodium Sulphate.*	
0	− 1.21	0	− 1.21
0.25 Molar........	− 0.84	0.25 Molar.......	− 1.60
0.5 "	− 0.56	0.5 "	− 1.72
1 "	− 0.56	1 "	− 1.80
2 "	+ 0.03	2 "	− 1.88
3 "	+ 0.60	3 "	− 1.92
Ammonium Sulphate.		*Magnesium Sulphate.*	
0	− 1.21	0	− 1.21
0.25 Molar........	− 1.61	0.25 Molar.......	− 1.46
0.5 "	− 1.76	0.5 "	− 1.52
1 "	− 1.90	1 "	− 1.53
2 "	− 2.04	2 "	− 1.39
3 "	− 2.15	3 "	− 1.15
4 "	− 2.24		

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[1] Smith, *J. Am. Chem. Soc.*, *37*, 722 (1915).

[2] Washburn, *Tech. Quarterly*, *21*, 360 (1908).

[3] Jones, Carnegie Institution of Washington, Publication No. 60 (1907).

TABLE II.

EFFECT OF SALTS UPON THE CONCENTRATION OF HYDROGEN ION OF 0.1 NORMAL HYDROCHLORIC ACID.

Conc. Salt.	Log. C_{H+}.	Conc. Salt.	Log. C_{H+}.
Sodium Chloride.		*Potassium Chloride.*	
0	− 1.038	0	− 1.038
1 Molar	− 0.88	1 Molar	− 0.95
2 "	− 0.72	2 "	− 0.85
3 "	− 0.52	3 "	− 0.75
4 "	− 0.36	4 "	− 0.63
Ammonium Chloride.		*Lithium Chloride.*	
0	− 1.038	0	− 1.038
1 Molar	− 0.94	1 Molar	− 0.81
2 "	− 0.87	2 "	− 0.60
3 "	− 0.75	3 "	− 0.35
4 "	− 0.65	4 "	− 0.12
Barium Chloride.		*Magnesium Chloride.*	
0	− 1.038	0	− 1.038
0.25 Molar	− 0.96	0.25 Molar	− 0.73
0.5 "	− 0.88	0.5 "	− 0.55
0.75 "	− 0.80	1 "	− 0.55
1 "	− 0.71	2 "	+ 0.005
		3 "	+ 0.68
		4 "	+ 1.37
Sodium Sulphate.		*Ammonium Sulphate.*	
0	− 1.038	0	− 1.038
0.25 Molar	− 1.51	0.25 Molar	− 1.52
0.5 "	− 1.65	0.5 "	− 1.72
1 "	− 1.79	1 "	− 1.90
2 "	− 1.86	2 "	− 2.05
3 "	− 1.89	3 "	− 2.14
		4 "	− 2.18
Magnesium Sulphate			
0	− 1.038	1	− 1.47
0.25 Molar	− 1.36	2 "	− 1.34
0.5 "	− 1.45	3 "	− 1.12

certain that this substance has considerable hydrating power, but this is masked in our results by the large amount of polymerization which the sulphates undergo."

The curve of the freezing point depression of magnesium sulphate plotted against concentration shows a depression to about 0.5 molar, from which point the depression decreases for higher concentrations. In this respect there is a slight similarity to its effect on hydrogen ion concentration, *i.e.*, it increases hydrogen ion concentration to 0.5 to 1 molar beyond which it decreases it. Magnesium chloride, however, gave a similar effect on freezing point depression, although not so pronounced as magnesium sulphate. We could not find anything in the hydrate theory as developed at present to account for the peculiar bend in the magnesium chloride hydrogen ion curve.

We do not believe that the figures for hydrogen ion concentrations in the presence of salts given in this paper, are the true values. They should be termed apparent concentrations of hydrogen ion as determined by the method in general use at this date.

For the determination of the hydrogen ion concentrations, a Wolff 15,000 bridge with a galvanometer to determine the null point was used. As hydrogen electrode, a No. 16 Browne and Sharp gauge platinum wire (platinized) fused in a glass tube inserted in the Clark[1] cell was used. The calomel element contained 3.5 molar potassium chloride solution saturated with calomel and was the same design as that described by Fales and Vosburgh.[2] The E.M.F. was determined by means of a Weston cell that had been checked by the Bureau of Standards. The hydrogen contained in a tank under pressure, was carefully washed through saturated mercuric chloride solution, alkaline permanganate, alkaline pyrogallol and a tower of cotton fibers. The measurements were made at room temperatures which varied between 22° and 26° C., the proper corrections being made. No correction for barometric pressure was made since it is so small. (See Harned, loc. cit.) No attempt was made to calculate and correct for the solution contact potential because we know of no satisfactory method of doing so, especially where solutions containing divalent ions are concerned. It is emphasized however, that the differences in effects reported in this paper cannot be attributed to solution contact potential. This point was demonstrated by Harned, and Fales and Vosburgh proved there is no contact potential at 25° C., between a saturated solution of po-

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[1] Clark, *J. Biol. Chem.*, *23*, 475 (1915).

[2] Fales and Vosburgh, *J. Am. Chem. Soc.*, *40*, 129 (1918).

tassium chloride (4.1 M) and hydrochloric acid solutions ranging in concentrations between 0.1 molar and 1 molar.

The salt bridge between the hydrogen and calomel elements used in our measurements was a saturated solution of potassium chloride.

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On the utilization of salep mannan.

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Some experiments on the utilization of salep mannan were reported in 1911.[1] It was found that this anhydride of mannose was not hydrolyzed by the enzymes of saliva, pancreatic and intestinal juice, nor by malt diastase, but disappeared almost completely from the human alimentary tract when eaten, the coefficient of digestibility in three out of four experiments being 100 per cent. and 94 per cent. in the fourth. Studies of the effect of fecal bacteria indicated that some of them could produce appreciable amounts of sugar from this polysaccharide, and stimulated further research as to its precise fate in the animal organism. Investigations were interrupted in 1914, when the war cut off the supply of salep, and what has been accomplished along several lines is now reported as it is doubtful when these studies can be resumed.

Four more determinations of the coefficient of digestibility were made, two on healthy young women and two on diabetics. The young women, consuming identical and uniform diets, free from cellulose, throughout a fore, mid, and after period, took in the mid period of three days 75 grams of salep mannan, equivalent to 61 grams of glucose. The coefficient of digestibility was 97 per cent. in one case and 95 in the other. A diabetic man given in one day 45 grams of salep mannan, with no other food but broth, coffee and whiskey, had a coefficient of 98 per cent. A diabetic boy fifteen years old, took in three days 33, 65 and 70 grams of

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[1] *Trans. Conn. Acad. Arts and Sciences*, XVI, pp. 247–382, 1911.