(4) The viscosity or internal friction increases as the charge of the particles approaches the zero point.

(5) The rate of swelling of gelatin increases as the concentration of electrolyte approaches 0.28 molar.

B—In the zone when the concentration of electrolyte added is 0.28 molar.

(1) The migration velocity of the anions is zero and that of the cations is exactly unity. The electrolytic deposit on the cathode is smooth and pure.

(2) The anions and the cations are being adsorbed by the colloid in proportion to their mobilities; as the anions generally migrate faster than the cations there is adsorption of a larger quantity of anions than cations.

(3) The velocity of motion of the colloidal particles in the electrostatic field is zero.

(4) The viscosity of internal friction is a maximum.

(5) The rate of swelling of gelatin is a maximum.

C—In the zone when larger additions of electrolyte are made.

(1) The migration velocity of the anions is increased as the electrolyte additions are increased and the velocity of the cations is decreased in the same proportion.

(2) The adsorption of positive and negative ions continues until the particles assume a negative charge when the cations are then being adsorbed in larger proportions.

(3) The particles migrate to the anode hence are negatively charged.

(4) The viscosity of the solutions gradually decreases as the charge of the particles increases.

(5) The rate of swelling of gelatin decreases as the concentration of the electrolyte added increases. At molar concentration of zinc sulfate gelatin is precipitated.

WAPPLER ELECTRIC CO.
LONG ISLAND CITY, N. Y.

THE SALT ERROR OF CRESOL RED.[1]

BY ROGER C. WELLS.

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In the course of a study of the water of Chesapeake Bay now being made by the U. S. Geological Survey in coöperation with the U. S. Bureau of Fisheries, it was desired to determine the hydrogen ion concentration of the water taken directly from the bay at various points, and for this purpose it was decided to use the colorimetric method involving comparison with standard tubes. As the salinity of the water of the bay is considerably lower than that of sea water it appeared necessary to make new determinations of the salt error of the indicator, cresol red, for the

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[1] Published by permission of the Director, United States Geological Survey.

salinities in question and at values ranging around 7.8 for P_H. Similar studies have previously been made for several indicators.[1] As is well known, the presence of much salt affects the color of most indicators to a certain extent, so that in making comparisons allowance should be made for the amounts of salt in the standard and the unknown. The results obtained in the present study show that with the buffer mixtures used—boric acid and sodium borate—there is a considerable difference in the P_H values for mixtures having the same color in the presence and absence of salts such as sodium chloride, this difference depending on the concentration of salt and also slightly on the concentration of buffer.

A short description of apparatus and methods will first be given.

Solutions.—Cresol red, or *o*-cresol-sulfone-phthalein, is one of the indicators recommended by Lubs and Clark[2] for the range $P_{H^+} = 6.50$ to 8.50. The material used was obtained from Hynson, Westcott & Dunning, Baltimore. It was made up one part to a thousand of 50% alcohol.

The buffer solutions of boric acid and borax were made up 15 g. to a liter and led to burets protected by soda-lime tubes. No precautions were taken to purify these substances, except to filter the solutions, as it was considered better to determine the P_H value of certain mixtures than to rely on solutions of definite content.

Practically all of the experiments on the salt error were made with sea-salts which were added in the form of a concentrated sea water containing 107.3 g. per liter. It was later found, however, that sodium chloride gave practically the same results, weight for weight.

Potassium chloride solution for the 0.1 *N* calomel electrode was saturated with calomel by shaking it in the thermostat at 25°.

Apparatus.—The indicator solution was taken in 0.30 cc. portions and made up to a volume of 30 cc. for each experiment. It was measured in the graduated 2 cc. buret shown in Fig. 1.

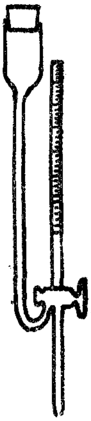

Fig. 1. Graduated 2 cc. buret.

The calomel electrodes were made up with paste prepared by Hulett's method. Three electrodes gave identical values after a week's standing.

