THE HYDROLYSIS OF SODIUM OXALATE AND ITS INFLUENCE UPON THE TEST FOR NEUTRALITY.[1]

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I. Introduction.

1. Purpose of the Investigation.—The use of sodium oxalate as a primary standard for acidimetry and oxidimetry was suggested in 1897 by Sörensen,[2] who described its preparation, testing and use, in subsequent papers.[3] Its general adoption as a standard has been hindered by the difficulty of securing from the manufacturers material of a purity conforming to the specifications prepared by Sörensen.[4] In order to determine the composition of sodium oxalate as purchased, and to secure, if possible, a material of the requisite purity to issue as a standard sample, specimens of sodium oxalate were obtained by purchase in the open market or directly from the maker, from two European and three American manufacturers. In the course of the subsequent tests, the methods described by Sörensen were found satisfactory, with the exception of that for the determination of sodium carbonate or sodium acid oxalate, in which discrepancies were found, which led to the following investigation. Sörensen's directions are given in the following paragraph, and an improved method, based on this investigation, is described in the final summary:

2. Sources of Uncertainty in Sörensen's Method.—Sörensen's method for testing the neutrality of the sodium oxalate is as follows: Introduce into a conical Jena flask about 250 cc. of water and 10 drops of phenolphthalein solution (0.5 gram phenolphthalein dissolved in 50 cc. alcohol and 50 cc. of water), and evaporate to 180 cc. while passing in a current of pure air, free from carbon dioxide. Allow to cool to the ordinary temperature and add 5 grams of sodium oxalate. Upon shaking carefully, while maintaining the current of air, the oxalate slowly dissolves. If the solution is red, not more than 4 drops of decinormal acid should

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[1] Published by permission of the Director of the Bureau of Standards.

[2] *Z. anal. Chem.*, 36, 639–43 (1897).

[3] *Ibid.*, 42, 333–59, 512–6 (1903).

[4] Merck, "Prüfung der Chemischen Reagenzien auf Reinheit," (1905); Krauch-Merck, "Chemical Reagents," (1907).

be required to render it colorless, while if the solution is colorless, it should acquire a distinct red color upon the addition of not more than 2 drops of decinormal sodium hydroxide.

Preliminary experiments showed that the following points in the above method required investigation:

(*a*) Is pure sodium oxalate neutral toward phenolphthalein, or is the hydrolysis sufficient to produce an alkaline reaction?

(*b*) Does sodium oxalate solution decompose on boiling, or is the increased alkalinity due to the action upon the glass?

(*c*) Is any excess of alkali present entirely in the form of Na_2CO_3, or may $NaHCO_3$ actually exist in a material heated to 240°?

(*d*) Under given conditions of titration, to what form should the excess of alkali or acid be calculated, and what errors in the use of sodium oxalate as an acidimetric or oxidimetric standard are caused by the presence of a given excess of acid or alkali?

II. The Hydrolysis of Sodium Oxalate.

1. Theoretical Considerations.—Souchay and Lenssen[1] stated that "the aqueous solution does not affect curcuma paper, but blues red litmus paper, especially on boiling." Sörensen[2] considered that the slightly alkaline reaction which most of his preparations showed toward phenolphthalein was probably due to a trace of sodium carbonate, though admitting the possibility of alkalinity due to hydrolysis, in the sense of the equation

$$Na_2C_2O_4 + H_2O = NaOH + NaHC_2O_4.$$

Since the apparent alkalinity of his samples (a maximum of about 0.05% Na_2CO_3) represented a negligible error when used as an acidimetric standard, Sörensen dismissed the subject without further study.

(*a*) *Calculation of the Theoretical Hydrolysis.*—The hydrolysis of sodium oxalate may be represented thus:

$$Na_2C_2O_4 + H_2O \rightleftarrows NaHC_2O_4 + NaOH$$

which may be expressed as follows in terms of ions:

$$Na_2C_2O_4 \rightleftarrows 2Na^+ + C_2O_4^{--}$$

$$C_2O_4^{--} + H_2O \rightleftarrows HC_2O_4^- + OH^-.$$

The hydrolysis may be considered as due entirely to the small value of the ionization constant of the second hydrogen of oxalic acid, which is only about one-thousandth of that of the first hydrogen of this acid.[3] In such a solution, therefore, $[HC_2O_4^-]$ is practically equal to $[OH^-]$, while $[C_2O_4^{--}]$ is equal to the product of the concentration of the salt and its ionization. Thus:

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[1] *Ann.*, **99**, 33 (1856).

[2] *Z. anal. Chem.*, **42**, 351 (1903).

