The

QUANTITATIVE ESTIMATION of CERTAIN BETA-NAPHTHOL SULPHONIC ACIDS SINGLY and in PRESENCE of ONE ANOTHER

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The QUANTITATIVE ESTIMATION of CERTAIN BETA-NAPHTHOL SULPHONIC ACIDS SINGLY and in PRESENCE of ONE ANOTHER.

OBJECT of RESEARCH.

The beta-naphthol sulphonic acids are used in large quantities as second components in the manufacture of azo dyes and as starting points for other intermediates. They are usually prepared by the action of sulphuric acid on beta-naphthol. It would appear, therefore, that a systematic study of the sulphonation of beta-naphthol would be of practical value in discovering conditions for obtaining the optimum yield of these sulphonic acids, since, on investigation of the literature, it is found that no such study has been published. The literature on the direct sulphonation of beta-naphthol and on its sulphonic acids is, in the main, descriptive of the preparation and separation of the acids for dye manufacture, and of the methods used in the elucidation of the structure of the compounds. No reference is found in the literature to work undertaken for the purpose of investigating the mechanism of the sulphonation reaction and of the conversion of one acid into another, nor has the sulphonation of beta-naphthol at various temperatures and concentrations of sulphuric acid been followed quantitatively. The patents, on the other/

the other hand, refer mainly to the manufacture of azo dyes from the acids.

It was with the object of studying these sulphonation reactions that the present research was undertaken; but, previous to such a study, it was necessary to have a method of estimating quantitatively the constituents in a sulphonation melt individually and collectively. The following paper records attempts to evolve such a method.

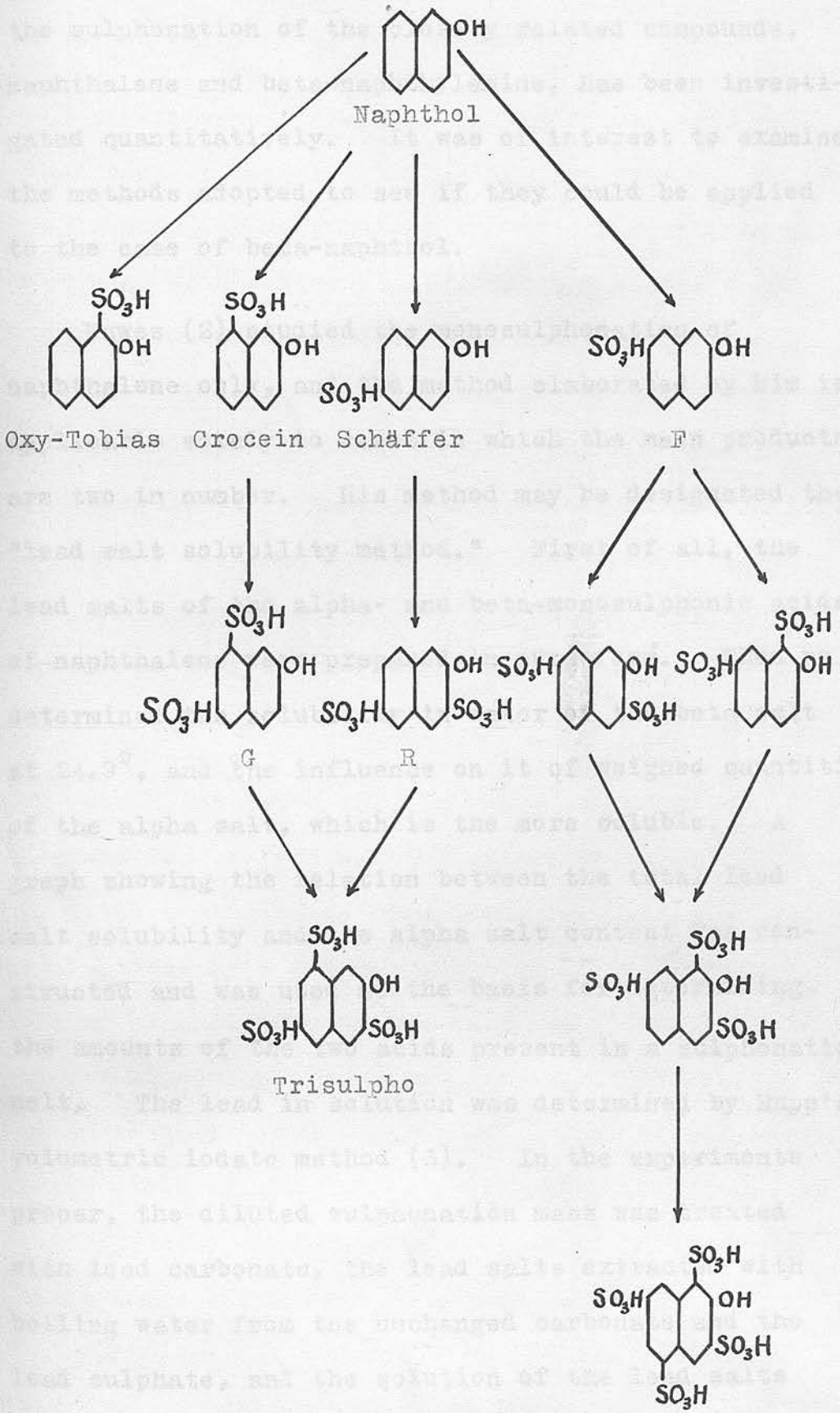
The SULPHONATION of BETA-NAPHTHOL.

It is well known that beta-naphthol dissolves in concentrated sulphuric acid and oleum with the evolution of heat, due to the formation of sulphonic acids. One of the nuclear hydrogen atoms combines with a hydroxyl group of the sulphuric acid to form water, and the residual sulphonic acid group (SO_3H) enters the molecule. The particular individuals obtained depend on the strength of the acid used, the ratio of it to the naphthol used, and the temperature employed.

