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A COLORIMETRIC COULOMETER

BY

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I sincerely wish to acknowledge Dr. T. C. Franklin's aid and encouragement in this problem. The problem was initiated on his suggestion, and his untiring efforts and direction brought about its completion.

I also wish to thank all the faculty of the Chemistry Department for their generous and unselfish work in the inauguration of an evening program at the University of Richmond for a Master of Science degree.

My sincere gratitude is extended to my wife for her continuous aid and encouragement.

INTRODUCTION

In the study of many electrochemical processes, such as, surface adsorption on electrodes, a simple, rapid, and relatively accurate coulometer that will measure .01 to 1.0 coulombs, would be extremely useful. This project was commenced to investigate the feasibility of an entirely different approach for coulometric analysis for application in this range.

This new type of coulometer utilizes a colorimeter for determining the amount of coulombs passed through a coulometer cell. Consequently, any electrode process which of its own nature is color-producing, or a process which, in turn, can actuate a color indicator, is a potential reaction for this colorimetric coulometer.

There are three classes of electrode reactions with these potentialities. They are:

(I) A process in which the color substance is either produced or removed by oxidation or reduction at the electrode.

(II) A process in which the solute, which subsequently reacts to form a colored substance, is either produced or removed. The solute may be a metallic ion that is either produced or deposited or a gas that is generated.

(III) A process in which the solvent reacts at the electrode. In the case studied the pH of water is altered by the generation of hydrogen or oxygen. This pH change is indicated by the color of an acid-base indicator.

Of these three processes, the first is a primary reaction for the coulometer, in that the colored substance itself is changed by oxidation or reduction at the electrode. The last two are secondary for the passage of current is indicated by a reaction of one of the electrode products or reactants, as the case may be, with a color indicator.

In this investigation all three of the above possibilities were examined. With the last two processes, color indicators had to be employed due to the inability of the fundamental electrode reaction to act as a color-producer. The coulometric efficiency and reproducibility of the reactions were studied, together with the effects of the variation of concentration of the color indicator and its solvent.

HISTORICAL

There are two classes of coulometers, the electromechanical type and the chemical type. The electromechanical type measures coulombs by the utilization of an ammeter with an integrating system for measuring the amount of time. They range in sensitivity and response time from a ballistic galvanometer to the intricate recorders exemplified in a Sargent-Heyrovsky Model XXI polarograph. A few of the laboratory integrating recorders are those designed by Bogan, Meites, Peters and Sturtevant[1]; Lingane and Jones[2], and Shaffer, Briglio and Brockman[3]. The chemical coulometers depend on the electrolytic deposition or dissolution of a chemical element. Since this investigation involves the study of a new approach to a chemical coulometer rather than the study of the capabilities of an electro-mechanical system, the discussions, references and comparisons will be made with respect to chemical coulometers, henceforth, referred to simply as coulometers.

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1. Bogan, Meites, Peters and Sturtevant, J. Am. Chem. Soc. 73, 1584 (1951)
2. Lingane and Jones, Anal. Chem. 22, 1220 (1950)
3. Shaffer, Briglio and Brockman, Anal. Chem. 20, 1008 (1948)

Since the establishment of the laws of electroysis by Faraday, a number of various types of coulometers have been introduced. Their accuracy and experimental conditions for employment have been established by extensive investigation. For example, the number of coulombs required to liberate one equivalent of a substance, known as the Faraday, has been experimentally determined with coulometers to the extent that its value is now limited by the known accuracy of the atomic weights of the elements. Few coulometers, however, will measure easily one coulomb or less, due to the small amount of product yielded by one coulomb at the electrode. To illustrate, the silver coulometer produces only 1.1180 mg. of silver per coulomb, and therefore, a very sensitive balance with good analytical procedures is required. The oxy-hydrogen coulometer liberates 0.1741 cc. of gas per coulomb which is extremely difficult to measure with any accuracy in such a small quantity.

The silver coulometer is the oldest type, and is also regarded as the "standard" of coulometers. Reliable measurements were made by Kohlrausch in 1886 with a silver coulometer, but the first accurate measurements were performed in 1908-1914. Some of the more notable investigations describing its accuracy and conditions are that of Smith, Mather and Lowry[4]; Richards and Anderegg[5] and Rosa and Vinal[6].

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[4]. Smith, Mather and Lowry, Phil. Trans. (A) 207, 545 (1908)
[5]. Richards, T. W., and Anderegg, F. O., J. Am. Chem. Soc. 37, 7 (1915)
[6]. Rosa and Vinal, Proc. Nat. Acad. Sci. 3, 59-64

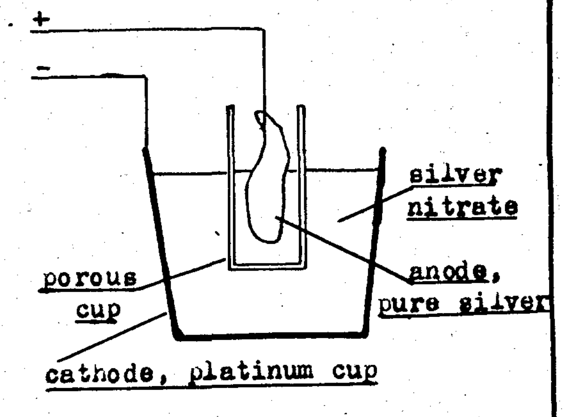

Figure 1

The principal design of the silver coulometer is as shown in Figure 1. Variations in this design center around the use of different types of cups of a porous material separating the anode and cathode; for cloth, filter paper, clay, porcelain, and glass have been utilized. These porous cups are employed to prevent one of the chief sources of error, "anode slime". "Anode slime" is a term applied to the small particles of silver which fall from the anode during deposition. Other errors in the silver coulometer involve the purity of the silver nitrate used for the electrolyte, and the removal of all inclusions of water and silver nitrate in the electroplated silver. Repeated crystallization from acidified solutions followed by fusion, is the procedure recommended for the purification of the silver nitrate; while ignition to a redness of the deposited silver is required to insure removal of all the inclusions. Under the proper conditions, reproducibility to .001-.002% is possible with a silver coulometer.

Kistiakowsky[7] claims an accuracy to within 0.1% with a simplified form of the silver coulometer, where the amount of silver removed by the current in the anode compartment is dissolved into a potassium nitrate solution and later determined volumetrically.

There are several references to silver micro-coulometers in the literature utilizing a sensitive balance to measure the small amount of deposited silver. Bose and Conrat[8] deposited silver on a thin platinum wire cathode with measurements as low as .229 coulombs with an accuracy of about 1%. Reevely and Gordon[9] used a microcoulometer that was a small scale design of the regular type silver coulometer. Their measurements ranged between 18-30 coulombs. One of the best methods proposed to allow measurements in the lower range is that of von Wartenberg and Schutza[10]. Silver plated from the normal silver nitrate solution has a coarse grain structure with a low adherence to the cathode. To circumvent this problem von Wartenberg and Schutza developed a bath which plates a fine grain structure of silver. The bath is prepared by dissolving silver oxide in hydrofluoric and boric acids.

Confirming evidence for the value of the Faraday by the silver coulometer was obtained with the iodine coulometer by Washburn and Bates[11]. The iodine coulometer uses a dilute solution of potassium iodide as the electrolyte. The starting position for the iodine coulometer is shown in Figure 2.

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7. Kistiakowsky, Z. Elektrochem., 12, 713 (1906)
8. Bose and Conrat, Techn. Hochsch., Dansig-Langfuhr
9. Reevely, W. O., and Gordon, A. R., Trans. Electrochm. Soc. 63, 5 pp.
10. von Wartenberg, H., and Schutza, H., Z. Elektrochem. 36, 254 (1930)
11. Washburn, E. W., Trans. Electrochem. Soc. 88 3 pp.

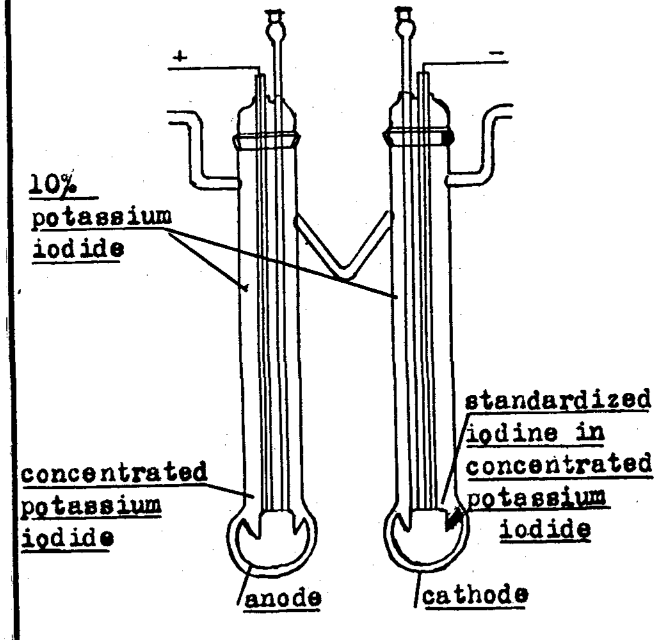

Figure 2

At the bottom of the anode compartment there is a concentrated solution of potassium iodide, while in the bottom of the cathode compartment there is a standardized solution of iodine in concentrated potassium iodide. The passage of current through the coulometer liberates iodine in the anode compartment, while iodide ions are generated at the cathode. To determine the number of coulombs passed, a titration of the iodine with arsenious acid may be made from either the anode or the cathode. Washburn and Bates demonstrated that "within the limit of error of the analysis the same amount of iodine is formed from iodide ions at the anode as is converted into iodide ions at the cathode".[11]

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11. Washburn, E. W., Trans. Electrochem. Soc. 88 3 pp.

In comparing the silver coulometer and the iodine coulometer, the following features are pointed out:

(1) The reproducibility of the two coulometers is about the same, .001 to .002%.

(2) The iodine coulometer does not require the special purification of materials necessary for the silver coulometer.

(3) The number of grams liberated per coulomb is about the same with a small advantage in favor of the iodine.

(4) The iodine coulometer is not affected by anode products or by inclusions.

(5) The reaction of the iodine coulometer is reversible while the silver coulometer is not.

(6) The manipulation of the silver coulometer is easier for moderate precision, however, for a high degree of accuracy both types are about equal.

For general laboratory use, the copper coulometer[12, 13, 14] or the oxy-hydrogen coulometer is recommended. The copper coulometer employs two copper electrodes immersed in a slightly acid solution of cupric sulfate. The copper liberated at the cathode is weighed to determine the number of coulombs passed through the cell. Careful analysis by Richards, Collins and Heimrod[12] illustrated that the copper coulometer agreed with the silver coulometer to within 0.03%. There are two chief sources of error with the copper coulometer:

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12. Richards, Collins, and Heimrod, Proc. Am. Acad. <u>35</u>, 123 (1899)
13. Datta and Dhar, J. Am. Chem. Soc. <u>38</u>, 1156 (1916)
14. Mathews, H. P. and Wark, I. W., J. Phys. Chem. <u>35</u>, 2345 (1931)

(1) Copper tends to oxidize in a neutral solution. This error is minimized by using a slightly acid solution with dissolved ethyl alcohol or tartaric acid to further hinder the oxidation.

(2) The copper electrodes dissolve, however, in an acid solution of cupric sulfate, especially in the presence of oxygen. For precise work this error must be taken into consideration, but it can be reduced by using the coulometer at a low temperature and in an atmosphere of hydrogen.

The oxy-hydrogen coulometer[15], [16] is one of the simplest to use. Figure 3 illustrates the coulometer of Lingane's design.

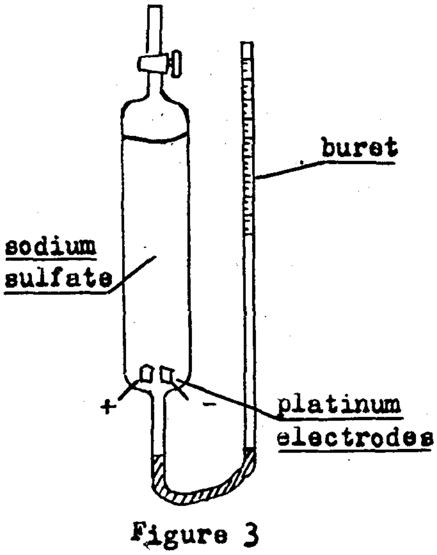

Figure 3

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[15] Lehgeldt, Phil. Mag. 15, 614, 621 (1908)
[16] Lingane, J. J., J. Am. Chem. Soc. 67 1916 (1945)

The passage of current will liberate hydrogen and oxygen at the electrode. The gas then displaces the electrolyte, pushing an equivalent amount of liquid up into the measuring column or buret. Allowing for the water vapor and the decrease in volume of the water as the solution is electrolyzed, one coulomb should liberate 0.1741 cc. of gas at S. T. P.

The above four coulometers are the principal designs. Coulometers of sodium, mercury, lead, aluminum, and vanadium have been employed. The sodium coulometer[17, 18] employs a fused electrolyte of sodium nitrate at 340° C. The electrodes are two glass tubes containing platinum wires inserted into cadmium at the cathode, and cadmium with a little sodium at the anode. With the passage of a current, sodium migrates into the glass at the cathode and out of the glass at the anode. The change in weight of the anode tube yields more accurate results than that of the cathode. Stewart obtained an accuracy better than 1:10,000 with a sodium coulometer.

Mercury coulometers[19] have been used mainly for commercial applications where large quantities of electricity have to be measured (Figure 4). In this coulometer the mercury is deposited on the carbon cathode from a mercuric iodide solution in potassium iodide. The mercury falls from the cathode into the calibrated measuring tube. After the experiment the mercury may be returned to the anode reservoir by tipping the entire cell. An accuracy of 1% is claimed for this type of coulometer.