The hydrogen electrode was mounted in a Clark cell[3] obtained from A. H. Thomas & Co. This cell could be shaken as long as desired by means of a motor and an eccentric rotating support constructed in the laboratory. The various cells were kept in a large double-chambered air thermostat fitted with observa-

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[1] Prideaux, "The Theory and Use of Indicators," London, 1917, p. 211. See also McClendon, "The Standardization of a New Colorimetric Method for the Determination of the Hydrogen Ion Concentration of Sea-water," *J. Biol. Chem.*, 30, 265 (1917).

[2] *J. Washington Acad. Sci.*, 5, 609 (1915).

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

tion windows, which ran continuously at 25°, the air being made to circulate continuously from the inner to the outer chamber by means of a small Sirocco fan. Hydrogen, made from zinc and hydrochloric acid, was passed over a hot tungsten filament and through a tower washed with dil. caustic soda solution.

The cadmium cell was compared with one at the Bureau of Standards. Two Leeds and Northrup resistance boxes were used as potentiometer by maintaining a gradient of one millivolt per ohm through 1500.0 ohms by means of an auxiliary resistance box and storage battery. The balance was obtained with a sensitive galvanometer which was read by means of a telescope and scale.

Procedure.—Each solution investigated was first brought as nearly as possible to the same color by comparison with one that was not changed throughout the course of the experiments. This was done by altering the proportions of boric acid and borax. The solutions were eventually made up to 30 cc. in small Erlenmeyer flasks by adding boric acid and borax solutions, and water, keeping the flasks stoppered as much as possible. When the matching was completed a portion of each solution was transferred to the hydrogen-electrode cell, which had first been filled with hydrogen and well rinsed with the solution. After shaking for 15 minutes, the gas was displaced by a stream of fresh hydrogen for 2 minutes, and then the shaking continued 5 minutes longer. Fresh contacts with 4.1 *N* potassium chloride solution were then made in wide tubes with the solutions in the 2 half-cells and the e. m. f. read immediately. The e. m. f. usually rose slightly on standing but the first readings were used.

From the e. m. f. the hydrogen ion concentration was calculated by the equation

$$P_{\mathrm{H}} = -\log[\mathrm{H}^+] = \frac{E - 0.3369}{0.0591}.$$

E represents the e. m. f. observed corrected to represent dry hydrogen at 25° and 760 mm. pressure. This correction, however, ranged only from +0.3 to +0.7 millivolt, as follows:

Pressure of H_2.	Correction.
750	+0.2
740	+0.4
730	+0.6
720	+0.8

Discussion of Results.—The results are shown in Table I and Fig. 2. Expts. 1*c* to 3*b*, inclusive, were made with only buffer present. They show that as the quantity of buffer is increased the solution becomes slightly more acid. The effect of salt is similar, but a given weight of salt, or sea salts, produces a much more acid solution than the same weight of buffer. All of the solutions represent the same color. In other words, the color of cresol red cannot be ascribed entirely to the hydrogen ion concentration, although that is the principal factor.

TABLE I.

Solutions Made up to 30 cc. to have same color with cresol red. P_H from e. m. f. Measurements with hydrogen and 0.1 N calomel electrodes at 25° C.

