HYDRATION AS AN EXPLANATION OF THE NEUTRAL SALT EFFECT.

By John Arthur Wilson.

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A mass of experimental data now available seems to indicate that the addition of sodium chloride to an acid solution results in an increase in hydrogen-ion concentration, whereas adding it to an alkaline solution causes an increase in concentration of the hydroxide ion.[1] This is of very great importance in the manufacture of leather, although probably not more so than in other fields of chemistry.

An interesting practical example of this property of salt is furnished by a series of experiments in chrome tanning recently carried out by the writer. A commercial chrome liquor (a solution of basic chromic sulfate and sodium sulfate) diluted to contain 17 g. of chromic oxide per liter was found to be capable of completely tanning certain pickled[2] calfskins in less than 2 days without any addition of alkali. A piece of chrome leather is considered fully tanned when it will remain apparently unaltered in boiling water for 5 minutes. In tanning successive lots of skins with this liquor, no difficulty was experienced in maintaining conditions so nearly constant that no difference could be detected either in the rate of tanning or in the properties of the resulting leather. The experiment was then repeated with all conditions exactly the same as before except for the addition of one lb. of sodium chloride per gallon (120 g. per liter) of chrome liquor. Measurements with the hydrogen electrode showed that an increase of about 50% in hydrogen ion concentration resulted from this addition of salt. After the skins had been in the liquor for 7 days, they were still not tanned and it was necessary to add a considerable amount of alkali to bring about complete tannage. A very similar effect is produced by adding hydrochloric acid instead of salt.

The effect of sodium chloride upon alkaline solutions is shown by adding salt to a lime liquor, which consists of a solution kept saturated with calcium hydroxide by means of a large excess and containing a comparatively small amount of sodium sulfide. The function of this liquor is to destroy the Malpighian layer of the epidermis of the skins so that the hair may simply be rubbed off by working on a suitable machine. Adding salt to such a liquor was found to increase the plumpness of the skins and to cause the hair to slip somewhat more easily. This same effect is produced by the addition of sodium hydroxide.

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[1] Poma, *Z. physik. Chem.*, 88, 671 (1914); Arrhenius, *ibid.*, 31, 197 (1899); Harned, This Journal, 37, 2460 (1915); Fales and Nelson, *ibid.*, 37, 2769 (1915); Thomas and Baldwin, *ibid.*, 41, 1981 (1919).

[2] The pickling process consists of subjecting unhaired skins to a bath of sulfuric acid and sodium chloride of definite strength until equilibrium is established.

The chrome tanning experiments noted above were a continuation of a series of simpler experiments by Wilson and Kern,[1] of which the following is typical. 0.1 *N* sodium hydroxide was added to 10 cc. of a filtered chrome liquor, with suitable agitation, until the first permanent turbidity appeared, due to precipitation of basic chromic salts, the amount required being 3.7 cc. To another portion of 10 cc. was added 0.04 gram molecule of sodium chloride; in this case 6.8 cc. of the standard alkali was required to start precipitation. Repeating the experiment, using in each case 10 cc. of the chrome liquor and 0.02 gram molecule of added salt, Wilson and Kern found different salts to have very different degrees of effectiveness in preventing precipitation, the order being $KCl < NH_4Cl < NaCl < MgCl_2 < MgSO_4 < Na_2SO_4 < (NH_4)_2SO_4$. The liquor containing potassium chloride required only 4.0 cc. of 0.1 *N* sodium hydroxide to start precipitation against 11.6 cc. for ammonium sulfate.

The order of these salts led Wilson and Kern to the conclusion that the effect was probably due to hydration of the added salt. Chrome liquors are all decidedly acid in reaction, and, if the added salt becomes hydrated at the expense of the solvent, the ratio of moles of acid to moles of solvent, and consequently the activity of the acid, will be increased, the more so the greater the degree of hydration of the added salt.

This explanation was regarded as sufficient until Thomas and Baldwin[2] proved by electrometric measurements that while chlorides actually do increase the hydrogen-ion concentration, not only of chrome liquors but of pure acid solutions as well, sulfates behave very differently, generally lowering the hydrogen-ion concentration, just the reverse of what might have been expected from the results of Wilson and Kern.

One remarkable feature of the results of Thomas and Baldwin is that when the logarithm of the concentration of hydrogen ion is plotted against concentration of added salt in the case of the alkali chlorides, the curves are apparently straight lines, of the general formula

$$\log [H^+] = \log a + bm \qquad (1)$$

where b is a constant, a the hydrogen-ion concentration with no added salt, and $[H^+]$ the hydrogen-ion concentration in the presence of m moles per liter of added salt.

Since all that remained to make this equation a valuable instrument for the rapid estimation and control of the hydrogen-ion concentrations of pickle liquors was the determination of b for various strengths of acid, the writer, assisted by Mr. Rudolph Olson, repeated the work of Thomas and Baldwin for other strengths of sulfuric acid and sodium chloride, using the same method and type of apparatus which they describe, excepting for the substitution of a Leeds & Northrup potentiometer for

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[1] *J. Am. Leather Chem. Assoc.*, 12, 445 (1917).