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17. Burt, R. C. Phys. Rev. 27, 813 (1926)
18. Stewart, O. J., J. Am. Chem. Soc. 53. 3366 (1931)
19. Schulte, Z. Elektrochem. 27, 745 (1921)

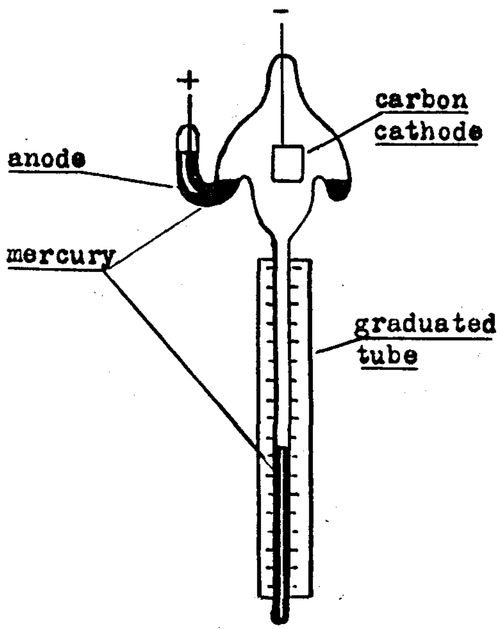

Figure 4

One of the unique designs of a microcoulometer involves a mercury coulometer. Wilson[20] measured quantities of electricity from a few hundred electrostatic units to one coulomb by observing the change in size of a mercury drop with a microscope. The mercury was deposited on the end of a fine platinum wire and its spherical growth with the passage of current was measured.

The lead coulometer was investigated by Fischer, Thiele, and Maxted[21].

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[20] Wilson, C. T. R., Proc. Cambridge Phil. Soc. 19, 345

[21] Fischer, Thiele, and Maxted, Z. Anorg. Chem. 67, 339

To obtain an adherent, unoxidized deposit lead salts of hydrofluoboric, hydrofluosilicic, and p-phenolsulphonic acids were employed. An accuracy comparable to the copper coulometer is claimed by the authors.

In the aluminum coulometer,[22] a high-purity aluminum anode dissolves under the action of the current in a sulfuric acid electrolyte at an efficiency of about 100%. Large currents can be measured with this type of coulometer.

A recent new type of titration coulometer[23] was devised on the anodic oxidation of VO^{++} to VO^{+++}. The amount of VO^{+++} produced at the anode is determined by a titration with ferrous ion. The authors state that an accuracy comparable to the silver coulometer is obtainable. The principle of this coulometer was proposed by MacNevin and Martin[24]. Improvement of the accuracy of the Faraday is possible through an oxygen-transfer reaction, such as, the vanadium oxide coulometer, since the atomic weights of the elements are taken relative to oxygen which is set at 16.0000. The oxygen-transfer coulometer will be based, therefore, on this atomic weight of oxygen, and future improvement of the Faraday's value will probably be attained through this type of coulometer.

An unusual method for measuring coulombs without weighing the deposit was developed by Muller.[25] This design consisted of an H-shaped cell with a platinum wire traversing the cathode chamber, and sealed at the top and bottom. The quantity of electricity was determined by the change in the resistance of the platinum wire due to the deposition of metal upon it.

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22. Tosterud, M. and Mason, R. B., Trans. Electrochem. Soc. 90, 6 pp.
23. Syrokomskii, V. S., and Nazareva, T. I., Zhur. Anal. Khim. 6, 15 (1951)
24. MacNevin, W. M., and Martin, G. L., J. Chem. Ed. 24, 587 (1947)
25. Muller, R., Physik. Z. 11, 978 (1910)

EXPERIMENTAL METHODS

The entire colorimetric coulometer with its measurement circuit is shown in the photograph, Figure 5.

COLORIMETRIC COULOMETER

A clinical type, Klett-Summerson colorimeter was used for all the colorimetric determinations in this investigation. The coulometer was designed around one of the colorimeter's sample tubes. To prevent interference of the electrodes processes with each other, a design was selected in which the electrodes of the coulometer were separated from each other by a salt bridge. This half-cell arrangement with the electrode in the colorimeter tube is illustrated in Figure 6. Since the maximum diameter of the tube was 12 mm., all the items for the half-cell were necessarily small.

The electrode and the stirrer were combined by the means of a rotating electrode assembly. A platinum wire (A) was used as the material for the electrode. It was sealed in a glass tube (B), as shown, in two places---one at the bottom of the tube, and the other near the center where the platinum wire was bent into a zig-zag shape, and rotation of the wire provided ample agitation of the solution in the colorimeter tube (C).

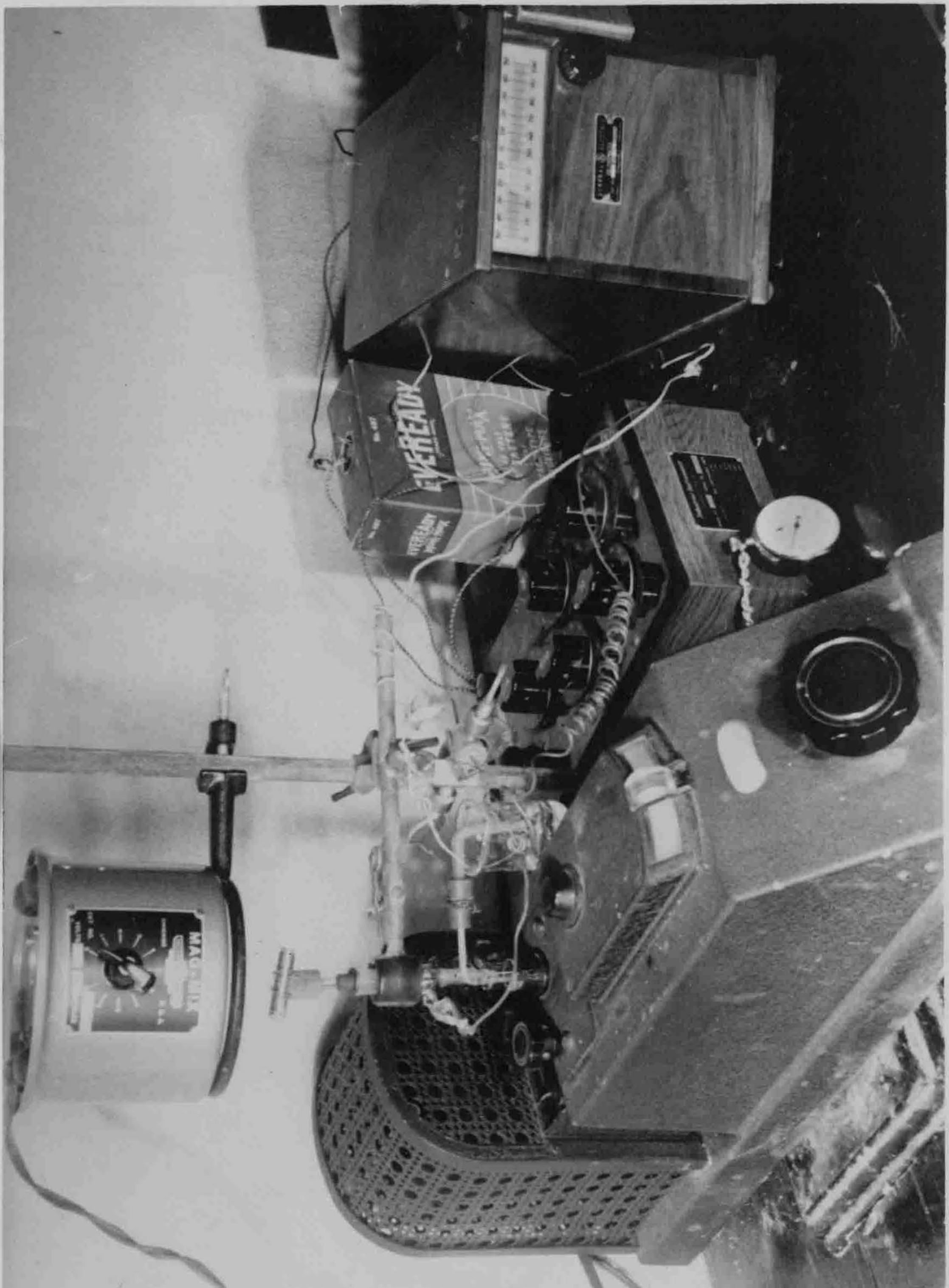


Figure 5

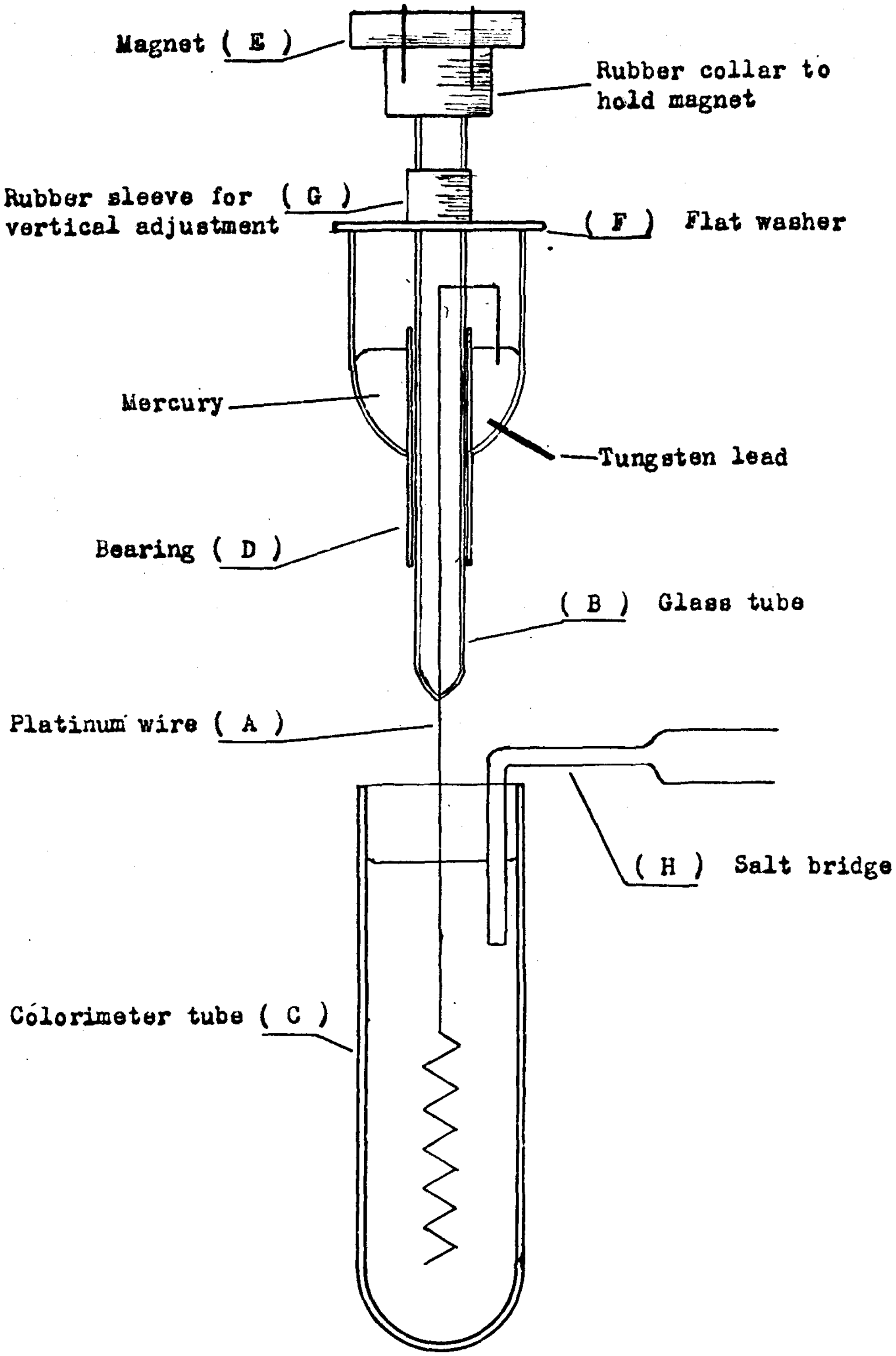

Magnet (E)
Rubber collar to hold magnet
Rubber sleeve for vertical adjustment (G)
(F) Flat washer
Mercury
Tungsten lead
Bearing (D)
(B) Glass tube
Platinum wire (A)
(H) Salt bridge
Colorimeter tube (C)

Figure 6

The bearing (D) for the stirring rod had an annular well at the top, and mercury was held in this well. The platinum wire after it emerged from the center of the tube was bent backwards and immersed in the mercury well. Continuous electrical contact was made between the mercury and platinum wire during rotation by this arrangement. The electrical contact to the mercury pool was made by means of a tungsten wire sealed through the outer wall of the well. This mercury pool system is the customary assembly for a rotating electrode.

Rotation of the electrode could be accomplished in two ways:

(1) The top of the stirring rod could be permanently fixed to a rotating power source, such as, the shaft of a stirring motor, or

(2) It could be an easily detached coupling to the power source, such as a pulley arrangement or a magnetic coupling. Since in this assembly, it was advantageous to remove the stirrer for each measurement from the colorimeter tube, the non-permanent type of coupling was chosen. A magnetic coupling was employed to rotate the stirring rod. A small magnet (E) attached to the top of the stirring rod was rotated by the influence of an inverted magnetic stirrer. The stirring rod received its vertical support from a flat washer (F) which acted as a thrust bearing. During rotation this flat washer rested on the top of the annular mercury well. Vertical positioning of the stirring rod was accomplished by a small rubber sleeve (G) located above the flat washer.