If the temperature is kept below 40°, and 2 mols of acid are used to 1 of naphthol, then the 2:1-naphtholmonosulphonic acid (Oxy-Tobias acid) is the chief product. On standing, such a mixture gives rise to two other monosulphonic acids, viz., the 2:8- (Crocein) and the 2:6- (Schäffer) acid, the Oxy-Tobias acid disappearing. Crocein acid is present in greater quantity at low temperatures, while Schäffer acid preponderates/

acid preponderates at higher temperatures (above about 50°). A greater proportion of sulphuric acid and higher temperatures lead to the production of disulphonic acids, viz., the 2:6:8- acid (G-acid) and the 2:3:6- acid (R-acid), so called because the former couples with diazo compounds to give yellowish azo dyes (Ger. gelb) while the latter gives red (rot) dyes. By using a still greater proportion of acid, higher temperatures and longer times, the 2:3:6:8-naphtholtrisulphonic acid is obtained along with disulphonic acids. Other acids have been recognised in the sulphonation melt, such as the 2:7-naphtholmonosulphonic acid (F-acid). Thus, it appears that at least two acids are obtained under any one set of conditions, the particular individuals depending on the time of reaction, concentration of acid and temperature. A very complete survey of the literature has lately been given by Forster and Keyworth (1) in a paper on the preparation of arylamine salts of these acids. The following scheme, taken from that paper, gives the formulae of these acids and shows how they are related to one another. Of the acids mentioned, this paper deals only with four, viz., Schäffer, Crocein, R and G.

SULPHONATION of BETA-NAPHTHOL.



PREVIOUS WORK on SIMILAR COMPOUNDS.

Although a detailed study of the sulphonation of beta-naphthol has not been recorded in the journals, the sulphonation of the closely related compounds, naphthalene and beta-naphthylamine, has been investigated quantitatively. It was of interest to examine the methods adopted to see if they could be applied to the case of beta-naphthol.

Euwes (2) studied the monosulphonation of naphthalene only, and the method elaborated by him is applicable solely to cases in which the main products are two in number. His method may be designated the "lead salt solubility method." First of all, the lead salts of the alpha- and beta-monosulphonic acids of naphthalene were prepared in pure form. Then he determined the solubility in water of the beta salt at 24.9°, and the influence on it of weighed quantities of the alpha salt, which is the more soluble. A graph showing the relation between the total lead salt solubility and the alpha salt content was constructed and was used as the basis for determining the amounts of the two acids present in a sulphonation melt. The lead in solution was determined by Rupp's volumetric iodate method (3). In the experiments proper, the diluted sulphonation mass was treated with lead carbonate, the lead salts extracted with boiling water from the unchanged carbonate and the lead sulphate, and the solution of the lead salts evaporated to dryness./

evaporated to dryness. The solubility of the salt mixture was determined as above and from it the proportions of the two acids present were found from the graph, previously constructed.

Experiments by workers in the Colour Investigation Laboratory of the U.S. Bureau of Chemistry (4) on the sulphonation of naphthalene and on its sulphonic acids have been mainly qualitative, but the vapour phase sulphonation of naphthalene has been studied under conditions leading to the formation of the 2:6- and the 2:7-disulphonic acids only. For the determination of these, Euwes' method (1) was employed, the particular graph required having been previously constructed from experimental data, specially determined. The lead content of the solutions was determined by precipitation as chromate.

Green and Vakil (5), in their study of the sulphonation of beta-naphthylamine, prepared the dry mixed sodium salts from the sulphonation mass. By treatment of a weighed quantity of these with boiling alcohol, the sodium salts of the 2:5-, 2:6- and 2:7-monosulphonic acids were dissolved leaving the sodium salt of the 2:8-acid, which was weighed. The silver salts of the 2:6- and 2:7-acids were found to be practically insoluble in cold water and thus furnished a means of separating these acids together. The precipitate of the silver salts was filtered off, dissolved in boiling water and the silver precipitated with hydrochloric/

with hydrochloric acid and weighed as chloride. The 2:5-monosulphonic acid was estimated by difference. The accuracy of the method was checked with known mixtures of the various pure salts.

In the paper of Forster and Keyworth already referred to (1), the preparation and properties of a number of the arylamine salts of beta-naphthol sulphonic acids were given, and a scheme of separation, using those salts, was deduced. A trial quantitative separation of R and G acids was carried out by dissolving weighed quantities of pure p-toluidine R and G salts in hot water and allowing the solution to crystallise. A quantitative yield (within 0.5%) of p-toluidine R salt separated out, and the p-toluidine G salt was recovered by evaporation, but evidence of slight hydrolysis was obtained. The authors suggested that the benzidine salts of Schäffer and R acids could be used for their quantitative separation, provided that no sulphate were present. The arylamine salts of the beta-naphthol sulphonic acids could not be titrated with standard sodium hydroxide solution using phenolphthalein as indicator; this method of quantitative estimation was available for other arylamine salts investigated, e.g. those of naphthalene sulphonic acids.

These methods were rejected for the following reasons. The lead salt solubility method is only applicable to conditions in which two sulphonic acids are formed,/

are formed, and it is quite probable that more than two are formed when beta-naphthol is sulphonated; also it entails the heating and drying of the salts. Such treatment might cause changes in the proportions of the isomers present. The same objection can be brought against the method of Green and Vakil. Also, it was desired, if possible, to develop a volumetric method in preference to a gravimetric, to shorten the time required for a determination.

VOLUMETRIC METHODS AVAILABLE.

There are two methods given in the literature, which conform to the restriction that no drastic treatment is involved in their use, viz.,

(a) titration with a standard solution of a diazotised amine,

(b) titration with a standard bromine solution, or with a standard solution generating bromine.

The sulphonic acids of beta-naphthol are mainly used in industry as second components of azo dyes; that is to say, they have the property of "coupling" with diazotised amines. This property can be used for their estimation quantitatively. An alkaline or weakly acid solution of the sulphonic acid, containing a known weight of it, is titrated at a suitable temperature (usually 0^{o}) with a standard diazo solution using the spotting test as a means of detecting the end point; or, a slight excess of diazo solution is added and/

added and the dye salted out, collected in a Gooch crucible, dried and weighed. The first method is the one generally used. The "spotting" test is described fully in the analytical section of Fierz-David's "Dye Chemistry" (6), and also the method of preparing the solutions and standardising them.

Now, since diazo solutions decompose more or less easily in daylight, and also in alkaline solution, and since coupling only takes place in alkaline or, in special cases, in weakly acid solution, this method will tend to give high results. Also the spotting test can only be carried out in good daylight, and is inclined to be indefinite in dilute solution, that is, when the end point is being reached. These disadvantages make this method somewhat uncertain, except after much practice.

It was decided, therefore, to investigate, in the first place, the bromination method, as far as it could be used for the present purpose.