[2] *Loc. cit.*

the Wolff bridge. The temperature, which was not controlled, varied between 18 and 22°. Our results for *N*, 0.1 *N*, and 0.025 *N* sulfuric acid, together with those of Thomas and Baldwin for 0.0005 *N* acid, are shown in Table I and Fig. 1.

TABLE I.—EFFECT OF NACL UPON HYDROGEN-ION CONCENTRATION OF SOLUTIONS OF SULFURIC ACID.

Moles NaCl per liter.	Log [H+] of *N*-H_2SO_4.	Log [H+] of 0.1 *N*-H_2SO_4.	Log [H+] of 0.025 *N*-H_2SO_4.	Log [H+] of 0.0005 *N*-H_2SO_4.
0.000	—0.36	—1.22	—1.72	—3.50
0.428	......	—1.13	—1.62	......
0.856	......	—1.04	—1.56	......
1.000	—0.15	......	......	—3.29
1.284	......	—0.96	—1.45	......
1.712	......	—0.87	—1.37	......
2.000	+0.03	......	......	—3.10
2.140	......	—0.77	—1.27	......
3.000	+0.24	......	......	—2.92
3.210	......	—0.55	—1.05	......
4.000	+0.45	......	......	—2.71
Value of *b*	0.20	0.21	0.21	0.20

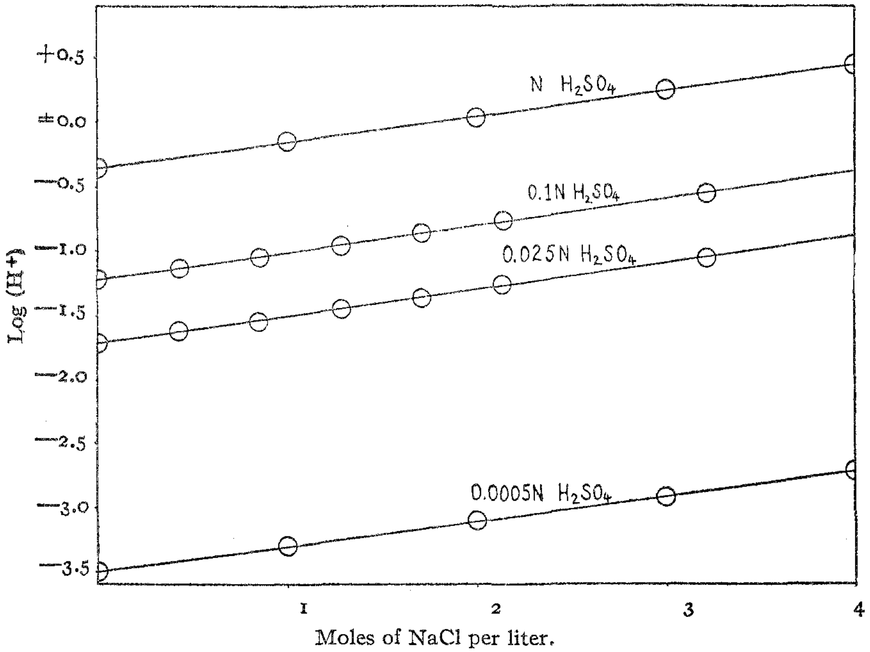

Fig. 1.

Apparently the curves are not only straight lines, but all 4 have the same slope, the average value for *b* being 0.205. The large percentage increase in hydrogen ion concentration upon the addition of 4 moles per liter of sodium chloride and the fact that it is practically the same, about 560%, for widely different strengths of acid, suggest that the effect must be due to some action of the salt upon the solvent, such as hydration. It is of course apparent that any increase in concentration of acid caused by hydration of the salt will result in a lesser percentage ionization of the acid, but at least 2 factors, other than hydration of the salt, will tend to cause an increase in hydrogen ion concentration, and these are the hydration of the acid itself and the fact that with increasing salt concentration there will be less total water, free and combined, per liter of solution. If these opposing tendencies exactly balance each other, that is, if they operate so that the percentage increase in hydrogen ion concentration found is equal to the percentage increase in concentration of total acid, then it is an easy matter to calculate the degree of hydration of the salt for any concentration. The fact that we get the same slope for all 4 curves seems to show that here the opposing tendencies are nearly balanced. Nevertheless, this may not prove true for other cases, so the safer plan would be to select acid solution so dilute as to make these opposing tendencies of negligible magnitude. It would appear, however, in the case of sulfuric acid, that $b = 0.205$ for sodium chloride in all concentrations of acid less than normal. Let us, therefore, calculate the degree of hydration of salt in a solution of acid so dilute that we may neglect the hydration of the acid and its partial volume and consider it totally ionized.

From Equation 1 $\log([H^+]/a) = bm$. But $[H^+]/a$ is the factor by which the acid concentration has been multiplied by adding m moles per liter of salt. Let w represent the total number of moles of water, free or combined with salt, in one liter of solution containing m moles of salt. The moles of free water then equal $wa/[H^+]$ and the moles of water combined with one mole of salt equal $(w/m) \times (1 - a/[H^+])$. Calling this latter value h, we have

$$h = w\,(1 - 10^{-bm})/m. \qquad (2)$$

Substituting 0.205 for b in Equation 2, we have calculated the degree of hydration of sodium chloride for several concentrations. (See Table II.)