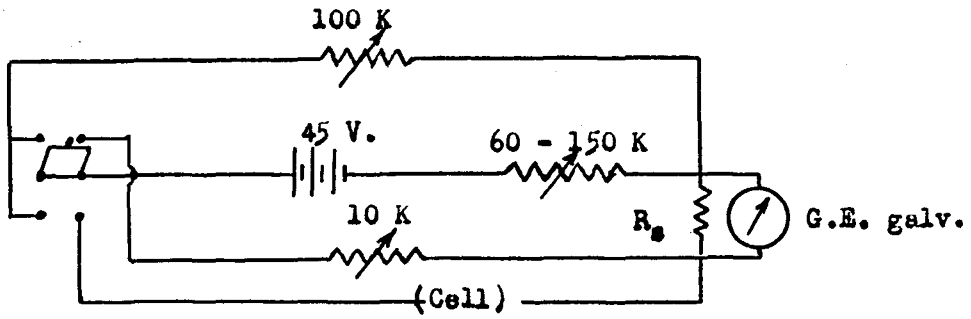
The salt bridge (H) was made of 2.5 mm. glass tubing for the end that was immersed into the colorimeter tube. The diameter of the salt bridge was increased to 6 mm. tubing about one inch away from the colorimeter tube to minimize the resistance of the bridge. The salt bridge was prepared with a saturated solution of potassium chloride in agar-agar.

According to Beer's law the logarithm of the transmittancy of light through a solution is directly proportional to the concentration of the absorbing solute. The scale for this Klett-Summerson colorimeter is marked in a logarithmic fashion, therefore, the colorimeter's readings are directly proportional to the concentration of the solute.

To prevent an error from the absorption of light by the electrode wire, the electrode was removed for each determination of a reading of the colorimeter. Also, precautionary measures were necessary for the first half hour of operation of the colorimeter, because there was a slight decreasing drift in the instrument's zero. After a half hour, the zero value of the colorimeter was reasonably steady.

ELECTRICAL COULOMETER MEASURING SYSTEM

The electrical circuit used to measure the quantity of electricity passed through the coulometer cell is shown below. The number of coulombs



passed in the cell was obtained by a controlled current flow for a measured amount of time.

A large resistor (60,000 to 150,000 ohms) was placed in series with the battery to reduce the current and to provide a stable current source. A large, variable resistor box (100,000 ohms) was placed in parallel with the cell to act as a bleeder resistor, thereby, providing a means for adjusting the current flow in the circuit arm of the cell to a constant value. The current was always passed through a dummy lead (10,000 ohms) first, and then switched rapidly into the cell before each measurement. The current in the cell was measured by a General Electric galvanometer, (Cat. No. 32C), which had been previously calibrated as a microammeter with several shunts (R_s) for different ranges.

OXY-COULOMETER

A minature version of Lingane's oxy-hydrogen coulometer was fabricated initially, however, the sensitivity of this instrument was not great enough to allow its use as a criterion for the small quantities of electricity employed.

PREPARATION OF MATERIALS

All the materials used in this investigation were the highest grade commercially available. Standard solutions were prepared by weighing the compounds on an analytical balance, and dissolving them in water purified by an ion-exchange resin in graduated volumetric flasks.

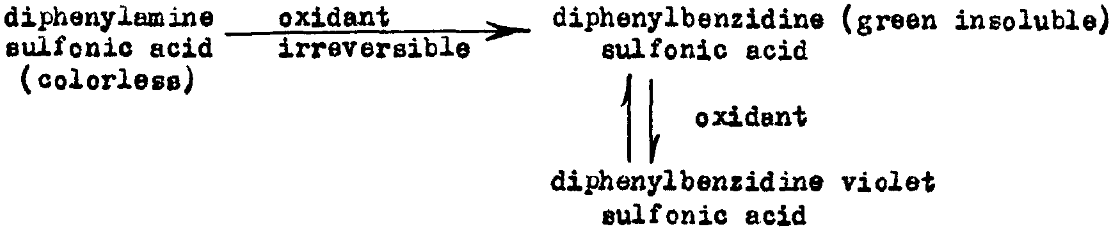
RESULTS AND DISCUSSION

In the Introduction, three classes of reactions are listed which summarize the possible electrode processes that could be used for a colorimetric coulometer. They are briefly (1) an oxidation-reduction process, (2) an alteration of the solute process, and (3) an alteration of the solvent process. The Results and Discussions are divided here into these three sections for presentation.

- - I - -

OXIDATION-REDUCTION PROCESS

The oxidation-reduction process was one of the first possible coulometer reactions that was investigated. The oxidation-reduction indicators of barium diphenylamine sulfonic acid and sodium 2,6 dichlorobenzene-one indophenol were tried. The normal oxidation of the diphenylamine dye proceeds from the colorless state to a violet, passing rapidly through an insoluble green precipitate.



$$\begin{tikzcd}
\text{diphenylamine sulfonic acid (colorless)} \arrow[r, "\text{oxidant}", "\text{irreversible}"'] & \text{diphenylbenzidine sulfonic acid (green insoluble)} \arrow[d, shift left, "\text{oxidant}"] \\
& \text{diphenylbenzidine violet sulfonic acid} \arrow[u, shift left]
\end{tikzcd}$$

It was found that the electrolytic oxidation of the dye stopped at the insoluble green form, therefore this reaction was not useful as a coulometer process.

Sodium 2,6 dichlorobenzene-one indophenol was the next oxidation indicator to be studied. A decided change occurred in the indophenol from the reduced blue to the oxidized pink form. Further investigation of this change, however, demonstrated that the color change was not due to the oxidation of the dye, but entirely due to a change in pH of the solution. When the same experiment was repeated in a Clark and Lubs buffer at a pH of 7.5, the color change did not occur. It was also observed that under these conditions, the electrolyzed indophenol precipitated out on the electrode.

The sensitivity of the indophenol to a pH change is indicative of an oxidation-reduction indicator. If HIn is the oxidized form of an oxidation-reduction indicator, and In is the reduced form, the reaction is expressed by

$$HIn \rightleftharpoons In + H^+ + e$$

In this system the potential acquired by an inert electrode, such as platinum, may be expressed as

$$E = E^\circ - \frac{RT}{\mathcal{F}} \ln \frac{a_{In} a_{H^+}}{a_{HIn}} \qquad (1)$$

$$= E^\circ - \frac{RT}{\mathcal{F}} \ln \frac{a_{In}}{a_{HIn}} - \frac{RT}{\mathcal{F}} \ln a_{H^+} \qquad (2)$$

It is readily recognized that the potential of the system is dependent not only on the oxidized and reduced states, but also upon the hydrogen ion concentration. A change of the hydrogen concentration resulting in an alteration of the potential of only 0.03 volts on either side of the E^0 value will result in approximately the maximum change in color that is detectable for the indicator.[26]

The indophenol was then tested in the buffer (pH = 7.5) with a solution of dioxane of 10% by volume to raise the solubility of the oxidized state of the indicator at the electrode. Preliminary results indicate that the oxidation of the indophenol did occur, but it proceeded in an irregular and non-linear fashion.

The reduction of potassium permanganate was the next reaction of this class that was investigated. This electrolytic reduction did occur in the prescribed manner (Table 1 and Figure 7). The normality of the permanganate had to be determined with o-phenanthroline ferrous sulfate as an indicator, since the color change of the permanganate was not great enough at this level in concentration for normal titrations. It should be pointed out that according to this standardization, 2.794 coulombs should be required to reduce the permanganate. The curve of trial No. 1 indicates that 2.8 coulombs were necessary for the total reduction of the permanganate, demonstrating that this reduction proceeded at approximately 100% current efficiency.

The shape of the unusual two-step curve in trial No. 1 was verified later by a second electrolytic reduction of permanganate (trial No. 2). Although in the interim period between the two trials, the strength of the permanganate had lowered, the general shape of the curve was repeated. Calculations based on the slopes of the two sections of the reduction curve (trial No. 1) for the electron change, yield values of 6.2

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[26] Glasstone, S., "Textbook of Physical Chemistry", D. Van Nostrand Co. Inc., New York, N. Y.

electrons necessary for the first straight portion, and 3.7 electrons for the second. These rough values of 6 and 4, however, do not suggest any readily known intermediate, and therefore, the only conclusion on the electrolytic reduction of potassium permanganate that can be drawn is that it proceeds in a two-step fashion.

The reduction of potassium dichromate in an acid medium was also investigated, but no apparent change in the dichromate occurred.

TABLE 1

Reduction of Potassium Permanganate

Standardization of solution (o-phenanthroline ferrous sulfate indicator)

	Sample 1	Sample 2
Weight of sodium oxalate	0.0120 g.	0.0117 g.
Mls. of $KMnO_4$ required	64.29	60.05
Normality of $KMnO_4$	2.78×10^{-3}	2.90×10^{-3}

Sample 2 is correct, since it was known that the end point had been passed slightly in Sample 1.

Coulometric Determination[a]

Trial 1			Trial 2		
Increments of coulombs passed	Total coulombs passed	Colorimeter readings	Increments of coulombs passed	Total coulombs	Colorimeter readings
0.0000	0.0000	338	0.0000	0.0000	318
0.0678	0.0678	338	0.0869	0.0869	316
0.1932	0.2608	327	0.1159	0.2028	304
0.2318	0.4926	313	0.1159	0.3187	292
0.2608	0.7334	286	0.1449	0.4636	284
0.4347	1.2681	235	0.1449	0.6085	269
0.0869[b]	1.3550	227	0.1449	0.7534	255
0.3043	1.6593	181	0.1449	0.8983	237
0.3478	2.1071	118	0.1449	1.0432	223
0.4492	2.5563	42	0.1449	1.1881	202
0.2029	2.7592	22	0.1449	1.3330	176
			0.1449	1.4779	154
			0.1449	1.6228	127
			0.1449	1.7677	99
			0.1449	1.9126	72
			0.1449	2.0575	49
			0.1449	2.1924	27
			0.0869	2.2793	17
			0.1159	2.3952	11

[a] -- Green filter, transmission limits 520-580 millimicrons
Trial No. 2 was performed several days after No. in order to obtain confirmation of break observed in curve No. 1 Normality of $KMnO_4$ dropped during this interval slightly due to decomposition

[b] -- Uncertain value

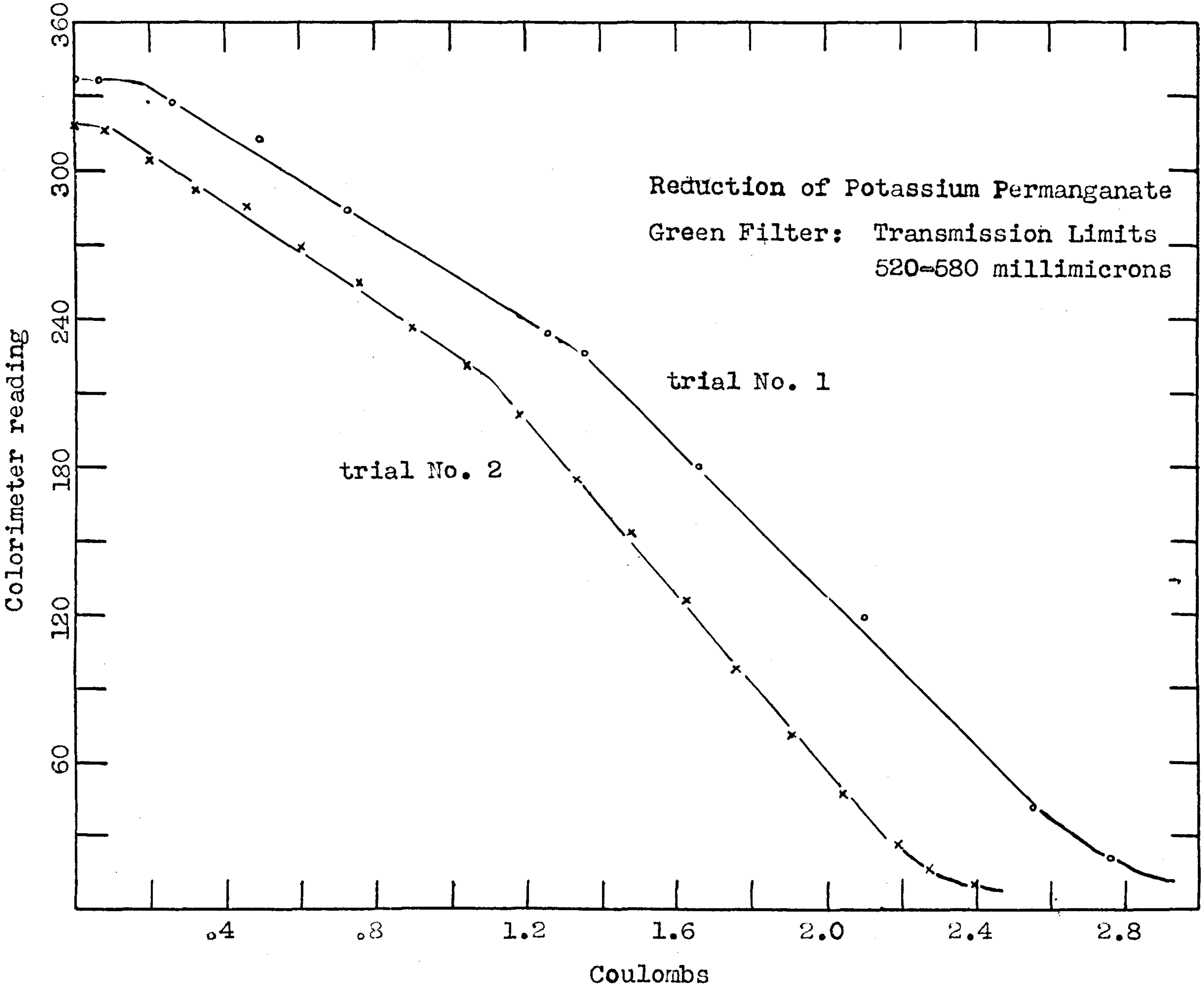
Reduction of Potassium Permanganate
Green Filter: Transmission Limits
520-580 millimicrons
trial No. 1
trial No. 2
Colorimeter reading
360
300
240
180
120
60
.4
.8
1.2
1.6
2.0
2.4
2.8
Coulombs

Figure 7

- - II - -

ALTERATION OF SOLUTE

The first reaction of this class that was studied was the generation of chlorine at the anode. From the coulometric titration with chlorine by Farrington and Swift[27], it was know that the generation of chlorine at the anode proceeded at a 100% efficiency from a 2 N hydrochloric acid solution. Also, Ellms and Hauser[28] proposed the use of o-tolidine for the sensitive determination of free chlorine in an acid solution.