[3] Chandler, THIS JOURNAL, **30**, 694–713 (1908).

$$[HC_2O_4^-] = [OH^-] \qquad K_{A_2} = \frac{[H^+][C_2O_4^{--}]}{[HC_2O_4^-]}$$

$$[C_2O_4^{--}] = \gamma C \qquad K_w = [H^+][OH^-]$$

where c = molar concentration of the solution, *i. e.*, the number of gram molecules in one liter of the solution.

γ = ionization of the salt.

K_{A_2} = dissociation constant for the second H of $H_2C_2O_4$.

K_w = dissociation constant for H_2O.

By substitution $[H^+] = \sqrt{K_{A_2}K_w/\gamma C}$.

To calculate $[H^+]$ for 0.1 *M* (molar) solution of sodium oxalate, the following values were employed:

$$K_{A_2} = 4.5 \times 10^{-5}.^*$$

$$K_{W25^\circ} = 1.1 \times 10^{-14} \text{ and } K_{W18^\circ} = 0.6 \times 10^{-14}.^\dagger$$

$$\gamma = 0.7.^1$$

		Round number employed.
from which	$[H^+]_{18^\circ} = 1.96 \times 10^{-9}$	2.0×10^{-9}
and	$[OH^-]_{18^\circ} = 3.06 \times 10^{-6}$	3.1×10^{-6}
	$[H^+]_{25^\circ} = 2.66 \times 10^{-9}$	2.7×10^{-9}
	$[OH^-]_{25^\circ} = 4.14 \times 10^{-6}$	4.1×10^{-6}

In the subsequent calculations the round numbers indicated have been employed.

(*b*) *Calculation of Standards for Comparison.*—For the purpose of comparison, standards of calculated alkalinity were prepared from mixtures of ammonium chloride and hydroxide, on the following basis:

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* Chandler [THIS JOURNAL, 30, 694–713 (1908)] found by partition experiments 4.1×10^{-5}, and by conductivity, 4.9×10^{-5}. The mean value 4.5×10^{-5} has been employed for both 18° and 25°, although determined by Chandler at 25°; since the temperature coefficient is probably less than the uncertainty in the value for 25°.

† Derived from the following values:

	25°, $K \times 10^{14}$.	18°, $K \times 10^{14}$.
Arrhenius, *Z. physik. Chem.*, 11, 805 (1893)	1.2	. .
Wijs & van't Hoff, *Ibid.*, 12, 514 (1893)	1.4	0.64
Löwenherz, *Ibid.*, 20, 283 (1896)	1.4	. .
Kanolt, THIS JOURNAL, 29, 1402 (1907)	0.8	0.46
Hudson, *Ibid.*, 31, 1130 (1909)	1.0	. .
Lorenz & Böhi, *Z. physik. Chem.*, 66, 733 (1909)	1.2	0.72
Heydweiller, *Ann. Physik*, 28, 503 (1909)	1.0	0.59
[Recalc. from Kohlrausch & Heydweiller, *Wied. Ann.*, 53, 709 (1894)]	——	——
Mean,	1.1	0.60

[1] Kohlrausch [*Leitvermögen der Elektrolyte*, p. 161 (1898)] and Noyes and Johnston [THIS JOURNAL, 31, 987 (1909)], both found for 0.1 *M* $K_2C_2O_4$ at 18°, $\gamma = 0.7$, which value has been assumed to hold for $Na_2C_2O_4$.

The ionization constant[1] of ammonium hydroxide at 25° $= 1.8 \times 10^{-5}$, *i. e.*,

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} \text{ and } \frac{[NH_4^+]}{[NH_4OH]} = \frac{1.8 \times 10^{-5}}{[OH^-]}$$

$$\therefore \frac{[NH_4^+]}{[NH_4OH]} = \frac{1.8 \times 10^{-5}}{4.1 \times 10^{-6}} = 4.4$$

Since, however, 0.1 N NH_4Cl is about 85% ionized[2] it is necessary to use $4.4 \div 0.85 = 5.2$ parts of 0.1 N NH_4Cl to 1 part 0.1 N NH_4OH to prepare a solution in which $[H^+]_{25°} = 2.7 \times 10^{-9}$.

A second comparison was made with 0.1 N sodium acetate, for which the following constants were employed:

$$K_{Ac} = 1.8 \times 10^{-5},^*$$

$$\gamma = 0.8$$

from which $$[H^+] = \sqrt{K_{Ac}K_W/\gamma C} = 1.6 \times 10^{-9},$$

i. e., 0.1 N sodium acetate should be slightly more alkaline than 0.1 M sodium oxalate.

Mixtures of 0.1 N sodium borate and hydrochloric acid, and of glycocoll and sodium hydroxide were also prepared, according to Sörensen[3] who calculated $[H^+]_{18°}$ for such solutions from e. m. f. measurements with a hydrogen electrode.[4] As his measurements were made at 18°, the observations were confined to that temperature.