Expt.	Boric acid solution. Cc.	Borax solution. Cc.	Salt solution. Cc.	Buffer. g/l.	Salt. g/l.	E. m. f. of cell.	P_H.
1c[a]	0.18	0.08	None	0.13	None	0.8159	8.10
1d	0.32	0.13	None	0.23	None	0.8276	8.30
1e	0.43	0.20	None	0.32	None	0.8241	8.24
1ea[a]	0.50	0.20	None	0.35	None	0.8094	7.99
1f	0.88	0.30	None	0.59	None	0.8243	8.25
2	1.35	0.55	None	0.95	None	0.8237	8.24
2a	1.80	0.63	None	1.21	None	0.8232	8.23
3	3.02	1.20	None	2.11	None	0.8237	8.24
3a	6.00	2.32	None	4.17	None	0.8207	8.18
3b	19.90	12.80	None	16.30	None	0.8152	8.09
4	0.57	0.20	0.10	0.28	0.36	0.8161	8.11
4a	0.50	0.18	0.20	0.34	0.72	0.8119	8.04
4b	1.70	0.70	0.10	1.20	0.36	0.8194	8.16
5	1.51	0.51	0.20	1.01	0.71	0.8169	8.12
6a	1.20	0.40	0.40	0.80	1.43	0.8146	8.08
8	0.54	0.21	0.41	0.38	1.47	0.8113	8.03
8a	0.62	0.20	0.56	0.41	1.98	0.8087	7.99
9	0.55	0.18	1.12	0.36	4.00	0.8060	7.94
10	1.70	0.62	1.68	1.19	6.00	0.8065	7.94
10b	1.10	0.30	2.00	0.70	7.18	0.8048	7.92
11	0.48	0.18	3.30	0.33	11.8	0.8019	7.87
12	6.50	0.20	5.03	0.35	18.0	0.8003	7.84
13	10.13	4.87	7.83	7.50	28.0	0.8007	7.85
18	0.55	0.21	7.83	0.38	28.0	0.7980	7.80
19	1.04	0.30	9.23	0.67	33.0	0.7985	7.81
20	1.04	0.30	11.40	0.67	40.8	0.7988	7.81
21	1.60	0.52	11.46	1.06	41.0	0.7964	7.78
22	0.48	0.28	20.98	0.38	75.0	0.7933	7.72
23	0.76	0.13	28.81	0.45	103.2	0.7897	7.67
24[b]	10.00	5.00	5.03	7.50	18.0	0.8059	7.94
25	0.47	0.20	5.03	0.34	18.0	0.8018	7.88
26	15.00	9.92	5.03	12.5	18.0	0.8063	7.94
27	10.00	5.30	7.54	7.67	27.0	0.8036	7.89
28[c]	10.13	4.87	7.82	7.50	28.0	0.8007	7.85

[a] Probably affected by CO_2 and not shown in Fig. 2.

[b] New standard color.

[c] Last standard color.

It is somewhat difficult to determine the salt effect at low concentrations on account of the necessity of having some buffer present to maintain a stable P_H value. But the total effect is not additive, as the presence of buffer with salt nullifies the effect of the salt to a certain extent. Several experiments (*e. g.*, Nos. 4, 4*a*, 4*b*, 5, 25, 26) were made to determine what allowance should be made for the action of the buffer on the salt but the effect appeared to be only about 0.07 in the P_H value for the extreme cases, so that no corrections seemed necessary when, as in most of the experiments, the weight of salt used was greatly in excess of the weight of buffer.

Fig. 2 is based on the weights of salt without any correction for the weight of buffer, for all experiments in which the weight of buffer was small in comparison with the weight of salt. The P_H values are plotted against $\log_2 S$, S being the salinity in g. per liter of sea salts (or buffer). The logarithm to base 2 was chosen in order to give the various concentrations more nearly equal importance in the figure.

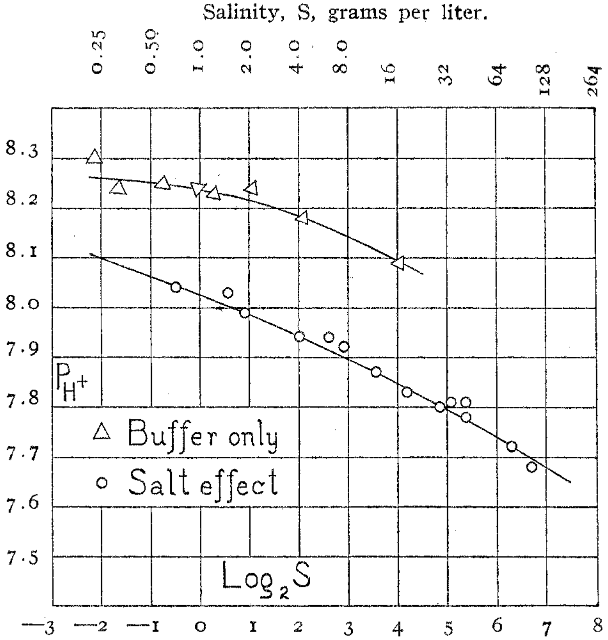

Fig. 2.—Salt effect at constant color.