With these two facts in mind this reaction was investigated, and a sensitivity almost five times better than that of an acid-base indicator method described laterwas obtained. Accurate determinations, however, were impossible due to the inherent fading of the chlorinated indicator. For rough approximations where one place accuracy is sufficient, this reaction would yield a possible sensitive method for determining a pulse current, provided, of course, that the colorimeter values for the o-tolidine were determined immediately. Although Ellms and Hauser[28] claim sufficient stability in color for a half-hour for the indicator, the fading tendency of the color is too fast for any accurate work with this reaction.

The dissolution and deposition of copper in a triethanolamine solution were investigated. (Table 2 and Figure 8) The copper-triethanol-

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[27] Farrington and Swift, Anal. Chem. 22, 889 (1950)
[28] Ellms and Hauser, J. Ind. Eng. Chem. 5, 915 (1913)

amine complex conforms to Beer's law within the range desired from 0 to 600 p.p.m.[29] The dissolution of the copper was conducted in a triethanolamine solution of 28.2% by weight. A calibration curve was determined for the copper in triethanolamine, and it indicated that this anode process was proceeding at 100% efficiency approximately. For example, the colorimeter gave the value of 130 for a concentration of copper that would have required 7.96 coulombs to dissolve. The corresponding experimental colorimeter reading shows a value of 140 for the same number of coulombs.

The deposition of copper was also tried, but early results did not indicate this as a favorable reaction for a coulometric process.

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29. Yoe and Barton, Ind. Eng. Chem., Anal. Ed. <u>12</u>, 456 (1940).

TABLE 2

Anodic Dissolution of Copper To Triethanolamine Complex[a]

Anodic Dissolution

Increments of Coulombs Passed	Total Coulombs Passed	Colorimeter Reading
0.290	0.290	28
0.580	0.870	40
0.870	1.740	55
0.870	2.610	66
1.912	4.522	95
3.480	8.002	142

Cupric Sulfate Calibration

Concentration of $CuSO_4 \cdot 5H_2O$	Colorimeter Reading	Coulombs Required by Calculation
13.64 g./L.	400	--
2.92 g./L.	270	22.57
1.03 g./L.	130	7.96

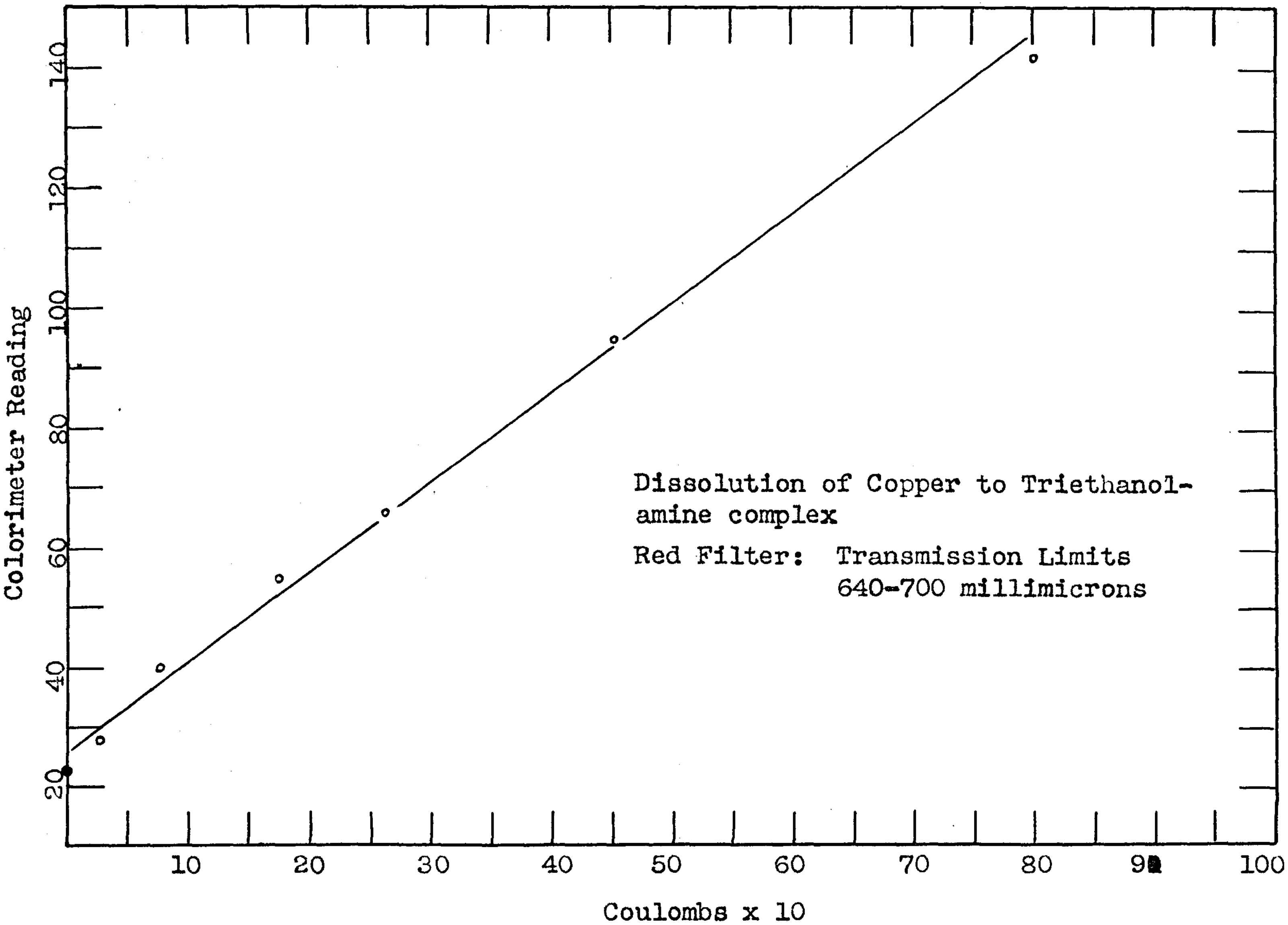

Dissolution of Copper to Triethanolamine complex
Red Filter: Transmission Limits 640-700 millimicrons
Colorimeter Reading
20
40
60
80
100
120
140
10
20
30
40
50
60
70
80
90
100
Coulombs x 10

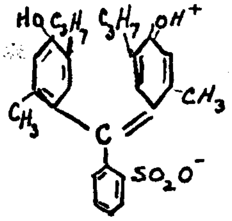
Figure 8

- - III - -

ALTERATION OF SOLVENT

The change in the pH of water by the removal of hydrogen or oxygen was the approach used in the study of this third process, the alteration of the solvent. Acid-base indicators presented one of the largest host of indicators for any one reaction, such as, the generation of hydrogen, chlorine, or a metal ion. In the subsequent discussion, the undissociated indicator molecule will be referred to as HIn and the anion as In^-.

THYMOL BLUE (THYMOLSULFONEPHTHALEIN)



pH range 8.0 - 9.6
yellow to blue

The data obtained with thymol blue is given in Tables 3 and 4, and Figures 9 and 10. In Figure 10, the colorimeter reading is plotted for the indicator as it increased from the the yellow acid form to the blue base form. At the top of the curve, it is known that the thymol blue is almost completely converted to In^-, while at the bottom or acid portion of the curve, the concentration of the In^- present is essentially zero. Consequently, if the indicator obeys Beer's law and the proper filter is selected to analyze the colored In^- content, the colorimeter readings of the acid state will be independent of the concentration of the indicator since there is so little In^- present. The colorimeter readings will be solely proportional to the In^- for the entire neutralization curve with the proper filter and obedience to Beer's law by the indicator. When the indicator has been completely neutralized, the readings will be equal to the initial concentration of HIn. The reverse situation will exist if the color absorption is due to the HIn molecule instead of the In-. That is, the colorimeter readings will be proportional to the concentrations of the acid state and independent of the concentrations of the alkaline state when HIn is the absorbing constituent.

The thymol blue system is a good example of the ideal situation where the In^- form is the only color absorbing state. The colorimeter values in Table 3 are all approximately zero regardless of the HIn concentration, illustrating the fact that the colorimeter readings are proportional to the minute concentrations of In^-. Figure 9 illustrates the linear relationship between the colorimeter reading of the completely neutralized indicator and the initial concentration of HIn. The HIn has been essentially converted to In^- completely in the alkaline region of the dye, and this linearity should exist.

To analyze for the proper coulometric performance of the indicator, the following relationship was derived. This relationship assumes that the colorimeter value for either the acid or base state of the indicator is independent of the concentration.

In the half-cell the hydrogen that is generated at the cathode is derived from either the water of the indicator. Since the solution is electrically neutral, this expression is true before any Faradays are passed through the cell.

$$[H^+] = [OH^-] + [In^-] \qquad (3)$$

With the passage of current the hydrogen ion concentration decreases in the cathode compartment, and the change is equal to the number of Faradays passed through the cell. The cathode compartment still remains electrically neutral due to the migration of the potassium ion from the salt bridge into the compartment. Equation (3) then becomes

$$[H^+] = [OH^-] + [In^-] - \text{Faradays passed} \tag{4}$$

Since the $[In^-]$ is proportional to the colorimeter reading, then

$$[In^-] = k\,Rd \tag{5}$$

where k is an instrument constant, and Rd the reading of the colorimeter.

Substituting (5) in (4) and rearranging

$$\text{Faradays passed} = k\,Rd + [OH^-] - [H^+] \tag{6}$$

From the equations for the equilibrium of an acid-base indicator, and for water, we have

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]}, \quad \text{and} \tag{7}$$

$$[OH^-] = K_w/[H^+] \tag{8}$$

Substituting (7) and (8) in (6) and eliminating

$$\text{Faradays passed} = k\,Rd + \frac{K_w\,[In^-]}{K_{HIn}\,[HIn]} - K_{HIn}\frac{[HIn]}{[In^-]} \tag{9}$$

Since the $[HIn] = [In^-]_{final} - [In^-]$ (10)

equation (9) becomes

$$\text{Faradays passed} = k\,Rd + \frac{K_w \quad Rd}{K_{HIn}(Rd_{final} - Rd)} - K_{HIn}\frac{(Rd_{final} - Rd)}{Rd} \tag{11}$$

Several points were calcutated with equation (11) and plotted in Figure 10. Fair agreement between the experiment and calculated values is obtained considering the fact that the true $K_{H_{I_n}}$ is not known due to the presence of the alcohol used to solubilize the indicator.

TABLE 3

Thymol Blue Indicator

Colorimeter Readings and Concentration of Indicator[a]

Concentration of Indicator (moles/L.)	% of Stock Solution	pH	Colorimeter Readings	
			Acid Form	Base Form
2.160×10^{-4}	100	4.03	9	164
1.727×10^{-4}	80	4.07	2	126
1.618×10^{-4}	75 (extra value for base form)			120
1.295×10^{-4}	60 (extra value for base form)			105
1.080×10^{-4}	50	4.26	3	96
0.864×10^{-4}	40	4.41	3.5	76
0.432×10^{-4}	20	4.72	3.5	37
0.216×10^{-4}	10	5.23	0	22

a - Red filter, transmission limits 640-700 millimicrons
pH of the water used for solution is 5.72
Alcohol concentration constant at 10% by volume

TABLE 4

Thymol Blue Indicator[a]

Variation of Colorimeter Reading with Coulombs Passed

- - - - - Experimental - - - - - - - - - - - - - -			- Calculated[b] -
Increments of Coulombs Passed x 10^2	Total Coulombs Passed x 10^2	Colorimeter Readings	Total Coulombs Passed x 10^2
0.00	0.00	3	
5.80	5.80	3	
5.80	11.60	2	
4.35	15.95	2	
4.35	20.30	30	
2.90	23.20	43	24.7
2.90	26.10	54	
2.90	29.00	68	28.1
2.90	31.90	78	
5.80	37.70	91	32.7
7.24	44.94	101	35.5
5.80	50.74	107	
8.70	59.44	112	41.1
8.70	68.14	119	51.1

a - Concentration of indicator is 1.727 x 10^{-4} moles/L.
Alcohol concentration is 10% by volume
Red Filter: Transmission limits 640-700 millimicrons

b - All calculated points based on 17.2 x 10^{-2} coulombs as the initial point for the neutralization of the indicator.