(*c*) *Choice of Indicator for Comparison.*—Preliminary tests showed that phenolphthalein is the only indicator that is sensitive in solutions of exactly this alkalinity. Alizarin, cyanin and dinitrohydroquinone all proved unsatisfactory for accurate matching, though the latter was sufficiently sensitive to confirm approximately the results with phenolphthalein. The indicator selected for the final comparison was, therefore, phenolphthalein, for which the most probable value[5] of K is 1.7×10^{-10}. In a solution in which $[H^+]_{25°} = 2.7 \times 10^{-9}$ this indicator should, therefore, be transformed into its salt to the extent of 5.9%.[6]

$$\frac{[H^+]\ [I^-]}{[HI]} = 1.7 \times 10^{-10}$$

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[1] Noyes and Sosman, "Electrical Conductivity of Aqueous Solutions," *Carn. Inst. Pub.*, 63, 228 (1908).

[2] Calculated from Kohlrausch, "Leitvermögen der Elektrolyte," p. 159 (1898).

* Noyes and Sosman, *loc. cit.*

[3] Sörensen, *Compt. rend. trav. lab. Carlsberg*, **8**, 1–168 (1910); *Biochem. Z.*, **21**, 131–304 (1910).

[4] Several of Sörensen's mixtures were checked electrometrically and colorimetrically by Auerbach and Pick, *Arbeit. Kais. Gesundheitsamte*, **38**, 243–74 (1911).

[5] Hildebrand, *Z. Elektrochem.*, **14**, 351 (1908). Wegscheider, *Ibid.*, 510 (1908). Rosenstein (Mass. Inst. Tech.), private communication from W. C. Bray.

[6] Noyes, THIS JOURNAL, **32**, 861 (1910).

$$\frac{[I^-]}{[HI]} = \frac{1.7 \times 10^{-10}}{2.7 \times 10^{-9}} = 6.3 \times 10^{-2} = \frac{5.9}{94.1}$$

These calculations are based upon the assumption that the ionization constant of phenolphthalein is the same at 18° and 25° and that the color of the indicator is not materially affected by the presence of neutral salts.

2. Experimental Part.

(a) *Purification and Preparation of Materials and Solutions.*

Air.—Air was freed from carbon dioxide by passage through two wash bottles containing 30% potassium hydroxide and a U tube with a ten-inch column of soda lime, followed by absorbent cotton.

Water.—The regular distilled water was re-distilled from alkaline permanganate. It was then boiled in a seasoned Jena flask for two hours in a stream of pure air and preserved in a Jena flask provided with a siphon and a soda lime guard tube. This water has a specific conductivity of 2×10^{-6} reciprocal ohms and evolved no carbon dioxide when a small portion was boiled for one-half hour in a stream of pure air, which after being dried with calcium chloride was passed through a weighed soda lime tube.

Sodium Oxalate.—Pure sodium oxalate was prepared from two commercial samples. One, designated A, contained originally (as determined in the final tests) 0.02% $NaHC_2O_4$, while that marked B contained 0.04% Na_2CO_3 and considerable CaC_2O_4. These materials were recrystallized in platinum, the solutions being electrically heated, and the surrounding atmosphere being kept as free from carbon dioxide as possible. The fine crystals obtained were sucked dry on a platinum cone, and dried in an electric oven at 240°. A portion of the product of the third recrystallization of B was dissolved in water and precipitated by the addition of double distilled neutral alcohol, the product being filtered out and dried as above. The following samples of sodium oxalate were thus obtained:

Water crystallization, A_1, A_2; B_1, B_2, B_3.

Alcohol precipitation B_4.

Since in subsequent tests these samples were found to produce almost the same colors with phenolphthalein, we may conclude that a single water crystallization eliminated practically all of the impurities above noted, and as a constant and uniform product was obtained by recrystallization of materials originally respectively acid and alkaline, it is reasonably certain that the product represented pure sodium oxalate.

Ammonium Chloride.—A normal solution was prepared from J. T. Baker's special ammonium chloride, dried at 110° for two hours. This material was found to contain no organic bases when tested according to Krauch.

Ammonium Hydroxide.—A decinormal solution was prepared from re-distilled ammonia and standardized against decinormal hydrochloric acid, which in turn was standardized gravimetrically by means of silver chloride. Methyl red was used as the indicator. The solution was preserved in a ceresin-lined bottle and measured in a burette closed with a soda lime tube.

Sodium Hydroxide.—Pure material was prepared from metallic sodium with exclusion of carbon dioxide.[1] The resulting strong solution was titrated against standard hydrochloric acid and diluted to 0.01 *N* solution, which was preserved in a ceresin-lined bottle.

Oxalic Acid.—A 0.01 *N* solution was prepared from J. T. Baker's crystallized oxalic acid.

Sodium Acetate.—Merck's crystallized sodium acetate was recrystallized in platinum. The products of the crystallizations were sucked dry on a platinum cone, dried between filter paper and finally air-dried.