Estimation by titration with a brominating solution depends on the fact that a nuclear hydrogen atom may be replaced by a bromine atom, an equivalent quantity of hydrobromic acid being formed at the same time. If, now, the number of atoms of bromine entering one molecule of an aromatic compound under a given set of conditions be known, then the amount of that substance in a mixture or solution can be estimated quantitatively/

estimated quantitatively by determining the quantity of bromine used up in bromination, provided that that substance is the only one present which reacts with bromine. The bromination may be carried out in one of two ways, viz., (a) by the indirect method, in which a known excess of the brominating solution is added and the bromine remaining at the end of the reaction determined, or (b) by the direct method, in which the brominating solution is run in from a burette, until a faint excess of bromine can just be detected by a suitable indicator, such as starch-iodide paper.

The indirect method is the one generally employed and many papers have appeared describing its use for determining single compounds, mostly of the benzene series. The main points of some of the more general papers are given in the following survey, in so far as they have bearing on the present work.

SURVEY of BROMINATION METHODS.

INTRODUCTION.

Many brominating agents have been evolved, but, for volumetric quantitative work, only four appear to be suitable. They are bromine water, bromine dissolved in potassium bromide solution, bromine dissolved in potassium or sodium hydroxide solution (Lloyd's hypobromite solution), and a mixture of bromide and bromate in solution (Koppeschaar's solution). In using either of the last two solutions, it is added to an acid solution of the substance to be brominated, when bromine is liberated, probably in a nascent condition. The first three brominating media mentioned have the disadvantage that bromine volatilises from them and, therefore, the solutions have to be frequently restandardised; they also have the objectionable odour of bromine. Redman and Rhodes (7) found that solutions of bromine in caustic potash (about 0.1N bromine) decreased in strength at the rate of about 0.3% per day, if kept in bottles provided with a syphon and air inlet. These three investigators state that the hypobromite solution is more stable if kept in a well-stoppered, brown glass bottle. Since a bromide-bromate solution has no free bromine in solution, it is quite stable.

From the above considerations, it appeared that the solution containing a mixture of bromide and bromate was the best brominating agent for the present purpose; references/

purpose; references are, therefore, given only to papers describing this method of supplying the bromine.

(Lately (8), the perbromides of pyridine and quinoline salts, dissolved in glacial acetic acid, have been used as brominating media for the determination of phenol and of the "iodine value" of fats and oils.)

INDIRECT METHOD.

The bromide-bromate mixture was first used by Koppeschaar in 1876 (9) for the determination of phenol. Landholt (10) some time previously had suggested that phenol could be determined by treatment with excess of bromine water, and by weighing the precipitated tribromphenol. Koppeschaar simplified this method to obviate the tedious drying in a desiccator by adding a known excess of bromine water of known strength to an aqueous solution of phenol, allowing the reaction to proceed for 15 - 20 minutes, and then adding potassium iodide solution. This reacted with the unabsorbed bromine, liberating an equivalent amount of iodine, which was titrated with standard sodium thiosulphate solution, using starch as indicator. Since the strength of the bromine water, relative to the thiosulphate solution, was known, the amount of unabsorbed bromine was calculated and hence the amount absorbed and the weight of phenol present.

In order to/

In order to obviate the use of the disagreeable and unstable bromine water, Koppeschaar further modified his method. This modification consisted in adding a standard solution containing a bromide and a bromate to the phenol solution, which was then acidified with hydrochloric acid. In this way, he was able to generate bromine in the phenol solution as required. The equation for the reaction is

$$KBrO_3 + 5KBr + 6HCl = 6Br + 6KCl + 3H_2O.$$

Koppeschaar prepared his mixture of bromide and bromate by adding excess of bromine to a solution of potassium hydroxide, evaporating to dryness and gently igniting the residue. After grinding up the residue to obtain a uniform product, he had a dry mixture of the salts in the proportions required by the above equation.

$$3Br_2 + 6KOH = KBrO_3 + 5KBr + 3H_2O.$$

To obtain a solution suitable for bromination, it was only necessary to dissolve a weighed quantity of the mixture in a standard flask. If the alkali were not pure, the bromide-bromate solution could be standardised by liberating the bromine from a definite volume of it, in presence of potassium iodide and titrating the liberated iodine with standard sodium thiosulphate solution. Koppeschaar also prepared and used the corresponding sodium salt mixture.

According to his results, the sodium mixture gave the more concordant results (maximum variation 0.5%) than the potassium mixture (maximum variation 1.5%), which in turn gave better results than bromine water (maximum/

water (maximum variation 2.5%). Koppeschaar suggests that this difference is due to some impurity in the potassium hydroxide, probably sulphate, which with hydrochloric acid would liberate sulphuric acid in some measure; and he states that he found sulphuric acid unsuitable for the liberation of bromine. This observation is not substantiated by any later worker, nor by the present writer.

Koppeschaar recommends the following concentrations of solutions:-

Sodium thiosulphate - 0.04N.
Bromide-bromate - 9 gm. mixture per litre.
Potassium Iodide - 125 gm. per litre.
Hydrochloric Acid - 5 c.c. concentrated acid in a combined volume of phenol and brominating solution of 125 c.c.

The time of bromination recommended is 15 -20 minutes.

Koppeschaar's method has been utilised by many workers; it is capable of wide application. Seubert (11) used potassium bromide and bromate in the same proportions as Koppeschaar, but modified the method in that he placed a known volume of brominating solution in a glass-stoppered flask, liberated the bromine with hydrochloric or sulphuric acid, and added the unknown phenol solution from a burette, until no colour was given by a test drop on potassium iodide-starch paper. Beckurts (12) recognised the formation of tribromphenolbromide in addition to tribromphenol. He used separate solutions of potassium bromate (M/100) and potassium bromide (M/10), adding equal volumes to the phenol solution (i.e. 100% excess bromide) and/

bromide) and using sulphuric acid to liberate the bromine; the "excess" method was employed.

Most of the subsequent papers on the bromination of phenol relate to this question of the formation and decomposition of tribromphenolbromide, a point which has no bearing on the present investigation. In passing, it may be noted that both Lloyd (13) and Olivier (14) found that excess of potassium bromide decomposed the tribromphenolbromide to tribromphenol. Probably this observation led to the use of a bromide-bromate solution containing excess of potassium bromide. Redman and Rhodes (7) state that the solution recommended in the United States Pharmacopoeia is one containing 3.5 gm. potassium bromate and 55 gm. potassium bromide per litre; theoretically, 3.5 gm. potassium bromate require 12.48 gm. potassium bromide, so that an excess of 42.5 gm. or 340% is used. This excess of bromide also serves as a solvent for the bromine.