Several e. m. f. determinations were made using half-saturated potassium chloride as connecting solution, in order to extrapolate according to Bjerrum's method, but the differences found between those obtained with saturated potassium chloride were too small to be worth considering.

Applications.—The principal object of the study was to prepare tubes of standard P_H value. When small amounts of buffer are used the solutions are quickly affected by carbon dioxide of the air or by glass of the containing vessels. It is therefore advisable to use a large amount of buffer and an insoluble glass. Ampules of Pyrex glass that can be closed by sealing have been found serviceable. For the work in hand it was decided to have the standard tubes require no correction when compared with unknown solutions having a salinity of 18 g. per liter of salt and very little buffer, but as the standard tubes were to contain 0.225 g. of buffer in 30 cc. or 7.5 g. per liter the quantity of salt in each standard tube was increased to 1.26 g in order to counterbalance the increased amount of buffer, this being the quantity of salt indicated by the curve of Fig. 2 to make a lowering of 0.07 in the P_H value over that for 18 g. of salt per liter with very little buffer present. Each tube was therefore made up to 30 cc. with water, after adding 0.3 cc. of indicator solution, 15 cc. of buffer solutions, and 1.26 g. of sodium chloride.[1] The correction when such tubes are compared with waters having other salinities are given in Table II.

TABLE II.

Corrections in Using Standard Color Tubes Containing 0.3 cc. of Cresol Red, 0.225 g. of Buffer and 1.26 g. of Salt in 30 cc.

Salinity of unknown g. per liter.	Correction to P_H marked on standard.
0.2	+0.27
0.5	+0.22
1.0	+0.19
2.0	+0.14
5.0	+0.09
10.0	+0.04
15.0	+0.01
18.0	0
20	—0.01
25	—0.03
30	—0.05
35	—0.06
40	—0.07
100	—0.15
200	—0.21

In making comparisons 0.3 cc. of indicator is placed in a tube similar to those containing the standards and made up to the 30 cc. mark with the water to be tested. Different lots of indicators may vary so much that it is best to make all comparisons with the same indicator solution as used in the standard tubes. When the matching of the standard and unknown is completed the value marked on the standard is recorded, to be corrected eventually for the salinity of the sample under scrutiny.

Before making up the standard tubes a few P_H determinations are made with various buffer mixtures, using connecting solutions with both standard and half-saturated potassium chloride in order to extrapolate if necessary. A curve is then constructed so that a mixture of any desired P_H value within range of the buffer solutions can quickly be pre-

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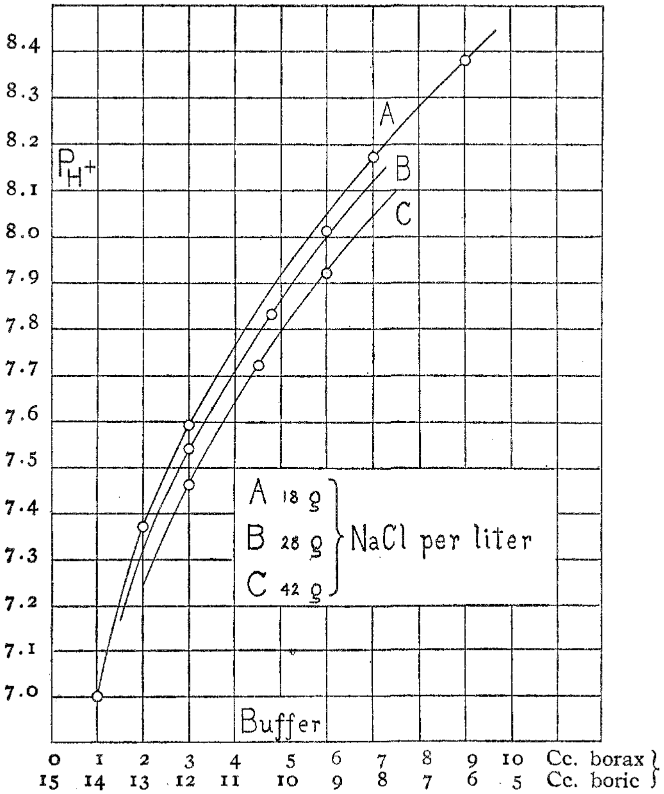
[1] If the action of the buffer here is to reduce the ionization of the sodium chloride it seems that the action should be due more to the borax than to the boric acid, but over the small range of P_H investigated this was not definitely proved.