Sodium borate ($Na_2B_4O_7$) solution was prepared from equivalent quantities of twice recrystallized boric acid, and pure sodium hydroxide.

Glycocoll (amino-acetic acid) solution was prepared according to Sörensen, by dissolving 7.505 grams glycocoll (Kahlbaum) and 5.85 grams NaCl in one liter.

Phenolphthalein.—A 1% alcoholic solution of the indicator was employed *i. e.*, about 0.03 *N*. In each comparison exactly 0.2 cc. of this solution was employed in a total volume of 150 cc., thus giving a solution in which the phenolphthalein is about 1/22000 *N*. According to McCoy,[2] the saturated aqueous solution of this indicator is about 1/11000 *N*. A solution of such concentration (*i. e.*, 0.4 cc. in 150 cc.) was, however, always turbid, so that the smaller concentration was employed, giving a color of convenient intensity for comparison. Alcohol was not present in amount sufficient to affect the color[3] of the indicator.

(*b*) *Stability of Sodium Oxalate Solutions.*—Before attempting to prepare and test pure sodium oxalate, it was necessary to determine the effect of heat upon its solution. Sörensen[4] found that a sodium oxalate solution became more alkaline upon boiling, whether in water that had previously been boiled or not, and equally in a stream of air, oxygen or nitrogen. He attributed the increased alkalinity to a decomposition in the sense of the equation

$$2Na_2C_2O_4 + H_2O = CO_2 + Na_2CO_3 + 2HCOONa,$$

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[1] Findlay, "Practical Physical Chemistry," p. 176 (1906).

[2] *Am. Chem. J.*, 31, 503 (1904).

[3] McCoy, *Ibid.*, 31, 503 (1904). Hildebrand, *Z. Elektrochem.*, 14, 351 (1908). THIS JOURNAL, 30, 1914 (1908).

[4] *Z. anal. Chem.*, 42, 352 (1903).

quoting Carles[1] who found that oxalic acid solution decomposed similarly if boiled in a stream of an inert gas.

That no appreciable decomposition takes place upon boiling sodium oxalate solution was shown by the following experiments:

Five grams of the salt were boiled with pure water in a stream of pure air, which was passed through calcium chloride and then through a weighed soda lime tube. The latter was reweighed at the end of two hours, replaced, and the solution acidified and again boiled to determine whether any sodium carbonate was formed in the boiling of the aqueous solution. The amount of carbon dioxide evolved on direct acidification was also determined. The apparatus and method were tested with known small quantities of sodium carbonate.

TABLE I.—EVOLUTION OF CARBON DIOXIDE ON BOILING SOLUTIONS CONTAINING FIVE GRAMS OF SODIUM OXALATE.

Exper.	Sample.	Solution.	Time. Minutes.	Weight of CO_2. Mg.
1	A	Acidified	15	0.3
2*a*	A	Aqueous	15	0.0
b	A	Aqueous	+120	0.2
c	A	Acidified	+15	0.2
3*a*	B	Acidified	15	1.3
b	B	Acidified	30	1.4
4*a*	B	Aqueous	15	0.6
b	B	Aqueous	+120	0.3
c	B	Acidified	+15	0.5

Since in experiments 1 and 2*b* practically the same amount of CO_2 was evolved on 15 minutes' treatment with acid as upon two hours' boiling with water, we may conclude that no appreciable decomposition takes place in two hours' boiling, though the solutions become markedly alkaline. The evolution of 0.6 mg. CO_2 in 4*a* is believed to be due to the presence of $NaHCO_3$ (or occluded CO_2) in this sample (p. 127).

(*c*) *Effect of Sodium Oxalate Solution on Glass.* — Further tests showed that there was no increase in alkalinity upon boiling the sodium oxalate solution for two hours in a platinum dish or in a quartz flask in a current of pure air (cf. Table II, 1*b*,*c*,*d*). The increased alkalinity noted by Sörensen must, therefore, have been due to the attack of the glass (Jena glass) employed by him. Since it was impracticable to employ entirely quartz flasks, tests were carried out to determine the relative effect of sodium oxalate solutions upon different kinds of glass. Flasks of several kinds of glass were prepared of approximately the same shape and size, with tubes ground in for the inlet and exit of the pure air (except the quartz flask). Two-gram portions of sodium oxalate were boiled with 125 cc. pure water and 0.2 cc. phenol-

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[1] *Compt. rend.*, **71**, 226 (1870).

phthalein solution in a stream of pure air. At the end of the test they were titrated with 0.01 *N* oxalic acid till the solutions were colorless. The results were as follows:

TABLE II.—EFFECT OF SODIUM OXALATE SOLUTIONS UPON GLASS. INCREASED ALKALINITY IN TERMS OF 0.01 *N* OXALIC ACID.