Two other papers on the determination of phenol by bromination may be mentioned. In the first of these, Redman and Rhodes (7) showed that phenol may be accurately determined by the indirect method with either Lloyd's hypobromite solution or Koppeschaar's solution (U.S.P. standard), the bromination period reduced to one minute, provided the mixture is shaken continuously.

The second paper is by Redman, Weith and Brock (15), and it contains particulars/

(15), and it contains particulars of 75 experiments showing the effect of acid concentration, time, temperature, amount of potassium iodide added, time for liberation of the iodine and excess of bromide-bromate solution on the accuracy of the method. Their conclusions are as follows:-

(a) An (hydrochloric) acid concentration of 0.48N is necessary during the bromination period, if the reaction is to be complete within one minute. Acid concentrations up to 1.12N do not affect the results; bromination at lower acid concentrations is only complete after longer periods.

(b) A temperature of 20 - 30° is necessary, if the bromination is to be complete in one minute using 0.64N acid; lower temperatures require longer periods.

(c) An excess of potassium iodide of 50% is sufficient for the displacement of the unabsorbed bromine; and shaking for one minute is sufficient for the liberation of the iodine.

(d) A 2% excess of bromide-bromate solution leads to accurate results, if the acidity and temperature given in (b) are used. An excess of 30% had no effect.

(e) The amount of bromide in the brominating solution may be reduced to 50% above that required by the equation. The solution recommended is one containing 2.76 gm. potassium bromate and 15 gm. potassium bromide per litre.

The phenol solution was very dilute during the bromination period (about 0.002N). If the above conditions were adhered to, it was possible to obtain results showing an error of 0.2%.

Another series of papers on the subject of bromination by the indirect method, using Koppeschaar's solution, appeared in the Journal of the American Chemical Society under the names of Francis and his collaborators (16). Francis was interested in the directive influence/

directive influence of groups on the substitution in the benzene ring. Large numbers of benzene derivatives were brominated for this purpose. It is pointed out in the first paper that, when bromine enters the ring, hydrobromic acid is liberated, and this will react with more bromic acid (potassium bromate and acid) to generate a further quantity of free bromine, which is available for bromination. The equation for the bromination of an aniline derivative under this scheme is given as

$$C_6H_4XNH_2 + KBrO_3 + 2KBr + 3HCl = C_6HBr_3XNH_2 + 3KCl + 3H_2O,$$

assuming trisubstitution.

A solution containing this smaller quantity of bromide was tried and found to be successful in practice. The principle is, of course, only applicable in the case of substitution reactions. The following details are taken from the paper.

"0.13N Bromide-Bromate Solution.- 3.5 gm. potassium "bromate and 13 gm. potassium bromide are dissolved "for each litre of solution. When the solution is "to be used for analyses involving substitution only, "5.5 gm. of potassium bromide per litre is sufficient. "The solution is standardised by titration against a "sample of pure aniline.

"0.1N Sodium Thiosulphate.- 25 gm. of crystallised "sodium thiosulphate are dissolved in each litre of "solution. The resulting solution is standardised by "titrating the iodine liberated when a definite volume "of the bromide-bromate solution is acidified and "potassium iodide added.

"Details of Analytical Procedure.

"One millimole of the sample is dissolved in 10 to "25 c.c. of water, dilute sulphuric acid or alcohol, "and a slight excess, 2 to 5 c.c., over the calculated "amount of 0.13N solution of bromide-bromate is added. "The solution is acidified with about 7 c.c. of 50% "sulphuric acid. This gives the pale yellow colour "of an excess of bromine, the odour of bromine and "usually a precipitate. A few drops of saturated "potassium iodide solution are added, thereby liber- "ating iodine/

"ating iodine which is titrated back with 0.1N sodium "thiosulphate solution, using starch as an indicator."

The time during which the bromination was allowed to proceed is not stated, but it is observed that one determination may be carried out in ten minutes; probably five minutes was the period allowed for the bromination.

Recently, an attempt has been made to evolve a uniform method of brominating quantitatively amines and phenols; a method, which would be suitable for the accurate determination of as many compounds as possible, and necessitate the fewest deviations in the case of individual compounds. To this end, Day and Taggart (17) carefully purified their materials and calibrated their weights and apparatus. The standard method given is as follows:-

"A quantity of the substance sufficient for ten "analyses is weighed out, dissolved in water, dilute "sodium hydroxide(for phenols and sulphonic acids), "or dilute hydrochloric acid (for amines), and the "solution diluted to 250 c.c. A 25 c.c. aliquot is "pipetted out into a 500 c.c. iodine flask, followed "by 25 c.c. of 0.2N "bromine" solution (75 gm. of "potassium bromide and 5.6 gm. of potassium bromate "per litre) and then diluted with 50 c.c. water. 5 "c.c. of concentrated hydrochloric acid are added and "the flask is stoppered at once. It is shaken for "one minute and then allowed to stand, with occasional "agitation, for a definite interval. (This varies from 5 to 30 minutes.)

"The flask is well cooled under the tap or in ice "water and 5 c.c. of 40% potassium iodide solution "are poured into the trough. The stopper is partly "dislodged, whereupon the iodide solution is drawn "into the flask with no loss of bromine. The flask "is thoroughly shaken, the stopper removed, and the "neck of the flask and stopper washed with water. "The free iodine, equivalent to the excess of bromine "taken, is titrated with 0.1N thiosulphate solution, "using 5 c.c. of 0.5% starch solution near the end "point of the titration."

A blank/

A blank determination was also carried out. A weight of sample was taken such that the 25 c.c. of "bromine" solution exceeded the theoretical amount by about 100%. The results obtained in the determination of the 25 compounds tabulated varied between 99.75 and 99.98 per cent.

In some cases, it was found that the method did not lead to accurate results. This could be traced either to oxidation as well as bromination, or to precipitation of partially brominated products. In the first circumstance, the difficulty could be got over, in some cases, by using Callan and Henderson's direct method (see below), but the authors have the objection that this method tends to be tedious, since a wait of 2 to 4 minutes is necessary for each drop in the vicinity of the end point. They only recommend it, in cases where the indirect method is inapplicable, due to oxidation. The second difficulty could be overcome by adding chloroform as a solvent. Previously, Francis had suggested (16) alcohol for this purpose, but this solvent reacts with bromine to a slight extent. Beta-naphthol, the only compound of the naphthalene series investigated, required the addition of chloroform (about 5 c.c.) as solvent, in order that the excess method should give accurate results. Certain compounds could not be analysed by the bromination method due to ease of oxidation.

DIRECT METHOD.