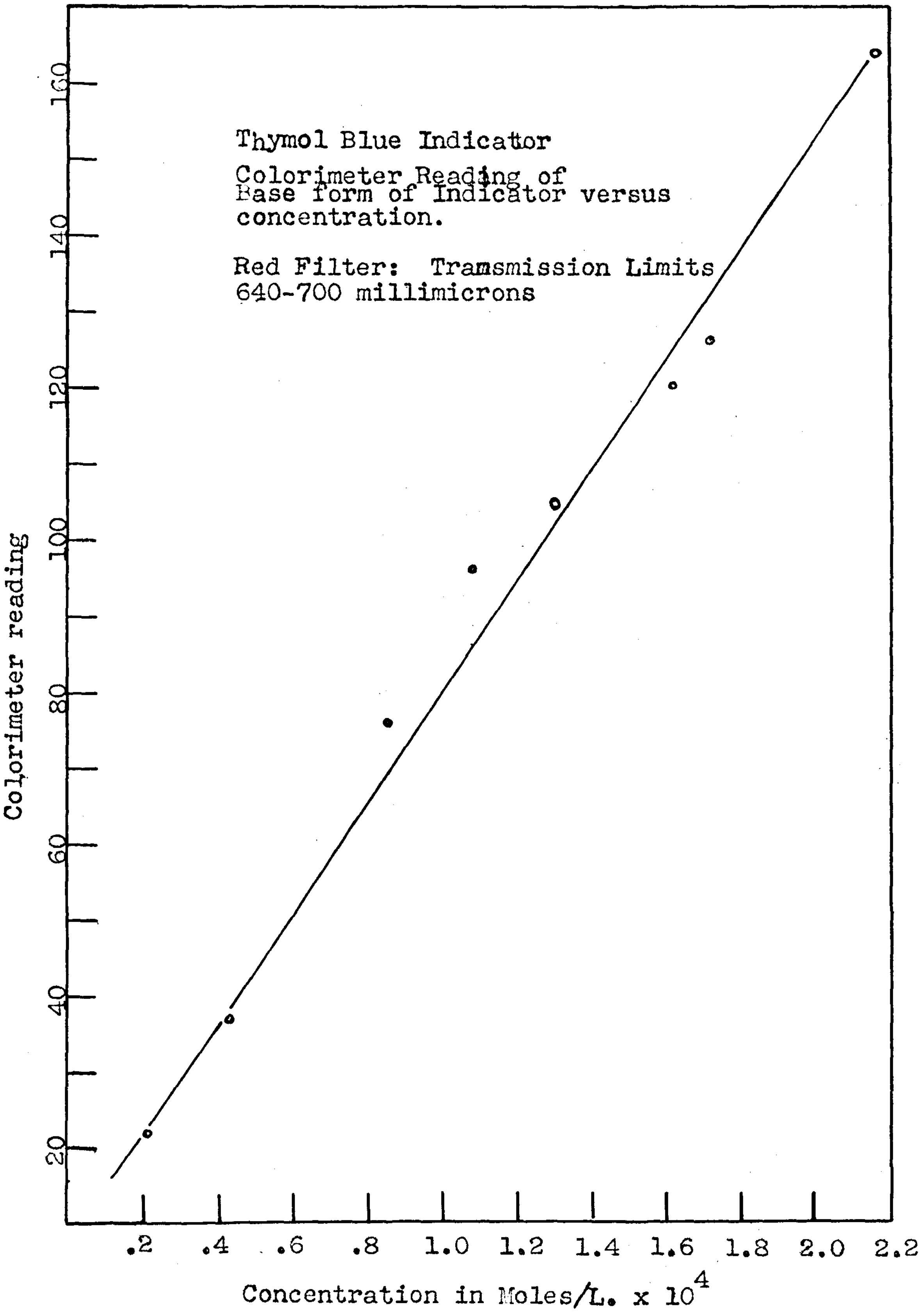

Thymol Blue Indicator
Colorimeter Reading of Base form of Indicator versus concentration.
Red Filter: Tramsmission Limits 640-700 millimicrons
Colorimeter reading
20
40
60
80
100
120
140
160
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Concentration in Moles/L. x 10⁴

Figure 9

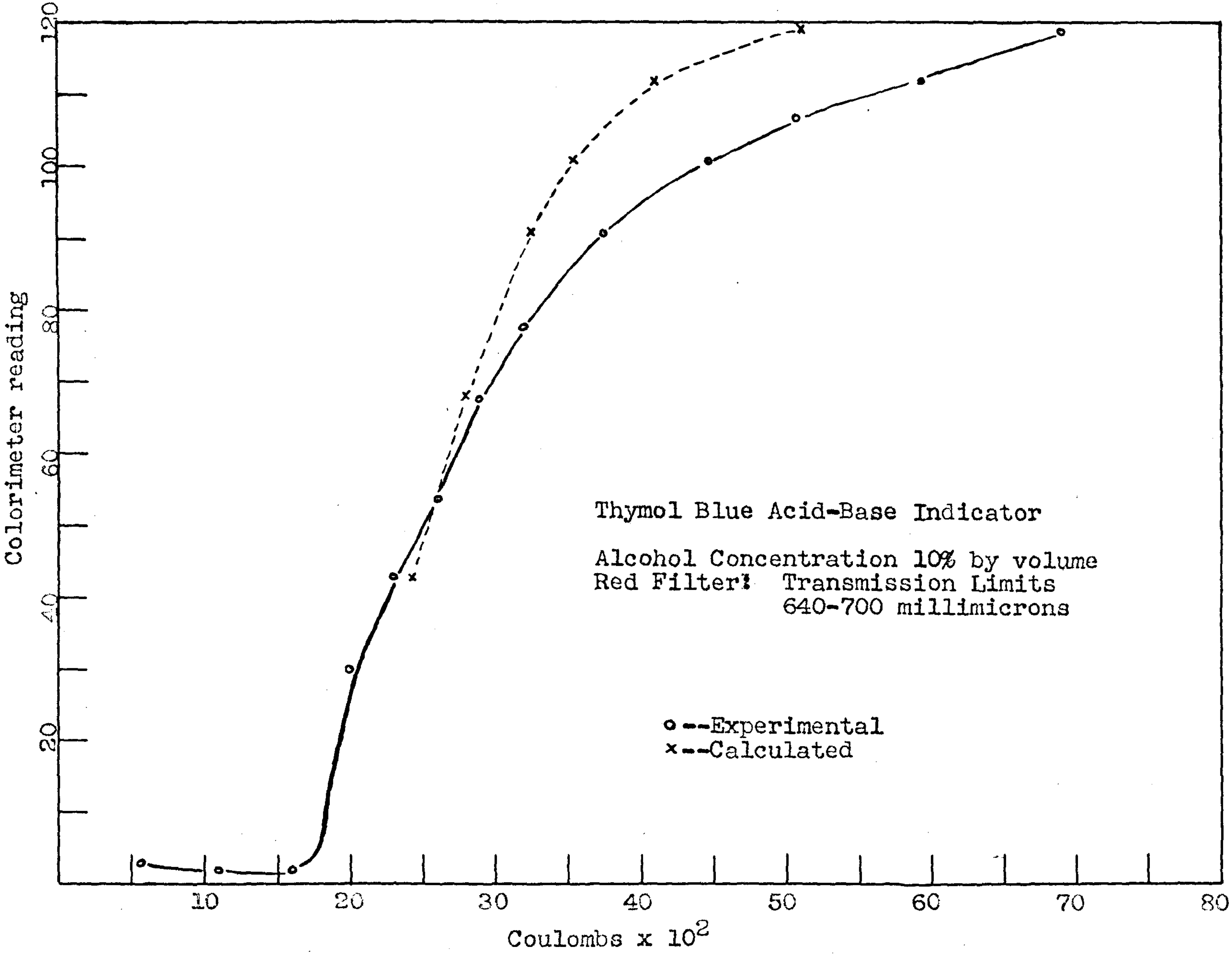
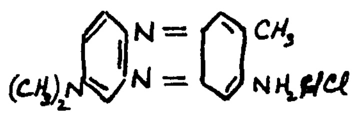

Thymol Blue Acid-Base Indicator
Alcohol Concentration 10% by volume
Red Filter: Transmission Limits 640-700 millimicrons
o --Experimental
x --Calculated
Colorimeter reading
20
40
60
80
100
120
Coulombs x 10^2
10
20
30
40
50
60
70
80

Figure 10

NEUTRAL RED

(Amino-dimethyl-amino toluphenazin-hydrochloride)



pH range 6.8 - 8.0

red to yellow

The data for neutral red is presented in Tables 5, 6, and 7 and in Figures 11, 12, and 13. Since the color transformation for neutral red is from the red acid form to a yellow base form, the major color absorbing form of the indicator is the HIn molecule that was measured in this analysis.

In Figure 11, a plot showing the colorimeter readings for the acid and alkaline forms versus concentration is given. This plot indicates a relationship between the colorimeter values and the concentration of neutral red for both the acid and alkaline states. In contrast to the thymol blue system described above, the complete transmittancy by either the HIn or the In^- constituent does not occur in this case. With neutral red the base form should have been independent of the concentration, but due to the limitation of the filters, complete transmittancy was not obtainable with the base state.

This introduces a new angle to the coulometric interpretation of the data. This problem was approached on the assumptions, that (1) the colorimeter reading of the acid state is due to the HIn concentration, (2) the reading of the base state is due to the In concentration, and (3) the reading is proportional to the combination of these two effects for the region between these two limits. A linear relationship is also assumed for these two effects for the intermediate region of the neutralization of the indicator. On these assumptions the following equations were derived.

The readings at all times are given by the following equation:

$$Rd = Rd_{In^-} + Rd_{HIn} \tag{12}$$

$$\text{and} \quad Rd_{In^-} = \frac{[In^-]}{k_{In^-}}; \qquad Rd_{HIn} = \frac{[HIn]}{k_{HIn}} \tag{13}$$

where k_{In^-} and k_{HIn} are the instrument constants for the $[In^-]$ and $[HIn]$ respectively.

$$\text{Since } [HIn] = [HIn]^\circ - [In^-] \tag{14}$$

the combination of equations (12), (13) and (14) yields

$$Rd = \frac{[In^-]}{k_{In^-}} + \frac{[HIn]}{k_{HIn}} = \frac{[In^-]}{k_{In^-}} + \frac{[HIn]^\circ - [In^-]}{k_{HIn}}$$

$$= \frac{k_{HIn}[In^-] - k_{In^-}[In^-] + k_{In}[HIn]^\circ}{k_{In} \times k_{HIn}} \tag{15}$$

$$k_{In} \times k_{HIn} \times Rd = [In^-](k_{HIn} - k_{In}) + k_{In}[HIn]^\circ \tag{16}$$

Let $k_{HIn} - k_{In} = k_2$ and $k_{In} \times k_{HIn} = k_1$

$$\text{Then } [In^-] = \frac{k_1 Rd \quad k_{In^-}[HIn]^\circ}{k_2} \tag{17}$$

Since $[HIn]^\circ - [HIn] = [In^-]$, and starting with

$$Rd = \frac{[In^-]}{k_{In}} + \frac{[HIn]}{k_{HIn}} = \frac{[HIn]^\circ - [HIn]}{k_{In}} + \frac{[HIn]}{k_{HIn}} \tag{18}$$

the following relationship is obtained in the same manner as (16):

$$[HIn] = \frac{k_1 Rd - k_{HIn}[HIn]^\circ}{k_2} \tag{19}$$

Combining equations (17) and (19), we have

$$\frac{[HIn]}{[In^-]} = - \frac{k_1 Rd - k_{HIn}[HIn]^\circ}{k_1 Rd - k_{In}[HIn]^\circ} \tag{20}$$

Repeating equation (9) where the

$$\text{Faradays passed} = [In^-] + \frac{K_w[In^-]}{K_{HIn}[HIn]} - \frac{K_{HIn}[HIn]}{[In^-]} \tag{9}$$

and substituting (17) +(20) in (9) we have

$$\text{Faradays passed} = \frac{k_1 Rd - k_{In^-}[HIn]^\circ}{k} - \frac{K_w}{K_{HIn}}\left[\frac{k_1 Rd - k_1[HIn]^\circ}{k_1 Rd - k_{HIn}[HIn]^\circ}\right] + K_{HIn}\left[\frac{k_1 Rd - k_{HIn}[HIn]^\circ}{k_1 Rd - k_{In}[HIn]^\circ}\right] \tag{20}$$

Theoretical calculations for neutral red based on equation (21) are given in Table 6, showing the relationship between these and experimental values.

Equation (21) is the final expression for an equation for the neutralization of an indicator exemplified here by neutral red. The influence of the HIn after neutralization or the In$^-$ before neutralization in the absorption of the transmitted light, is never completely eliminated by the filter.

With all of these acid-base indicators it would be advantageous to know if the electrode processes of oxidation or reduction have any harmful effects on the indicator. The possibility of using the indicator repeatedly with an electrolytic neutralization from the acid to the base form, and from the base to the acid form, was investigated. In Figure 13, a graph is given showing these subsequent electrolytic processes conducted on neutral red. It was found that neutral red was destructively oxidized at the anode, while no harmful reduction effects occurred at the cathode. The colorimeter reading for the HIn concentration was lowered after each successive oxidation and reduction, indicating a drop in the concentration of the absorbing HIn molecule of the neutral red.

A polarogram was taken on a Sargent-Heyrovsky Model XXI polarograph to determine if any side reactions were occuring in these acid-base indicator systems in conjunction with the generation of hydrogen at the cathode. The polarogram indicated that no reactions other than hydrogen liberation existed.

The stability of these acid-base indicator solutions were studied progressively with the other investigations. It was found that the stability was different for the various indicators, for example, solutions of o-cresol red were stable for a period of three days or more, while neutral red solutions would indicate a drop after one day.