Expt.	Glass.	Sodium oxalate.	Time. Min.	Volume of 0.01 *N* $H_2C_2O_4$. cc.
1*a*	Quartz	A	120	0.0
b	Quartz	F	120	0.5[1]
c	Quartz	F	60	0.5
d	Quartz	F	10	0.4
2*a*	Durax	A	120	0.5
b	Durax	A	120	0.5
c	Durax	F	120	0.7
3*a*	Jena Geräte	A	120	4.9
b	Jena Geräte	A	120	4.6
c	Jena Geräte	F	120	5.1
4*a*	German soft	A	120	6.8
b	German soft	A	120	6.7
c	German soft	F	120	6.5
5*a*	Resistance	A	120	8.7
b	Resistance	A	120	6.6
c	Resistance	F	120	8.5
6*a*	Jena Verbund	F	120	4.1

From Table II it is evident that the Durax glass[2] is not appreciably attacked by neutral or faintly alkaline sodium oxalate solutions during two hours' boiling, *i. e.*, much longer than is required to expel any CO_2 from the solution. For the subsequent experiments, vessels of quartz, platinum, or Durax glass were, therefore, employed. It may be noted that in none of the flasks did the solution acquire more than a very faint pink color at the end of 15 minutes, though the Jena Geräte glass was most rapidly attacked, and is least suited for this purpose. As the successive tests of each glass were made on the same vessels with approximately equal results there is no marked evidence of "seasoning" of the glass by several hours' boiling.

(*d*) *Presence of Sodium Bicarbonate in Sodium Oxalate.*—Sörensen dismissed the question of the existence of sodium bicarbonate by stating that it could not possibly be present in material dried at 240°, since it decomposes at or below 100°. In the course of the testing, however, it was found that several of the samples when dissolved in pure water

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[1] All the 2-hour results for F have been corrected for this "original" alkalinity.

[2] Durax glass made by Schott & Gen. is furnished only in the form of tubing, which formerly was distinguished by a longitudinal blue line, which has recently been changed to a green line. Verbund glass, formerly made with no distinguishing mark, now has a blue line. This information was secured directly from the maker, and is of importance in view of the confusion of terms in some of the recent catalogues of glassware.

containing phenolphthalein were colorless, or nearly so, but after a few minutes' boiling became strongly pink and remained pink on cooling, indicating the presence of an appreciable excess of alkali, which would have been overlooked if tested according to Sörensen. Such samples, *e. g.*, B, evolved carbon dioxide upon boiling the aqueous solution, and upon boiling with acid evolved a total amount of carbon dioxide greater than would correspond to the titrated alkalinity, if calculated as Na_2CO_3. From Table III it may be seen that in every case the gravimetric and volumetric results agreed more closely if calculated to $NaHCO_3$ than to Na_2CO_3 and that in all but E, the carbon dioxide is apparently even in excess of that calculated for $NaHCO_3$.

TABLE III.—DETERMINATION OF EXCESS ALKALI IN SODIUM OXALATE.

		Grav. detn. of CO_2. Calculated as		Vol. detn. of alkali. Calculated as	
Expt.	Sample.	Na_2CO_3. %.	$NaHCO_3$. %.	Na_2CO_3. %.	$NaHCO_3$. %.
1	B	0.065	0.051	0.036	0.057
2	C	0.291	0.230	0.107	0.171
3	D	0.308	0.244	0.120	0.192
4	E	1.31	1.05	0.70	1.11

It is evident, therefore, that if such samples were tested with the object of making corrections for accurate work, appreciable errors might arise if the alkalinity were calculated to Na_2CO_3. For samples containing less impurity than B, the differences would be entirely negligible.

With our present means of analysis, it is impossible to state whether such "excess" carbon dioxide (above Na_2CO_3) is present as $NaHCO_3$ or in some occluded form. That it is not readily given off at 240° was shown in E, which lost only 0.14% in two hours' heating at 240°, though it contained about 0.4% of such excess "carbonic acid." When we consider that as usually prepared (by neutralization of oxalic acid with sodium carbonate) the salt separates from a solution charged with carbon dioxide; it is not impossible that the latter should be occluded in it, in a form in which it is not readily expelled at high temperatures, just as water has been shown to exist in materials heated to high temperatures.[1]

(*e*) *Colorimetric Comparisons.*—All of the solutions for comparison were prepared in 300 cc. flasks of Durax glass with a long, narrow neck to facilitate exclusion of carbon dioxide. Before being used, these were boiled for two hours with pure water, allowed to soak in water for 36 hours, and were filled with 0.1 *M* sodium oxalate (or solutions of approximately the same alkalinity) for several days before the final tests were made.