In the last decade of last century, Vaubel examined the bromination of many compounds of the aromatic (homo- and heterocyclic) series and he published his results in several German journals. He was primarily interested in the constitution of and rules of substitution in the benzene ring, but he realised that his method was also applicable to the quantitative estimation of many compounds. He subsequently collected his results and published them in book form (18). The method adopted was to add a sufficient quantity of potassium bromide and sulphuric acid to an aqueous solution of the substance, and to run in standard potassium bromate solution, until free bromine could be detected in the liquid, for example by starch-iodide paper. Callan and Henderson, in a paper on the use of potassium bromate in volumetric organic analysis (19), give practically Vaubel's method. Significant details are as follows:-

0.2-0.5 gm. of the sample is dissolved in a suitable solvent - water, dilute acid or alkali, glacial acetic acid - and the volume is made up to about 250 c.c.

"To the solution prepared as above, 10 c.c. of a "20% potassium bromide solution and 5 to 10 c.c. of "concentrated hydrochloric acid are added, the mixture "brought to the required temperature and N/5 potassium "bromate (5.567 gm. per litre) run in slowly, until a "drop withdrawn on a glass rod gives a reaction on "starch iodide paper persisting for 2 to 4 minutes "after the last addition of bromate solution. It is "important that the final test on starch-iodide paper "should not be made immediately after the addition of "bromate, although in the earlier part of the titration "this is immaterial."

The paper/

The paper contains particulars of the most suitable temperatures at which to carry out the titration of selected compounds. One of three ranges of temperature was found to be suitable, viz., 15^{o}- 20^{o}, 30^{o}-40^{o}, and 60^{o}-70^{o}.

The bromometric method has been used by Pamfilov and co-workers in the estimation of aniline, especially in small concentrations. Indigocarmine (indigo sulphonic acid) was used as internal indicator (20), owing to difficulties encountered with starch-iodide paper as external indicator. This indicator had been previously used by Francois (21) in the estimation of aniline. (Methyl orange can be used in the same way. Both these substances are bleached by bromine.) It was found that the indicator was quite suitable, if bromine water were used in neutral or slightly acid solution, but that as the acidity was increased, the indicator brominated more readily than the aniline near the end point, so that further additions of indicator became necessary. In this instance, no indications are given of the bromide-bromate mixture used nor the amount of acid employed.

APPLICATION of POTENTIOMETRIC METHOD to DIRECT METHOD.

Later, Pamfilov and Kisselva (22) showed that the bromometric method could be adapted for potentiometric determination: the potential of a platinum wire immersed in the aniline solution was measured. As long as/

As long as the solution was free from bromine (i.e. as long as the aniline was absorbing bromine), the potential remained steady or showed a gradual rise, but, as soon as the solution contained the least excess of free bromine, the potential rose suddenly and further additions of bromine or brominating solution caused little or no further change from this higher value. This method was regarded as the better, since the least excess of bromine could be detected. It was noticed that neutral bromine water caused the greatest rise in potential and that the rise decreased somewhat on increase of acidity. As in the other paper, the directions are not too definite. The solution was allowed to stir for one minute after the addition of a fresh portion of brominating solution before determining the potential of the electrode. The volume of solution to be brominated was about 50 c.c.

Lately, Callan and Horrobin (23) have substituted the potentiometric method for the determination of the end point in the method previously elaborated by Callan and Henderson (19). This paper will be referred to later.

QUANTITATIVE BROMINATION of NAPHTHOL SULPHONIC ACIDS.

The quantitative bromination of naphthol and naphthylamine sulphonic acids was first investigated by Vaubel (24). The method is summarised in Lunge and Keane's "Technical Methods" (25) as follows:-

"In performing the estimation, an aqueous solution "of a weighed quantity of the impure sulphonic acid "is treated with potassium bromide and a sufficient "amount of sulphuric acid, and standard potassium "bromate is run in until a persistent excess of brom- "ine is observed. The operation is performed at "ordinary temperature. With regard to their capacity "for absorbing bromine, the sulphonic acids can be "arranged in three classes:-

"1. Those which absorb at the most only one atom of "bromine and give a sharp end point.
"2. Those which absorb more than one atom of bromine "and give an indistinct end point in consequence "of the slower absorption of the second and the "third atoms of bromine.
"3. Those which absorb little or no bromine under "the conditions mentioned above."

Of the acids under consideration in the present investigation, Schäffer and R belong to the first class, while Crocein and G belong to the third. It is further stated:-

"The last acids, the 2:8- and the 2:6:8- derivatives, "absorb bromine at a higher temperature, and the "property can be employed for their estimation. At "65°-75° they readily absorb one atom of bromine, and "any volatilisation of the halogen is so inconsider- "able as not to affect the estimation. The temper- "ature must not be allowed to fall much below 65°, "since it is then difficult to detect the end point.

"Mixtures of these acids and the corresponding 2:6- "or 2:3:6- derivatives cannot, however, be estimated "by first determining the Schäffer acid and the R acid "at ordinary temperatures, and then warming and "estimating the 2:8- and the 2:6:8- acids, because the "presence of the Crocein or the G acid renders it "difficult to detect the end point at the conclusion "of the first reaction.

"Such mixtures can be estimated, however, by deter- "mining the total sulphonic acid by bromination and "then estimating the R acid or the Schäffer acid by "coupling with diazo compounds....."

The only other paper in which this method of estimating beta-naphthol sulphonic acids is specifically mentioned is that of Callan and Henderson (19). The significant paragraphs are:-

"In the naphthalene series, the method is of considerable value in the cases of isomers; thus, for example, R salt absorbs bromine quantitatively at room temperature, while the isomeric G salt at this temperature does not brominate at all.

. . . . .

"Schäffer's acid brominates at room temperature taking up one bromine atom in position 1, while Crocein does not brominate under these conditions."

These two statements seem to contradict the statement of Vaubel, that such mixtures cannot be estimated in this way. It is significant that Vaubel used sulphuric acid and Callan and Henderson hydrochloric acid.

BROMINATION of BETA-NAPHTHOL SULPHONIC ACIDS.

Very little work on the separation of the products of the action of bromine on beta-naphthol sulphonic acids has been reported; there follows a summary of the work which has been published.