TABLE 5

Neutral Red Indicator

Colorimeter Readings and Concentration of Indicator[a]

Concentration of Indicator (moles/L.)	% of Stock Solution	Colorimeter Readings Acid Form	Colorimeter Readings Base Form
4.32×10^{-5}	100	--	103
1.728×10^{-5}	40	278	51
8.64×10^{-6}	20	147	28
4.32×10^{-6}	10	71	16

a - Green filter, transmission limits 520-580 millimicrons

TABLE 6

Neutral Red Indicator[a]

Variation of Colorimeter Reading with Coulombs Passed

A		B		C			D	
Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading	Theoretical Coulombs Passed[b] x 10^2	Total Coulombs Passed x 10^2	Colorimeter Reading
10.00	900	0.00	278	0.00	147		0.00	71.5
15.50	645	2.17	278	0.46	145		5.56	69.8
17.71	568	4.34	270	1.10	145		12.30	60.0
20.03	510	6.51	260	3.42	145		16.72	55.5
22.35	450	8.68	251	4.87	130	.160	21.36	49.0
25.33	375	10.85	237	7.04	124		28.32	41.0
28.00	315	13.02	224	8.49	119		37.60	24.0
30.67	266	15.19	207	10.66	113		42.24	20.0
33.34	222	17.36	197	12.83	106		46.88	18
36.01	185	19.53	185	15.00	100	.392		
38.68	142	21.70	170	17.17	93			
41.35	113	23.87	155	19.34	88			
44.02	104	26.04	139	21.95	78			
46.69	103	28.21	123	24.56	71	.605		
		30.38	106	27.17	61			
		32.55	90	29.78	51			
		34.72	74	32.39	42			
		36.89	57	35.00	32			
		39.06	53	37.61	28			
		41.23	51					

A - Concentration of neutral red is 4.32 x 10^{-5} moles/L.
B - " " " " " 1.728 x 10^{-5} moles/L.
C - " " " " " 8.64 x 10^{-6} moles/L.
D - " " " " " 4.32 x 10^{-6} moles/L.

a --Green filter, transmission limits 520-580 millimicrons

b -- Theoretical number of coulombs according to equation (21) for the colorimeter indicated.

TABLE 7

Neutral Red Indicator[a]

Destruction of Neutral Red by Electrolytic Oxidation

Step 1		Step 2		Step 3		Step 4	
Increasing pH		Decreasing pH		Increasing pH		Decreasing pH	
Coulombs Passed x 10^2	Colorimeter Reading	Coulombs Passed x 10^2	Colorimeter Reading	Coulombs Passed x 10^2	Colorimeter Reading	Coulombs Passed x 10^2	Colorimeter Reading
		20.30	48	1.45	212	17.40	45
00000	276	18.85	49	4.35	210	15.95	46
2.90	268	17.40	51	5.80	204	14.50	58
5.80	263	15.95	63	7.25	200	13.05	92
8.70	250	14.50	98	8.70	192	11.60	118
11.60	193	13.05	133	10.15	170	10.15	143
13.05	159	11.60	165	11.60	150	8.70	160
14.50	111	10.15	182	13.05	101	7.25	171
15.95	67	8.70	200	14.50	71	5.80	172
17.40	54	7.25	212	15.95	49	2.90	172
20.30	48	4.35	212	17.40	45	0.00	172
		1.45	212				

The increments of coulombs passed through the cell are reported in the following fashion. The total number of coulombs is given in Step 1; in Step 2, the increments are subtracted from the total passed in Step 1; in Step 3, the increments are added to the remainder of Step 2; and Step 4 the increments are subtracted from the total in Step 3.

Green filter, transmission limits 520-580 millimicrons

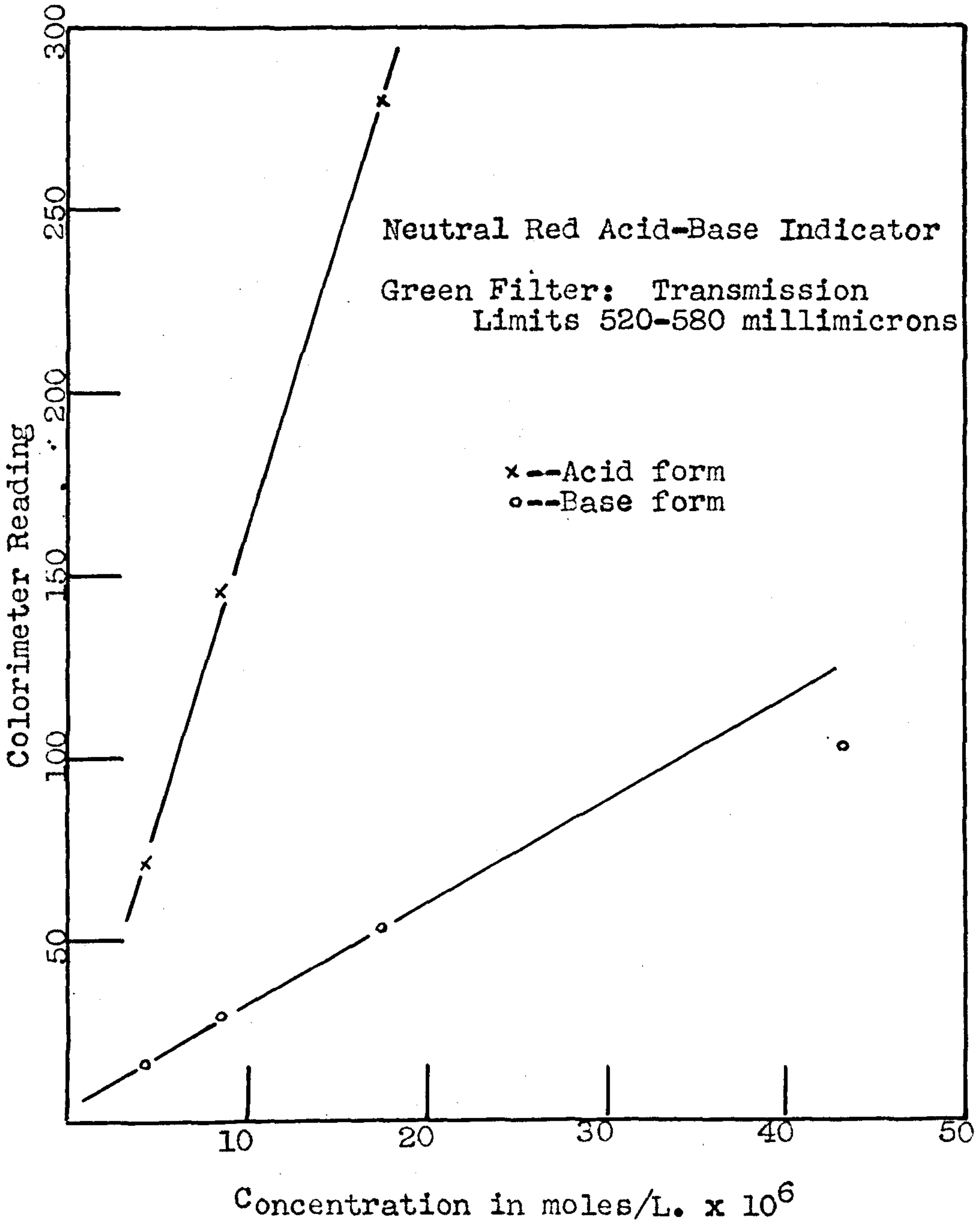

Neutral Red Acid-Base Indicator
Green Filter: Transmission Limits 520-580 millimicrons
× --Acid form
o --Base form
Colorimeter Reading
300
250
200
150
100
50
10
20
30
40
50
Concentration in moles/L. x 10^6

Figure 11

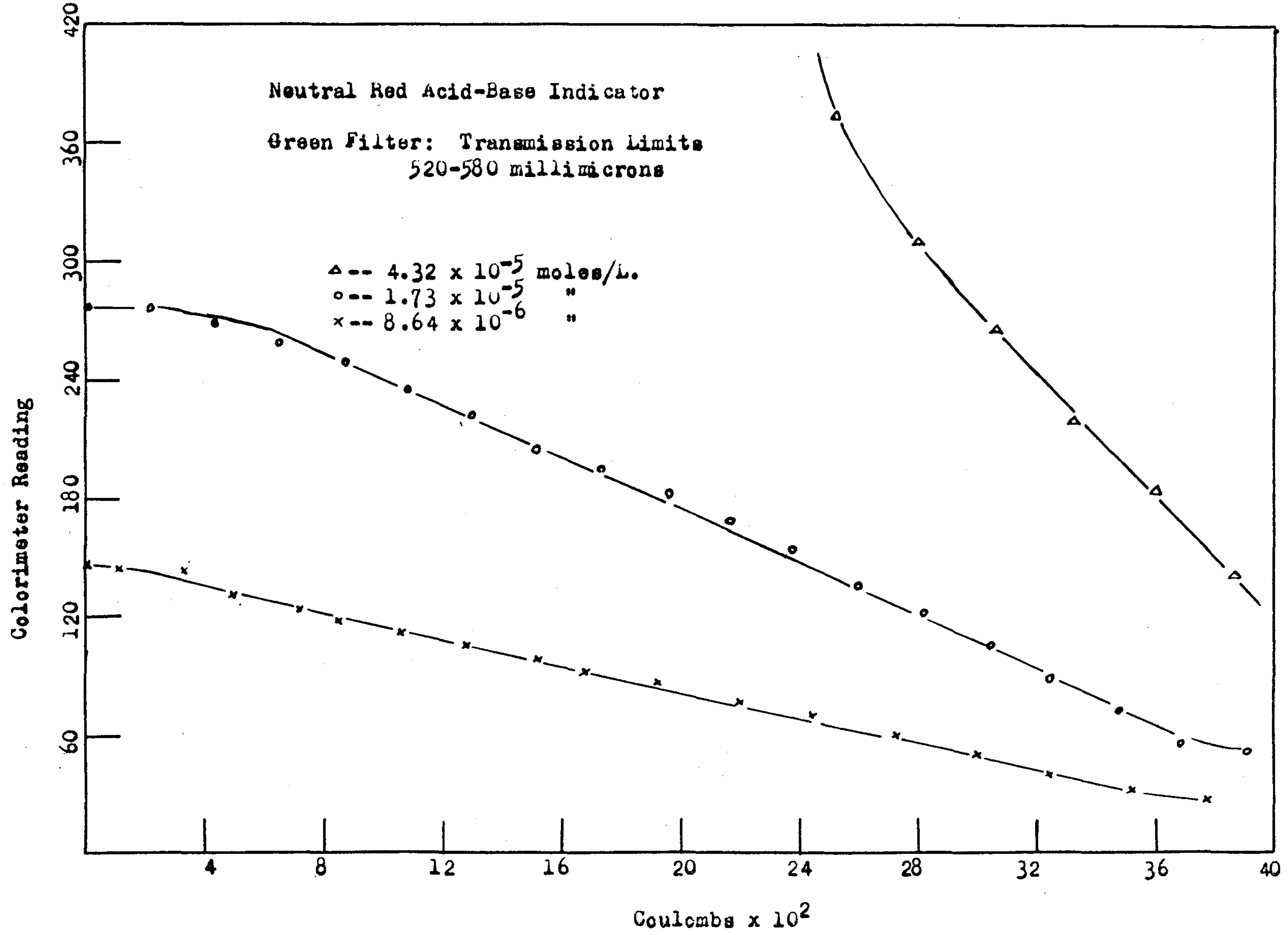

Neutral Red Acid-Base Indicator
Green Filter: Transmission Limits
520-580 millimicrons
△ -- 4.32 x 10⁻⁵ moles/L.
○ -- 1.73 x 10⁻⁵ "
× -- 8.64 x 10⁻⁶ "
Colorimeter Reading
420
360
300
240
180
120
60
4
8
12
16
20
24
28
32
36
40
Coulombs x 10²