Decimolar solutions of sodium oxalate were prepared by dissolving two grams of the salt in 150 cc. of pure water, to which was added 0.2

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[1] Richards, THIS JOURNAL, **33**, 888 (1911).

cc. of phenolphthalein. The solutions were boiled for ten minutes in a stream of pure air, which was continued during their cooling to room temperature. The flasks were then closed with rubber stoppers and placed in a thermostat adjusted to the desired temperature (±0.2°).

Ammonium Chloride Hydroxide.—Solution of the calculated alkalinity ($[H^+]_{25°} = 2.7 \times 10^{-9}$) was prepared by mixing 15.0 cc. *N* ammonium chloride, 28.8 cc. 0.1 *N* ammonium hydroxide and 0.2 cc. phenolphthalein and diluting to 150 cc., the resultant solution being decinormal with respect to the salt, *i. e.*, ammonium chloride. In the determinations of the value of the ionization constant for phenolphthalein given above, Hildebrand[1] and Rosenstein[2] employed solutions not over 0.05 *N*, with respect to ammonium chloride, in order to reduce the neutral salt effect.[3] In these tests it was hoped that by making all the solutions 0.1 *N*, the neutral salt effect would be largely eliminated. (From the standpoint of hydrolysis, 0.1 *M* sodium oxalate may be considered as 0.1 *N*.)

From Sörensen's chart, mixtures of 7.06 cc. of 0.1 *N* $Na_2B_4O_7$ and 2.94 cc. 0.1 *N* HCl, or of 9.34 cc. glycocoll solution and 0.66 cc. 0.1 *N* NaOH, produce solutions in which $[H^+]_{18°} = 2.0 \times 10^{-9}$ (*i. e.*, $10^{-8.7}$). Mixtures in these proportions were prepared with a total volume of 150 cc.

Phenolphthalein solutions of calculated transformation were prepared[4] by adding an accurately measured amount (0.2 cc.) of phenolphthalein to 150 cc. of water containing 10 cc. of 0.1 *N* sodium hydroxide, whereby the indicator was completely transformed into its red salt. Measured portions of this solution were then diluted to 150 cc. to produce the standards representing the desired percentage transformation. In each solution for comparison or titration, it is, of course, necessary to have exactly 0.2 cc. of the original phenolphthalein solution in the same total volume.

The following comparisons were made by direct optical matching of the solutions in the Durax flasks, which were all of the same shape and size. Attempts to use a colorimeter proved unsatisfactory, owing to the very light colors of the solutions and to very rapid fading of the sodium oxalate and acetate solutions upon exposure to air and even slight absorption of carbon dioxide. The results are expressed in percentage transformation of phenolphthalein, the standards for which did not vary appreciably in color between 18° and 25°.

[1] *Z. Elektrochem.*, **14**, 351 (1908).

[2] Private communication from W. C. Bray.

[3] Michaelis and Rona, *Z. Elektrochem.*, **14**, 251–3 (1908); *Biochem. Z.*, **23**, 61–7 (1909). Bohdan v. Szyszkowski, *Z. physik. Chem.*, **58**, 420 (1907). Sörensen and Palitzsch, *Biochem. Z.*, **24**, 387 (1910).

[4] Noyes, THIS JOURNAL, **32**, 826.

TABLE IV.—COLORIMETRIC COMPARISONS.

			Color. % transformation of phenolphthalein.			
			25°.		18°.	
Expt.	Solution.	Composition or ratio.	Calc.	Obs.	Calc.	Obs.
1	$Na_2C_2O_4$ B_1	0.1 M	5.9	3.5	7.8	4.0
2	$Na_2C_2O_4$ B_2	0.1 M	5.9	3.5	7.8	3.5
3	$Na_2C_2O_4$ B_3	0.1 M	5.9	4.0	7.8	4.0
4	$Na_2C_2O_4$ B_4	0.1 M	5.9	4.0	7.8	4.0
5	$Na_2C_2O_4$ A_1	0.1 M	5.9	4.0	7.8	4.0
6	$Na_2C_2O_4$ A_2	0.1 M	5.9	4.0	7.8	4.0
7	$Na_2C_2O_4$ B_1	0.2 M	7.8	6.0	10.2	6.0
8	$NaC_2H_3O_2$	0.1 N	9.6	3.0	12.7	3.5
9	$NaC_2H_3O_2$	0.1 N	9.6	3.0	12.7	3.5
10	NH_4Cl NH_4OH	5.2 1.0	5.9	6.5	9.8	8.5
11	NH_4Cl NH_4OH	6.7 1.0	...	...	7.8	5.0
12	$Na_2B_4O_7$ HCl	7.06 2.94	...	...	7.8	5.5
13	$Na_2B_4O_7$ HCl	6.84 3.16	...	...	6.8	4.0
14	Glycocoll NaOH	9.34 0.66	...	...	7.8	6.5
15	Glycocoll NaOH	9.52 1.48	...	...	5.9	4.0