Armstrong and Graham (26) investigated the action of bromine on Schäffer acid fairly thoroughly. When 1 mol of the potassium salt was treated with 1 mol bromine (as bromine water), the sparingly soluble monobromo derivative was precipitated in crystalline form. The corresponding calcium salt was prepared in the same way. With twice the quantity of bromine, a dibromsulphonate was obtained; this was more soluble. Three molecules of bromine and one of the potassium salt did not lead to the production of a tribromo derivative, but to a mixture of the compounds obtained by the action of 2 mols and 4 mols respectively. Using an acetic acid solution of the potassium salt, Armstrong and Graham allowed 4 mols of bromine to act on 1 mol of the potassium salt of Schäffer acid. After the evaporation of the solvent, the residue was taken up with boiling water; a blood red solution resulted, from which dark yellow plates, having the formula $C_{10}H_4BrSO_6K$, crystallised out. This compound was formulated as potassium bromoxynaphthaquinone sulphonate. This salt could not be brominated further at 100° in aqueous solution.

In the concluding paragraph of this section of the paper/

the paper, the authors state that they prepared the barium salts of Griess's beta-naphthol disulphonic acids (R and G acids) and treated them with bromine. The results are tersely stated:-

"In the first instance, they yield monobromderiva-
"tives, but, apparently, they yield ultimately the same product as Schäffer's acid."

Smith (27), in a paper on steric hindrance in the naphthalene series, gave a method of preparing the monobromo derivative of Crocein acid. A saturated solution of the sodium salt was treated with an equimolecular quantity of bromine. Heat was evolved and the solution took on a green colour, which changed to a reddish brown. The precipitated bromo compound was recrystallised from water, giving white leaflets, which turned brown on exposure to air. The compound did not couple with p-toluenediazonium chloride, whereas the corresponding compound of Schäffer acid coupled to give a compound free from bromine.

While the present research was in progress, there appeared a paper on the bromination of certain alpha- and beta-naphthol sulphonic acids (28). The main portion of the paper relates to the bromination of the former. The beta-naphthol sulphonic acids investigated were Schäffer, R, G and 2-naphthol-3:6:7-trisulphonic acids. By the action of 1 mol of bromine in glacial acetic acid solution on 1 mol of the sodium salt of Schäffer acid, the sodium salt of 1-brom-2-naphthol-6-sulphonic acid was obtained; 2 mols of bromine led/

bromine led to the formation of a dibromo compound, the orientation of which is not given. A larger proportion of bromine had no further effect. These authors were unable to obtain a quinone (cf. Armstrong and Graham); they put forward the suggestion that the beta-naphthol used by the latter might have contained alpha-naphthol, the sulphonic acids of which are known to yield quinones readily by oxidation with bromine. The two compounds mentioned above were isolated and analysed quantitatively for bromine and sodium. The action of bromine on R and G acids is dismissed in few words:-

"A mono- and a dibromsubstitution derivative were "obtained from the sodium salt of 2-naphthol-3:6-di- "sulphonic acid and these are little characteristic.

"The sodium salt of 2-naphthol-6:8-disulphonic acid "yielded, with excess bromine, an easily soluble "derivative, which, on analysis, is a sodium salt of "a tribrom-2-naphtholmonosulphonic acid."

POTENTIOMETRIC TITRATIONS.

INTRODUCTION.

As much of the work described in this paper took the form of potentiometric titrations, some considerations of this method will not be out of place.

Electrometric titrations are of two kinds,

(1) conductometric, in which the conductivity of of the solution being titrated is measured after each addition of the titrating solution, and

(2) potentiometric, in which the potential of a suitable electrode immersed in the solution is measured after each addition of the titrating solution.

Both these methods have the advantage that they depend on the reading of electrical measuring instruments, such as galvanometers and voltmeters, and not on the colour change of indicators, where the end point is dependent on the personal factor and is often masked by turbidity or colour in the solution, bad light and so on. In fact, one of the advantages of electrometric titrations is that they enable one to carry out determinations with coloured or dirty solutions, which previously were impossible due to the presence of colour. In addition, they make possible the utilisation of reactions in volumetric analysis, for which a coloured indicator could not readily be found.

The end point of a titration can be easily found by plotting the conductivity or potential measured against the/

against the corresponding total volume added. Conductivity titrations yield graphs of the form given in figure 1, the end point being the volume corresponding to the minimum conductivity; figure 2 shows the type of graph obtained in potentiometric titrations, the end point being taken as the point of inflexion on the curve, that is the point where the change of potential with repect to the increment of reagent added is a maximum.

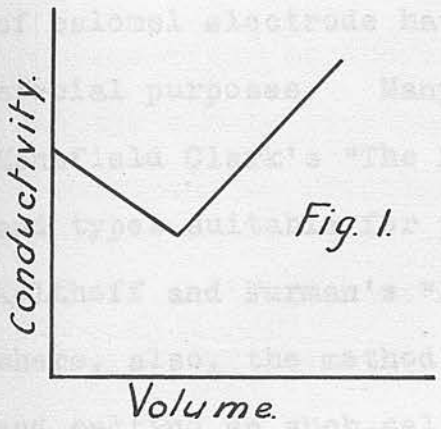


Fig. 1.

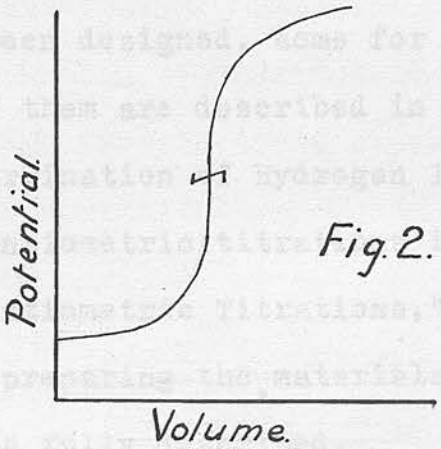


Fig. 2.

The potentiometric method was used in all the electrometric titrations described in this paper.

METHODS of MEASURING the POTENTIAL.

According to the theory of electromotive force, the potential of a metal electrode dipping into a solution depends on the concentration of ions of that metal in the solution. It is found that inert electrodes, such as a platinum wire, when placed in solutions take up a definite potential with respect to the solution; this is possibly due to their acting as air or oxygen electrodes. Now, if this potential difference between/

difference between the electrode and the solution is to be measured, electrical connection must be made to the solution. No metal, so far as is known, has the same potential as the solution in which it is immersed; hence some device, having a constant reproducible potential must be called into use. This usually takes the form of the ordinary calomel half-cell; connection between the latter and the solution is made by a salt bridge. Many forms and variations of calomel electrode have been designed, some for special purposes. Many of them are described in Mansfield Clark's "The Determination of Hydrogen Ions" and types suitable for potentiometric titrations in Kolthoff and Furman's "Potentiometric Titrations," where, also, the method of preparing the materials and setting up such cells is fully described.