TABLE II.—CALCULATED VALUES FOR DEGREE OF HYDRATION OF NACL AT DIFFERENT CONCENTRATIONS.

Moles NaCl per liter. (m).	Total moles water per liter. (w).	Molecules water combined with one molecule of NaCl. (h).
4.0	51.1	10.9
3.0	52.3	13.2
2.0	53.5	16.3
1.0	54.6	20.5
0.1	55.4	25.5
0.01	55.5	26.1
0.001	55.5	26.2
0.000	55.5	26.2

The striking agreement between our value 26.2 for infinite dilution and Smith's[1] calculated value of 26.5 by quite another method confirms the idea that hydration of the salt is responsible for the increase in hydrogen-ion concentration noted.

When it is required to calculate the degree of hydration only for infinite dilution, Equation 2 may be greatly simplified, since

$$\lim_{m=0} h = w(10^{bm} - 1)/m = 2.30wb = 128b. \qquad (3)$$

Conversely, given the degree of hydration at infinite dilution, one may simply divide by 128 to get b and substitute in Equation 2 to calculate hydration values for any finite concentrations, provided of course the degree of hydration follows the rule expressed by Equation 2.

For the sake of comparison we made a set of determinations with N sulfuric acid and potassium chloride, the results of which are given in Table III. Since $b = 0.14$, the degree of hydration at infinite dilution would be 128 times as great, or 18, which is not far from Smith's value of 19.2.

TABLE III.—EFFECT OF KCL UPON HYDROGEN ION CONCENTRATION OF N SULFURIC ACID.

Moles KCl per liter.	Log [H+].
0.0	—0.36
1.0	—0.21
2.0	—0.09
3.0	+0.05
Value of b	0.14

Thomas and Baldwin's results with hydrochloric acid show greater slopes for the alkali chlorides in 0.004 N than in 0.1 N acid. For each salt the value of b is less in the stronger solution by about 15% of its value in the weaker one. Since complications introduced by the acid would naturally be less noticeable in more dilute solutions, the values of b in the weaker acid may be taken as more nearly representing the true index of hydration of the salts. Values for 128b in 0.004 N hydrochloric acid follow: potassium chloride, 15; ammonium chloride, 15; sodium chloride, 26; lithium chloride, 35; and barium chloride, 50. Smith's corresponding values are potassium chloride, 19.2; ammonium chloride, 20.3; sodium chloride, 26.5; and lithium chloride, 33.6. Considering the limits of accuracy of the method as employed, the fact that temperature was not controlled, and that hydration of the acid and the repression of its ionization were ignored, the similarity between these 2 sets of results seems more than a coincidence. In fact, the writer believes it strongly confirms, for chlorides, the earlier view that the neutral salt effect is due to hydra-

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[1] THIS JOURNAL, 37, 722 (1915).

tion and also the suggestion[1] that the Hofmeister series of the ions owes its nearly fixed order to the fact that the degree of hydration of the ions runs in the same order.

The peculiar behavior of the sulfates of sodium and ammonium in lowering the hydrogen-ion concentration of acid solutions, when one might have expected them to raise it very materially, may after all be found to be due to the same forces as bring about hydration. Their action can hardly be simply that of repressing the ionization of the acid because of their effect upon chrome liquors, whose resistance to precipitation by alkalies they increase very much more than chlorides do, and this in view of the fact that in some cases they lower the hydrogen-ion concentration to a point at which precipitation of basic chromic salts might be expected without any addition of alkali. The tendency of sulfates to form addition compounds may eventually afford an explanation.

The nearly quantitative agreement between hydration values of the alkali chlorides at infinite dilution given by Smith and those calculated in this paper from hydrogen-ion measurements seems to warrant a much more extensive pursuit of the subject and especially of the use of the electrometric method for studying hydration and its effect upon concentrated solutions.

MILWAUKEE, WIS.

THE ACTIVATION OF HYDROGEN PEROXIDE BY LIGHT.

BY HARRY A. CURTIS.

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Introduction.

In studying the photolysis of hydrogen peroxide at the University of Wisconsin several years ago, it was noted by the writer that the oxidizing power of dilute hydrogen peroxide is increased when the solution is exposed to the light from a mercury vapor quartz lamp. Later this activation of hydrogen peroxide was investigated further by the writer and one of his students, Mr. Benjamin D. Cornell, at the University of Colorado. The work was interrupted by the war before it had been carried to a logical conclusion, but it appears worth while to record the results obtained.

Method.

By working with a considerable number of dyes, a few were found which, under the conditions of the experiment, were not bleached to any great extent by either light alone or the peroxide alone, but which were bleached colorless after a few hours exposure to light in the presence of

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[1] *J. Am. Leather Chem. Assoc.*, 13, 179 (1918).