3. Conclusions from the Comparisons.—From Table IV, the following conclusions may be reached:

a. The color produced by phenolphthalein in sodium oxalate solutions is not appreciably affected by changes in temperature between 18° and 25°.

b. As noted by Hildebrand[1] the colors produced in given mixtures of ammonium chloride and ammonium hydroxide are markedly affected by slight temperature changes, making such solutions unsuitable for practical comparison standards.

c. The colors produced in sodium acetate solutions[2] are far lighter than those calculated from the constants employed.

d. The color of the sodium oxalate solution is matched closely by solutions No. 13 and No. 15, in which, according to Sörensen's chart, $[H^+]_{18^\circ}$ is respectively 2.35×10^{-9} (or $10^{-8.63}$) and 2.7×10^{-9} (or $10^{-8.57}$). On the basis of Sörensen's e. m. f. measurements, $[H^+]_{18^\circ}$ for 0.1 *M* $Na_2C_2O_4$ may therefore be considered as equal to 2.5×10^{-9} (or $10^{-8.6}$); and $[OH^-]_{18^\circ}$ as equal to 2.4×10^{-6} (or $10^{-5.62}$). In other words the salt is hydrolyzed at 18° to the extent of 0.0024%.

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[1] *Z. Elektrochem.*, 14, 351 (1908).

[2] Salessky, *Z. Elektrochem.*, 10, 204 (1904), found that *N*-$NaC_2H_3O_2$ solution was far less alkaline toward phenolphthalein than was indicated by calculation.

e. In all the solutions except No. 10, the colors with phenolphthalein are markedly less than those calculated from the ionization constant 1.7×10^{-10}.

4. Discussion of Discrepancies.—Extended discussion of the causes of the discrepancies between the various calculated and observed colors would be of little interest, owing to the uncertainties in the values of the constants employed, especially that of phenolphthalein.[1] The value accepted depends practically upon the ammonium chloride-hydroxide mixtures, used by Hildebrand and Rosenstein, since the individual values of Wegscheider are far from concordant. If the ionization constant of phenolphthalein were calculated from experiments 12 to 15, on the basis of Sörensen's e. m. f. measurements, the value $K = 1.1 \times 10^{-10}$ would be obtained, which agrees more closely with McCoy's value of 0.8×10^{-10}. Salm,[2] however, obtained the value $K = 8.0 \times 10^{-10}$ by measurements with the hydrogen electrode. The discrepancies in the present work are in accord with the results of Hildebrand, who found unexplainable irregularities in the value of K with less than 8% transformation. These discrepancies may be due to the fact that phenolphthalein acts as a dibasic acid, as shown by Acree[3] and Wegscheider.[4]

In view of these uncertainties the reaction of pure sodium oxalate may best be defined empirically as equal to 4% phenolphthalein transformation in 0.1 M solution, and 6% in 0.2 M solution, standards which are readily reproducible and are free from any assumptions as to the value of the constants.

III. Determination of Excess Alkali or Acid in Sodium Oxalate.

1. Error Caused by Neglecting Hydrolysis.—Having shown that pure sodium oxalate (0.1 M) produces a pink color equivalent to 4% phenolphthalein transformation, accurate results in testing its neutrality will be obtained by titrating to such a standard color rather than to colorless. In order to determin the magnitude of such a correction, the following tests were made. Two gram samples of sodium oxalate dissolved as in the previous tests were titrated with 0.01 N oxalic acid or 0.01 N NaOH (*a*) to the standard color and (*b*) to colorless. The difference in the volume of 0.01 N acid or alkali required was always 0.3 cc., equivalent to 0.016% Na_2CO_3, 0.025% $NaHCO_3$, or 0.017% $NaHC_2O_4$, on the assumption that in the cold the end point is reached when $NaHCO_3$ is formed. The error involved in titrating 4 g. in the same volume to colorless instead of the normal color for 0.2 M solution (6% phenolphthalein) is 0.6 cc., *i. e.*, the percentage error is about the same. In general, therefore, any errors

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[1] Noyes, THIS JOURNAL, 32, 859 (1910).

[2] *Z. Elektrochem.*, 10, 344 (1904).

[3] *Am. Chem. J.*, 39, 528 (1908).

[4] *Z. Elektrochem.*, 18, 510 (1908).

through titration to colorless are likely to be negligible, and far less than those caused by the presence of excess of carbon dioxide in the samples, or the attack of the glass during the boiling for its expulsion.

2. *Calculation of Impurities Present.*—The question as to the form in which the excess of alkali exists in a given sample cannot be determined without a detailed study of each sample. From the experience with numerous samples, most accurate results will probably be obtained by calculating the alkalinity to $NaHCO_3$. In the case of samples containing less than 0.10% alkali, the differences will be negligible, *i. e.*, not over 0.04%. Samples containing much more than 0.10% of alkali are unsuitable for standardizing, even with a correction. Excess of acidity may be calculated as $NaHC_2O_4$.