Figure 12

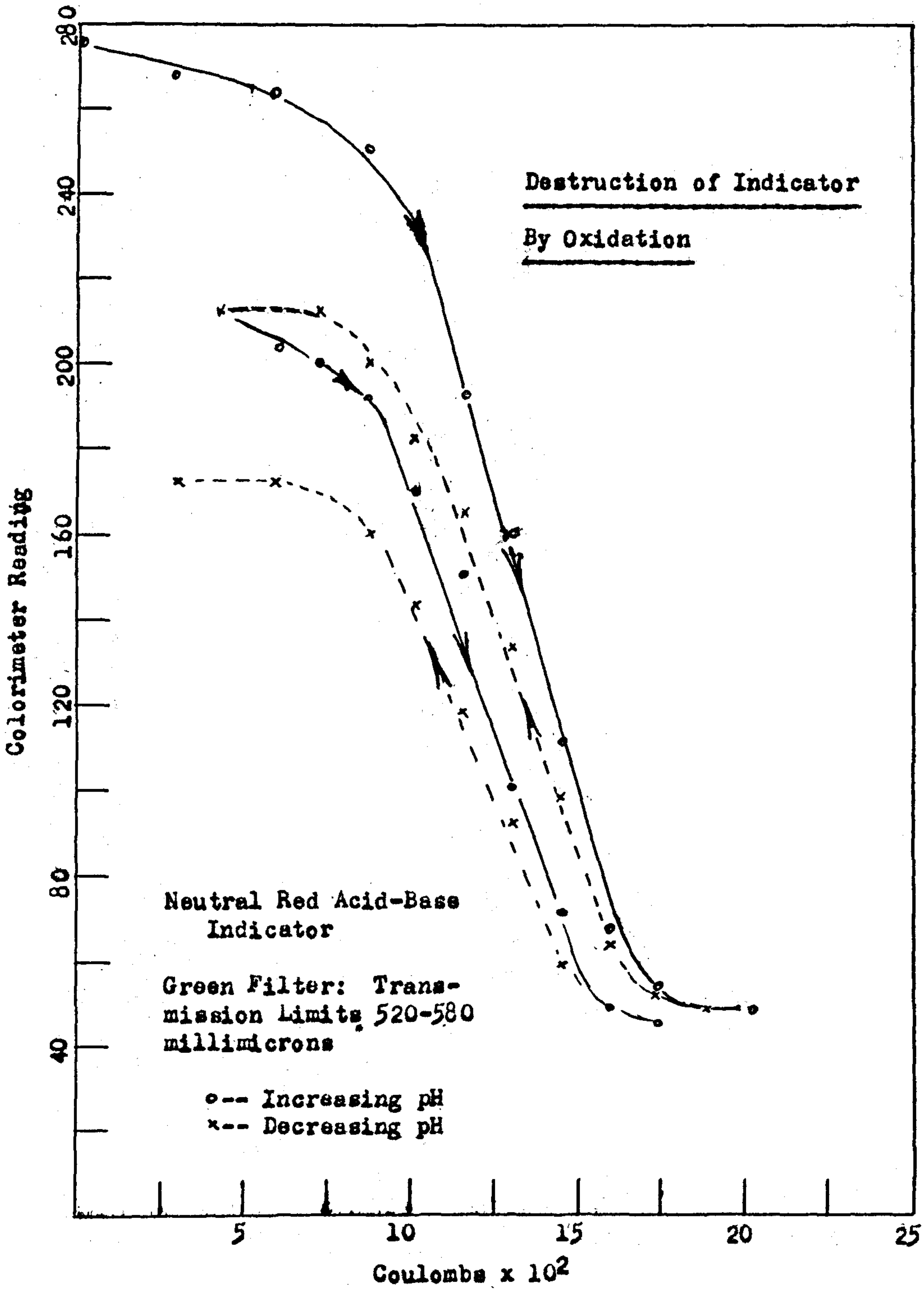
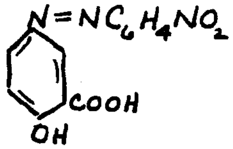

Destruction of Indicator
By Oxidation
Neutral Red Acid-Base Indicator
Green Filter: Transmission Limits 520-580 millimicrons
o-- Increasing pH
x-- Decreasing pH
Colorimeter Reading
280
240
200
160
120
80
40
5
10
15
20
25
Coulombs x 10^2

Figure 13

ALIZARIN YELLOW R

(Sodium salt of p-nitranilineazosalicyclic acid)



pH range 10.1 - 11.1

yellow to lilac

An investigation was conducted with alizarin yellow R to determine the conformance of indicators in the high pH range to this coulometric method of analysis. The data for this indicator is given in Table 8 and Figure 14. Although alizarin yellow produced the typical indicator curve, its sensitivity was not good due to a slow break on the base side of the neutralization curve.

TABLE 8

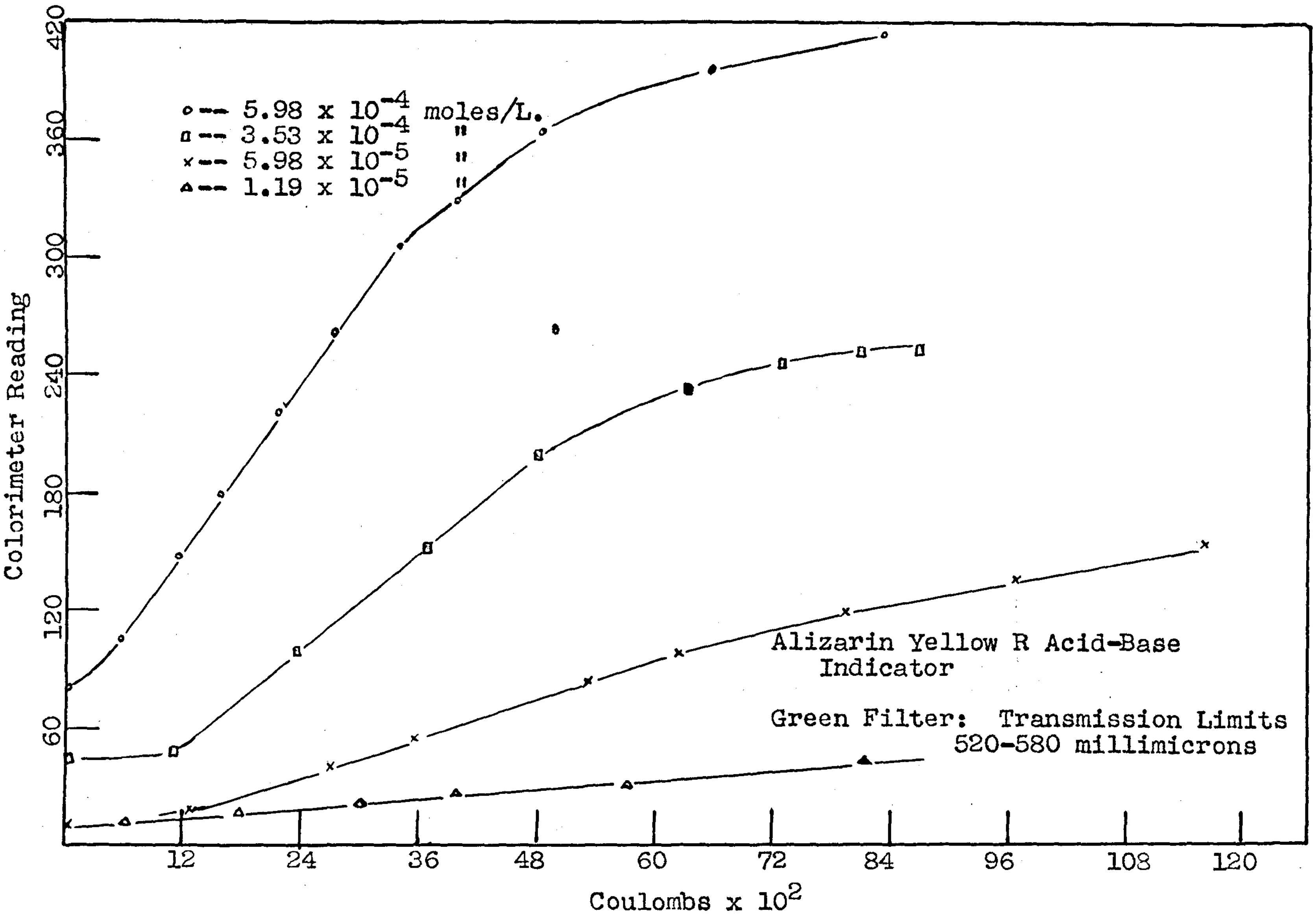
ALIZARIN YELLOW R INDICATOR[a]

Variation of Colorimeter Reading with Coulombs Passed

A		B		C		D	
Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading
0.00	80	0.00	47	0.00	10	0.00	8.0
5.80	106	5.80	46	5.80	10	5.80	10.5
11.60	148	11.60	49	12.56	17	14.50	14.0
15.95	180	18.84	79	18.36	26	20.30	17.5
21.75	222	23.67	98	27.06	40	30.93	22.5
27.55	262	28.02	126	35.76	55	40.59	27.0
34.65	307	32.37	146	44.46	70	57.98	34.0
40.45	330	36.72	152	53.16	84	82.61	46.5
49.15	364	42.52	173	61.86	98	98.55	51.5
66.05	398	48.32	200	70.56	110	113.04	57.0
83.44	415	55.56	216	79.26	120		
		64.26	234	96.65	139		
		72.96	248	114.04	155		
		81.66	254	134.33	172		
		87.46	254	148.82	182		
				177.80	199		
				200.98	199		

A - Concentration 5.98×10^{-4} moles/L.
B - " 3.53×10^{-4} moles/L.
C - " 5.98×10^{-5} moles/L.
D " 1.19×10^{-5} moles/L.

a -- Green filter, transmission limits 520-580 millimicrons

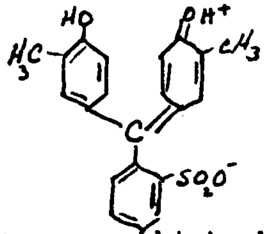


Alizarin Yellow R Acid-Base Indicator

Green Filter: Transmission Limits 520-580 millimicrons

Figure 14

O-CRESOL RED (o-cresolsulfonephthalein)



pH range 7.0 to 8.8

yellow to red

A series of curves were obtained with o-cresol red which did not fit either of the two previous possibilities for the relationships between the colorimeter reading and the concentration of the indicator as illustrated by thymol blue and neutral red. The data for this indicator is given in Tables 9 and 10 and Figures 15 and 16. Since o-cresol red changes from yellow to red in an acid to base neutralization, the concentration should be proportional to the red base form of the indicator only in the ideal situation. It was found that the colorimeter reading was related to the concentration of the indicator with the acid form in a manner similar to that exemplified by neutral red. The colorimeter readings for the base form of the indicator were not related to the concentration in any previously known manner, instead a steep curve with a limit was obtained. A similar shaped curve with a limit was obtained with variations in the alcohol concentration used to dissolve the indicator. It should be also pointed out here that the concentration curve of the acid form is not perfectly linear, but a slight curvature exists in the upper portion of the curve.

An explanation for these deviations was sought in the chemical structure of the compound given below;[30]

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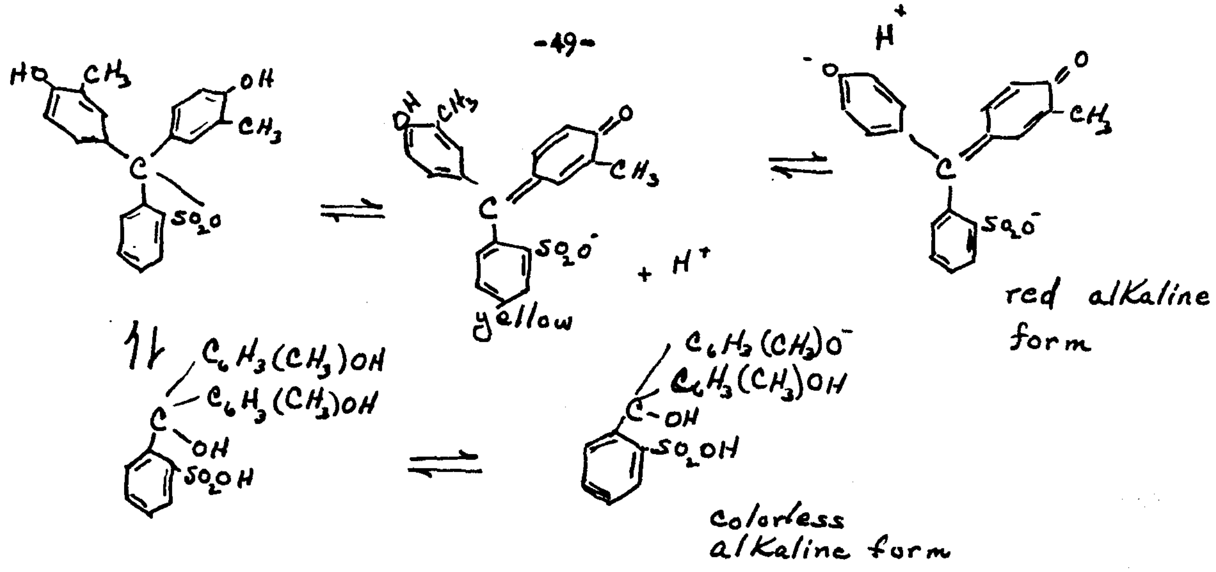
[30] "Acid-Base Indicator" Kolthoff, I. M., and Rosenblum, C., The MacMillan Company, New York, N. Y.



One possible explanation for the limiting portion of the curve for o-cresol red may be the formation of the strong alkaline form of the indicator as given above. Sulfonephthaleins exhibit a property similar to phenolphthalein in that they are decolorized by an excess of alkali. This equilibrium of the colorless strong alkaline form of the indicator may aptly explain the anomaly of the limiting value for the alkaline form of the indicator.

Another possibility for the explanation of the limit of the curve may lie in the instrument. The barrier cells of the colorimeter may not be sensitive enough to detect any further difference in this low transmission range.

An explanation for the curvature of the colorimeter readings with the acid form of the indicator is the association of the indicator with itself.

TABLE 9

o-Cresol Red Indicator

Colorimeter Readings and Concentration of Indicator[a]

Concentration of Indicator (moles/L.)	% of Stock Solution	pH	Colorimeter Readings Acid Forms	Colorimeter Readings Base Forms
4.15×10^{-4}	100	3.70	164	377
3.32×10^{-4}	80	3.80	144	377
2.08×10^{-4}	50	4.02	101	370
1.66×10^{-4}	40	4.15	83.0	358
0.830×10^{-4}	20	4.45	45.5	338
0.415×10^{-4}	10	4.85	25.5	274

a - Green filter, transmission limits 520-580 millimicrons
Alcohol concentraton constant at 10% by volume.

TABLE 10

o-Cresol Red Indicator[a]

Variation of Colorimeter Readings with Coulombs Passed

A.		B.		C.	
Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading	Total Coulombs Passed x 10^2	Colorimeter Reading
0.00	25.5	0.00	45.5	0.00	83
5.80	25.5	5.80	45.5	5.80	80
11.60	55	11.83	81	11.60	80
14.50	109	14.73	139	17.40	124
15.95	143	17.63	227	20.30	203
18.85	188	20.53	284	23.20	277
21.75	220	23.43	318	26.10	328
24.65	238	26.33	334	31.90	358
30.455	252	32.13	338	40.59	358
36.25	264	43.73	338		
47.85	274				
59.45	274				

a - Green filter, transmission limits 520-580 millimicrons
Alcohol concentration constant at 10% by volume

A - Concentration 0.415×10^{-4} moles/L.
B - " 0.830×10^{-4} moles/L.
C - " 1.66×10^{-4} moles/L.