In carrying out a titration, the potential difference between the mercury in the calomel half-cell and the platinum wire in the solution being titrated is measured after each addition of reagent. Since the potential of the calomel cell is constant, any change in the potential difference noticed is due to a change in potential of the indicator electrode (platinum wire). This potential difference cannot be measured by a voltmeter, even of high resistance, since such an instrument is a current operated device, and the chemical action at the electrodes producing this current would be sufficiently great to destroy the equilibrium/

the equilibrium; polarisation would take place, with the result that a true value of the potential difference would not be obtained. Hence some form of compensation method must be adopted.

An electrostatic voltmeter can be used since it requires no current to operate it. For accurate work, a potentiometer is used; the method of using this instrument is fully described in Kolthoff and Furman's "Potentiometric Titrations." Descriptions are also given of the construction of instruments from the simple stretched wire form to those capable of measuring to fractions of a millivolt.

For ordinary purposes, the circuit can be simplified by using the Hildebrand modification. This was adapted by Hildebrand (29) from a circuit used for the separation of metals electrolytically (30). The circuit diagram is given in figure 3. The main

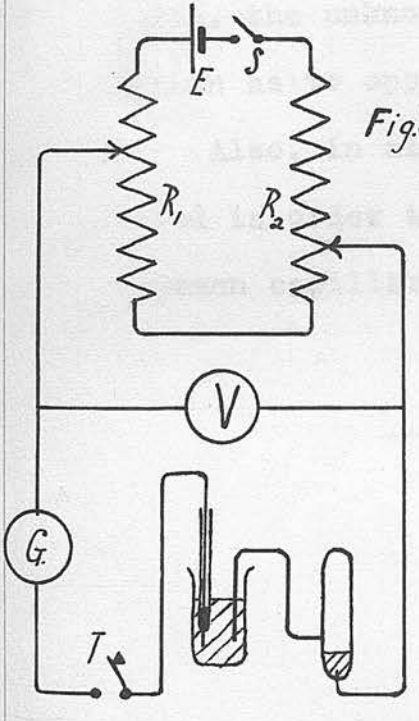


Fig.3.

circuit contains two variable resistances, R_1 having a high value and R_2 a low value, in series with a switch, S, and a dry cell, E. The shunt circuit is connected across the sliding contacts of the rheostats, and consists of the cell, the e.m.f. of which is to be measured, in series with a galvanometer, G, and a tapping key, T. A

voltmeter is permanently/

voltmeter, V, is permanently connected across the contacts of the rheostats; an instrument reading to 0.002 volt is suitable.

The method of operation is as follows. The switch, S, is closed, and current flows through R_1 and R_2, the voltmeter, V, indicating the potential drop across the contacts of the rheostats. The sliding contacts are altered, until, on depressing the tapping key, T, no current flows in the galvanometer, G. (R_1 provides a coarse adjustment and R_2 a fine adjustment.) Then the voltage is read off on the voltmeter, V; this is the e.m.f. of the cell in the shunt circuit. As in the case of measurement with a potentiometer, no current is taken from the cell when the circuit is balanced, the current actuating the voltmeter being derived from the cell, E.

It should be noted that, in all potentiometric circuits, the unknown cell is connected in such a direction as to oppose the current in the shunt circuit. Also, in all circuits where a galvanometer is included in order to indicate the presence of current, a Lippmann capillary electrometer may be used in its place.

APPLICATION of the THERMIONIC VALVE to POTENTIOMETRIC TITRATIONS.

As has been indicated above, it is essential to employ a method in the use of which no current is taken from the "unknown" cell, i.e. the cell formed by the indicator electrode, the solution being titrated and the calomel half-cell. Such a condition obtains in the case of the grid-bias battery of a thermionic valve, when no grid current is flowing. The anode current is a function of the potential of the grid with respect to the filament, and, if the valve is operating on the straight portion of its grid-anode current characteristic, the anode current is proportional to the potential of the grid. If a cell, the e.m.f. of which changes, is inserted as a grid bias cell and the grid is, in addition, sufficiently biassed negatively to prevent the flow of grid current, the changes in voltage of the cell can be noticed by the changes in the anode current. Now, since it is only the change in potential that is important in potentiometric titrations, the change in anode current can be taken as a measure of the change of potential of the indicator electrode. Since the total change in anode current is usually only a fraction of a milliampere in such cases, and there is a steady current of the order of 2 to 4 milliamperes, it is usual to employ a microammeter and to arrange that the initial steady current in it is balanced out by a similar current in the opposite direction. In such an/

such an arrangement, changes of anode current only are measured.

The method was first described by Goode (31) in 1922; the circuit diagram is given on the opposite page. The method has been used frequently since then, sometimes with small alterations (32).

In some cases, when the grid potential-anode current characteristic is not absolutely linear, it is necessary to calibrate the arrangement. This method of following titrations potentiometrically, which is an adaptation of the well known Moullin voltmeter, has the advantage over those described, that it requires no adjustments during the titration. Suitable increments of the reagent are simply added and the microammeter read off after the elapse of a selected interval.

The valve may be used in a totally different manner, viz., as a sensitive galvanometer requiring no current from the "unknown cell" for its operation (33). The plate current, indicated on a suitable milliammeter, is adjusted to a suitable value by altering the potential of the grid with the usual "potentiometer" device across the filament battery. The unknown cell is switched into the grid circuit and the anode current falls. By means of a battery and variable resistance, the e.m.f. of the "unknown cell" can be counterbalanced and the anode current brought up to/

brought up to its original value. A voltmeter in the grid circuit then reads the e.m.f. of the cell. This arrangement requires one adjustment for each reading and is independent of the characteristics of the valve, the anode potential and the filament current, provided these remain constant over the period during which the titrations are being carried out. This method possess the anomaly that a sensitive instrument, the thermionic valve, is made subservient to a less sensitive instrument, the voltmeter; but the method has the advantage that no current is taken from the "unknown cell" during the adjustment of the circuit.

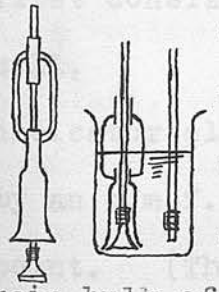
DIFFERENTIAL POTENTIOMETRIC TITRATION.