In the above calculations we have assumed that 1 cc. 0.01 *N* acid[1] is equivalent to 0.00106 g. Na_2CO_3 or 0.00168 g. $NaHCO_3$, while 1 cc. 0.01 *N* NaOH is equivalent to 0.00112 g. $NaHC_2O_4$, in accordance with the following equations:

Upon boiling the original solution

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$

and upon titration in the cold

$$2Na_2CO_3 + H_2C_2O_4 = Na_2C_2O_4 + 2NaHCO_3,$$

while

$$NaHC_2O_4 + NaOH = Na_2C_2O_4 + H_2O.$$

3. *Effect of Impurities on Standardizing Value.*—The errors caused in the use of sodium oxalate by a given amount of such impurities are as follows: When the sodium oxalate is used as an acidimetric standard, Na_2CO_3 causes a positive error to the extent of 21% of its amount, *i. e.*, the material is apparently stronger than 100%. $NaHCO_3$ causes a negative error of 25% of its amount, while $NaHC_2O_4$ produces a negative error of 67% of its amount; that is, the same quantity of alkali is present (after ignition) in 134 parts $Na_2C_2O_4$, 106 parts Na_2CO_3: 168 parts of $NaHCO_3$, or 224 parts of $NaHC_2O_4$. If sodium oxalate is to be used as an oxidimetric standard, either Na_2CO_3 or $NaHCO_3$ is an inert impurity, *i. e.*, its effect is proportional to its amount. $NaHC_2O_4$ causes a positive error of 16% of its amount, since 112 parts of $NaHC_2O_4$ have the same reducing power as 134 parts of $Na_2C_2O_4$. The same relations may be expressed as follows: In order to have an error in titration of not over 0.10%, the following amounts of impurities may be present: in alkalimetry, 0.48% Na_2CO_3, 0.40% $NaHCO_3$, or 0.15% $NaHC_2O_4$; in oxidimetry 0.10% Na_2CO_3 or $NaHCO_3$, or 0.63% $NaHC_2O_4$. For use as a general standard, however, the lowest of each of these values is the maximum permissible for the given degree of accuracy.

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[1] It is immaterial whether oxalic acid or some stronger acid be employed, since the latter, in small amount, would immediately liberate its equivalent of oxalic acid.

IV. Summary.

1. The solution of pure sodium oxalate is alkaline.

2. Decimolar sodium oxalate solution produces a color with phenolphthalein equivalent to 4% transformation of the indicator, and fifth molar a color equal to 6% transformation. The most probable value of $[H]_{18°}$ for such solutions is 2.5×10^{-9} and 2.0×10^{-9}, respectively.

3. The use of calculated standards of (*a*) phenolphthalein, (*b*) ammonium chloride and hydroxide, (*c*) sodium acetate, (*d*) borax and hydrochloric acid, or (*e*) glycocoll and sodium hydroxide, for determining the normal alkalinity of sodium oxalate is inaccurate, due either to uncertainty in the values of the constants, to undetermined influences of the salts, or the abnormal ionization and hydrolysis phenomena.

4. The value of the ionization constant K for phenolphthalein is probably less than 1.7×10^{-10} for solutions in which it is transformed to the extent of less than 8%, *i. e.*, the only solutions adapted to direct optical comparison.

5. Sodium oxalate solution does not decompose appreciably on boiling.

6. Sodium oxalate solutions readily attack glass, "Durax" glass being the least affected of the kinds tested.

7. Commercial samples of sodium oxalate, dried at 240°, may contain $NaHCO_3$ or even occluded CO_2.

8. The following method for testing the neutrality of sodium oxalate is recommended to replace that given by Sörensen. Evaporate 200 cc. of water in a quartz or Durax glass flask to 150 cc. in a current of pure air, free from carbon dioxide. Add exactly 0.2 cc. phenolphthalein solution (1% solution in alcohol), and 4 g. of sodium oxalate. Continue to boil for ten minutes, then cool to room temperature while maintaining the air current. If pure, the solution should have a pink color equivalent to 6% phenolphthalein transformation. (Such a standard may be prepared by adding 0.2 cc. phenolphthalein to 150 cc. of water containing 10 cc. of 0.1 N sodium hydroxide, and diluting 9 cc. of this solution to 150 cc.) Each cc. of $N/100$ acid or alkali required to titrate to the standard color indicates the presence respectively of approximately 0.04% $NaHCO_3$ or 0.03% $NaHC_2O_4$. One or two water recrystallizations in platinum will usually be sufficient for the preparation of the pure salt from materials containing a moderate excess of alkali or acid.

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