pared. Some figures obtained in standardizing buffer mixtures are given in Table III, which also shows the variations caused by different amounts of salt while the quantity of buffer remains constant. The results are reproduced in Fig. 3.

TABLE III.—SALT EFFECT WITH TOTAL BUFFER CONSTANT.

Expt.	Water. Cc.	Boric acid. Cc.	Borax. Cc.	Sodium chloride.[a] Cc.	Indicator. Cc.	P_H.
32	12.64	14.00	1.00	2.06	0.30	7.00
33	12.64	13.00	2.00	2.06	0.30	7.37
31	12.64	12.00	3.00	2.06	0.30	7.59
30	12.64	8.00	7.00	2.06	0.30	8.17
34	12.64	6.00	9.00	2.06	0.30	8.38
36	11.51	12.00	3.00	3.19	0.30	7.54
43	11.51	10.20	4.80	3.19	0.30	7.83
35	11.51	9.00	6.00	3.19	0.30	8.01
40	9.90	12.00	3.00	4.80	0.30	7.46
41	9.90	10.50	4.50	4.80	0.30	7.72
42	9.90	9.00	6.00	4.80	0.30	7.92

[a] Containing 0.2628 g. per cc.



made up to 30 cc. together with indicator and salt.
Fig. 3.—Salt effect with buffer constant.

It is possible that the salt effect may be used in certain cases to produce definite hydrogen ion concentrations with certain buffers where the buffer mixtures alone do not cover the P_H value desired.

Remarks.—A few difficulties connected with the work here described may be mentioned. When small quantities of buffer were used the colors were often dimmed by the action of carbon dioxide from the air before the e. m. f. could be measured. Moreover, in the course of the first experiments, extending over about 3 weeks, a slow drift toward the acid side was detected about the third week in the solution serving as the constant standard color for comparison, so that the results were not as concordant as they might have been and were therefore discarded. Whether this was caused by fading of the indicator in the solution serving as standard color, by evaporation of the stock solution of indicator, or by changes in the stock buffer solutions could not be ascertained. It may have been due to all 3 causes. Fresh color standards made up like the first were slightly redder and gave slightly higher P_H values. By starting with a standard having a given P_H value, however, the curves shown in Fig. 2 were constructed before any changes could be detected. Under any circumstances it is probably advisable to keep the standard tubes in the dark when not in use in order to avoid the bleaching action of light. It is not certain that the indicator suffers no change over long intervals but it certainly does not fade out entirely.

It may be noted that to reproduce definite P_H values the dilution of a given borate buffer mixture must be controlled as well as the proportions of boric acid and borax, and the amount of salt.

U. S. Geological Survey,
Washington, D. C.

[Contribution from the Chemical Laboratory of the University of Illinois.]

THE REACTION BETWEEN CHLORINE AND AMMONIA, II.[1]

By William A. Noyes and A. B. Haw.

Received July 12, 1920.

Some years ago one of us, working with A. B. Lyon,[2] showed that a considerable amount of nitrogen trichloride may be formed by the action of chlorine on a dilute solution of ammonia. An equation representing a somewhat complicated reaction was given to account for the result obtained and in the discussion it was suggested that in this reaction, and probably in others which are not usually considered as ionic, molecules separate into positive and negative parts as they react.

W. C. Bray and C. T. Dowell[3] have pointed out that the complicated,

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[1] Abstract of a thesis submitted to the University of Illinois in partial fulfilment of the requirements for the degree of Master of Science.

[2] Noyes and Lyon, This Journal, 23, 460 (1901).

[3] Bray and Dowell, *ibid.*, 39, 907 (1917).