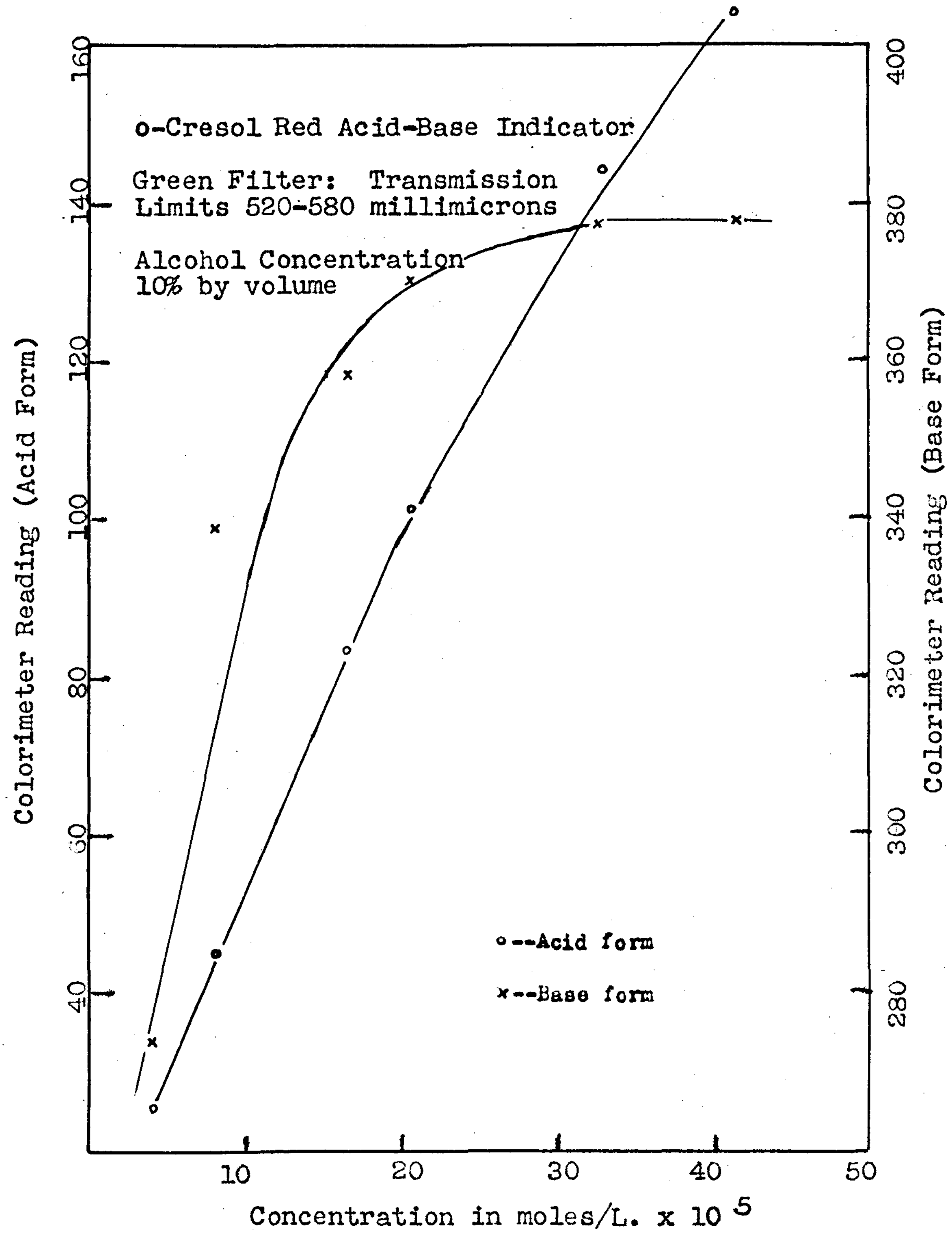

o-Cresol Red Acid-Base Indicator
Green Filter: Transmission Limits 520-580 millimicrons
Alcohol Concentration 10% by volume
o--Acid form
x--Base form
Colorimeter Reading (Acid Form)
160
140
120
100
80
60
40
Colorimeter Reading (Base Form)
400
380
360
340
320
300
280
10
20
30
40
50
Concentration in moles/L. x 10 -5

Figure 15

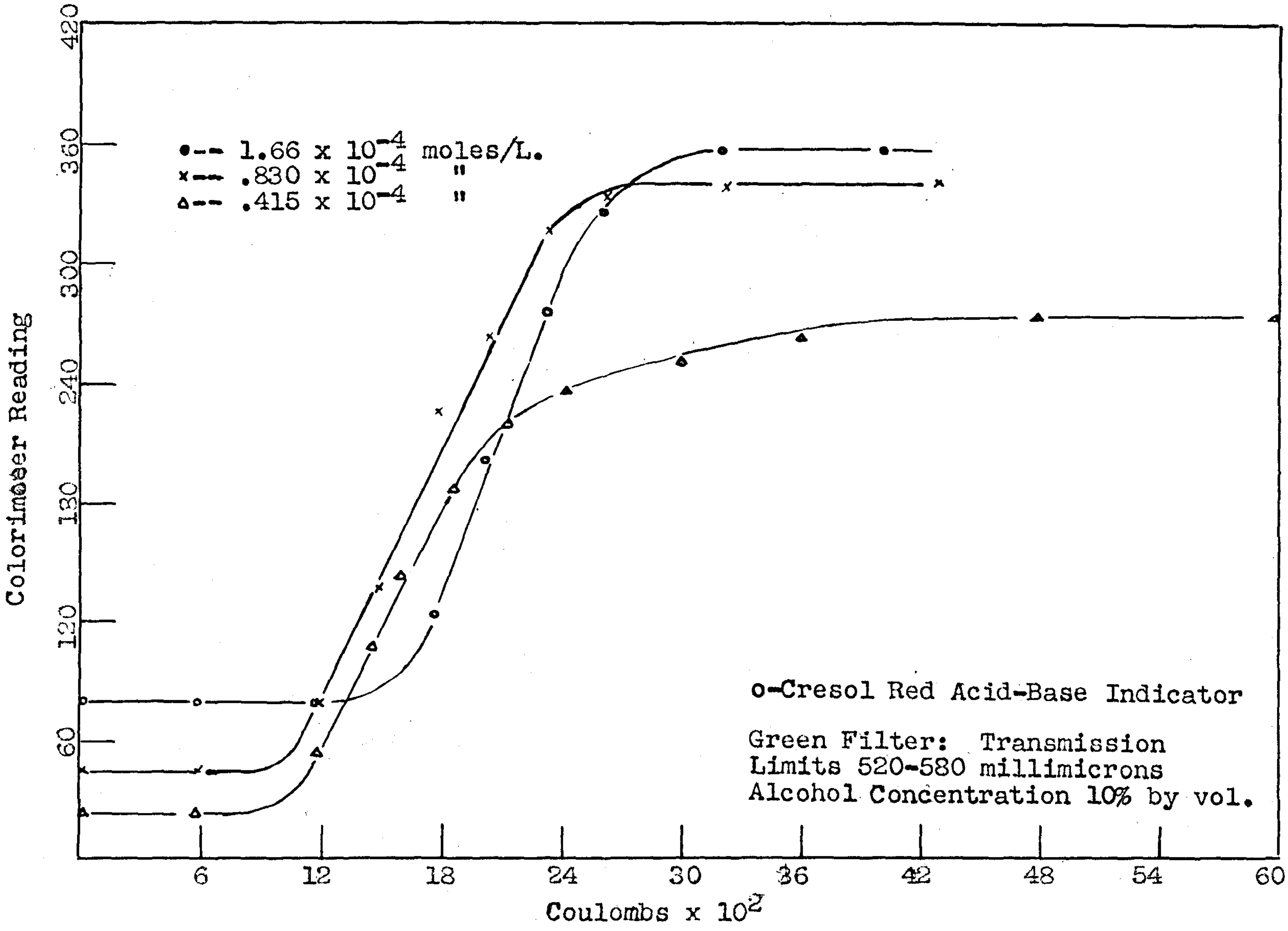

420
360
300
240
130
120
60
Colorimeter Reading
●—— 1.66 x 10^{-4} moles/L.
×—— .830 x 10^{-4} "
△—— .415 x 10^{-4} "
o-Cresol Red Acid-Base Indicator
Green Filter: Transmission
Limits 520-580 millimicrons
Alcohol Concentration 10% by vol.
6
12
18
24
30
36
42
48
54
60
Coulombs x 10^2

Figure 16

CONCLUSIONS

1. For the desired range of operation from 0.01 to 1 coulombs, the reactions for the first two processesthat were investigated were not sensitive enough. Bothe the "oxidation-reduction process", illustrated by the reduction of potassium permanganate, and the "alteration of solute" process, illustrated by the dissolution of copper operated most favorably from 1 coulomb and above.

2. Coulometric measurements within the desire range are possible with the "alteration of solvent" process, exemplified by the pH change of water as measured by the acid-base indicator method.

3. For the practical application of the acid-base indicator system, a brief standardization curve for the neutralization of the indicator should be performed. Each solution is stable for at least a day and maybe longer depending on the indicator employed.

4. The pH of the indicator solutions should be increased electrolytically to the lowest acid-form concentration on the steepest portion of the neutralization curve. In this region the system is most sensitive and the curve is linear.

5. All readings of the coulometer should be take as soon as possible with the stirrer removed after each experiment. The highly unbuffered solution of the indicator is susceptible to the CO_2 in the air and other contaminants. The indicator can be expected, however, to be constant for ten minutes or more in its most sensitive portion of neutralization

6. From the standpoint of maximum color change per quantity of electricity, o-cresol red is the most favorable indicator.

SUMMARY

1. All three possible reactions for a colorimetric coulometer were investigated.

2. The systems of sodium 2,6 dichlorobenzene-one indophenol, barium diphenyl amine sulfonic acid, potassium dichromate, and potassium permanganate were studied as "oxidation-reduction" processes. The potassium permanganate was the best example, operating at an efficiency of about 100% in the range of 1 to 5 coulombs.

3. The systems of chlorine--otolidine, and copper-triethanolamine were studied as "alteration of solute" processes. The dissolution of copper to a triethanolamine complex was the best reaction investigated for an "alter- of solute" process with an efficiency of approximately 100% in the range of 1 to 10 coulombs.

4. The pH change of water was the process studied in the "alteration of solvent" process. Several pH indicators including thymol blue, neutral red, alizarin yellow R, and o-cresol red, were studied and the experimental relationships between the acid and base forms versus concentration were obtained. The theoretical equations were derived for the relationship between the colorimeter readings and the number of coulombs passed. These acid-base indicator systems permit measurements in the range of 0.01 to 1.0 coulombs.

BIBLIOGRAPHY

1. Bogan, Meites, Peters, and Strutevant, J. Am. Chem. Soc. 73, 1584 (1951)

2. Bose and Conrat, Techn. Hochsch., Dansig-Langfuhr

3. Burt, R. C., Phys. Rev. 27, 813 (1926)

4. Datta and Dhar, J. Am. Chem. Soc. 38, 1156 (1916)

5. Ellms and Hauser, J. Ind. Eng. Chem. 5, 915 (1913)

6. Farrington and Swift, Anal. Chem. 22, 889 (1950)

7. Fischer, Thiele and Maxted, Z. Anorg. Chem. 67, 339

8. Glasstone, S., "Textbook of Physical Chemistry", D. Van Nostrand Co. Inc. New York, New York

9. Kistiakowsky, Z. Elektrochme., 12, 713 (1906)

10. Kolthoff, I. M. and Rosenblum, G., "Acid-Base Indicators", The MacMillan Company, New York, New York

11. Lehgeldt, Phil. Mag. 15, 614, 621 (1908)

12. Lingane, J. J., J. Am. Chem. Soc. 67, 1916 (1945)

13. Lingane and Jones, Anal. Chem. 22, 1226 (1950)

14. Mathews, H. P. and Wark, I. W., J. Phys. Chem. 35, 2345 (1931)

15. Muller, R., Physik. Z. 11, 978 (1910)

16. MacNevin, W. M., and Martin, G. L., J. Chem. Ed. 24, 587 (1947)

17. Reevely, W. O. and Gordon, A. R., Trans. Elektrochem. Soc. 63, 5pp.

18. Richards, Collins, and Heimrod, Proc. Am. Acad. 35, 123 (1899)

19. Richards, T. W. and Anderegg, F. O., J. Am. Chem. Soc. 37, 7 (1915)

20. Rosa and Vinal, Proc. Nat. Acad. Sci. 3, 59-64

21. Schulte, Z. Elektrochem. 27, 755 (1921)

22. Shaffer, Briglio and Brockman, Anal. Chem. 20, 1008 (1948)

23. Smith, Mather and Lowry, Phil Trans. (A) 207, 545 (1908)

24. Stewart, O. J. , J. Am. Chem. Soc. 53, 336 (1931)

25. Syrokomskii, V. S., and Nazareva, T. I., Zhur. Anal. Khim. 6, 15 (1951)

26. Tosterud and Mason, Trans. Electrochem. Soc. 90, 6 pp.

27. Von Wartenberg, H., and Schutza, H. Z. Elektrochem. 36, 254 (1930)

28. Washburn, E. W., Trans. Electrochem. Soc. 88, 3 pp.

29. Wilson, C. T. R., Proc. Cambridge Phil. Soc. 19, 345

30. Yoe and Barton, Ind. Eng. Chem. Anal. Ed. 12, 456 (1940)