It was stated previously that the end point of a titration is taken as the point of inflexion of the potential - volume curve, i.e. the point where $\Delta E/\Delta$c.c. is a maximum. Hostetter and Roberts showed (34) that if the value of $\Delta E/\Delta$c.c. (change of potential per c.c. at the point considered), for each addition of reagent in the vicinity of the end point, is plotted against the total volume added, a curve in the form of a cusp is obtained, and the point of the cusp corresponds to the end point.

Arrangements have been devised for measuring the value of ΔE directly. The first was described by Cox (35). The solution to be titrated was divided equally into/

equally into two parts, which were placed in separate beakers provided with similar indicator electrodes (platinum wires); electrical connection between the two beakers was made by a moist strip of filter paper. The titrating agent was added from two burettes, one for each beaker, and the addition was so regulated that there was a constant difference (0.02 c.c.) between the readings on the burettes. After each addition, the potential between the electrodes was measured by means of a potentiometer, since the e.m.f. produced was very small, being in fact the e.m.f. of a concentration cell. The point where the potential difference was greatest was taken as the end point. The practical difficulty of this method is the keeping of a constant difference between the readings of the two burettes.

The method was much improved by MacInnes and Jones (36). By means of a special piece of apparatus,



a sketch of which is given, a small quantity of the solution being titrated was isolated round a platinum gauze electrode, another platinum electrode being in the main bulk of the solution. Only one burette was necessary. The potential difference between the electrodes was measured after each addition of reagent, and then the entrapped liquid was allowed to mix with the remainder of the solution and a new portion confined. In this way, the error introduced by confining a portion/

ing a portion is extremely small. The authors state that, for many practical titrations, the use of a potentiometer may be dispensed with, the electrodes being simply connected to a galvanometer. There was no deflexion (current) until the region of the end point was reached; the largest deflexion indicating the end point.

SIMPLIFIED METHODS.

In addition to the straightforward methods outlined above, a number of simplifications have been described from time to time; these have been designed to avoid the use of either the calomel half-cell or the potentiometer or both. A full bibliography is included in a recent paper(37) on still another simple reference electrode.

Only two such methods will be described. The first consists in opposing the e.m.f. produced by the cell,

indicator electrode/soln. being titrated/ref. electrode,

by an e.m.f. equal to that of the cell at the end point. (This e.m.f. can be calculated or found by direct measurement.) A galvanometer or capillary electrometer connected in circuit indicates the end point by a reversal of polarity; a tapping key is also provided.

The second method is a variation of the first. The solution/

The solution to be titrated is connected by a salt bridge to a solution duplicating the conditions at the end point; similar indicator electrodes are placed in each solution. At the end point, the potentials of the two half-cells just balance and on completing the circuit through a tapping key and galvanometer, capillary electrometer or sensitive voltmeter, no deflexion is shown. The advantage of these two methods is that a potentiometer is dispensed with; but the chief disadvantage is that each titration reaction requires a different counter e.m.f. or end point half-cell.

Callan and Horrobin (38) in their paper on the application of potentiometric methods to technical make extensive use of the second method. In bromide-bromate titrations, the "end point solution" was prepared by adding a drop of N/5 potassium bromate to an acid solution of potassium bromide. They found this suitable in the titration of certain compounds detailed, but unsuitable, for reasons given in the paper, in the titration of R salt, the only compound of the naphthalene series mentioned.

These simplified methods can only be applied after the straightforward potentiometric method (or its Hildebrand modification) has been studied, when any peculiarity of the titration is noticed. The requirement for the possibility of utilising a simplified method is that the end point always corresponds to the same potential of the indicator electrode.

OUTLINE of EXPERIMENTAL WORK and CONCLUSIONS.

After pure specimens of the salts of the sulphonic acids had been obtained, the accurate estimation of them was tried by titration with a bromide-bromate solution. First of all, Schäffer salt and G salt were titrated, using Callan and Henderson's method (liberating the bromine with hydrochloric acid). Schäffer salt titrated well at ordinary temperature, the reaction proceeding rapidly and a good end point being given. The G salt on the other hand, when titrated by the same method, except that a temperature of 65°-70° was used (as recommended by Vaubel), led to indefinite results; the "spotting" on starch iodide paper being irregular.

At this juncture, the abstract of Pamfilov and Kisselva's paper on the titration of aniline potentiometrically appeared in "Chemical Abstracts." There seemed to be no fundamental reason why this method could not be applied to the titration of beta-naphthol sulphonic acids and so eliminate the difficulties involved in the use of starch iodide paper as indicator. The first titrations tried were encouraging and it was therefore decided to experiment further. Two changes were made in the procedure at this point. The volume of the solution to be titrated was reduced to 50 c.c. (the volume used by Pamfilov and Kisselva) and potassium bromide was dissolved in the same solution as the potassium bromate. With these alterations, a series of titrations/

was carried out. The experiments showed that (a) Schäffer salt gave a good curve at ordinary temperatures, i.e. one showing a large potential jump at the end point and (b) R salt also gave quite a good curve at ordinary temperature, but the most satisfactory result was obtained at 35°. In the case of G salt, variable results, depending on the temperature used, were obtained; but it seemed that 50° was sufficiently elevated and 65°-70° too high. When mixtures of Schäffer and G salts, and R and G salts were brominated at ordinary temperature, no rise in potential corresponding to the Schäffer or R salt content was obtained, but a jump was obtained corresponding to the total sulphonate content, when the temperature was raised to 65°-70°.

A return to the starch iodide paper method of detecting the end point was made, and the results confirmed those obtained by the potentiometric method. G salt interfered with the recognition of the end point corresponding to the Schäffer or R salt content of mixtures, although it itself did not seem to brominate at ordinary temperature. G salt alone, however, brominated quite well at 45°-50°, and the end point was easily detected at that temperature. The Schäffer-G and R-G "totals" at 45°-50° were, however, rather indefinite.

These observations suggested that it was something other than the indicators that was giving rise to the difficulties,/

difficulties, and, in consequence, experiments were tried, to find out if the acid liberating the bromine had some effect on the bromination of the sulphonic acids. Accordingly, sulphuric acid was substituted for the hydrochloric acid used hitherto, and this proved to be the solution of the problem of being able to titrate Schäffer or/and R salt in presence of Crocein or/and G salt, for it was found that a high concentration of sulphuric acid prevented the bromination of Crocein and G salts. A few experimental titrations with starch iodide paper as indicator proved this.

In order to discover the effect of concentration of sulphuric acid on the rate of bromination of the Schäffer salt in a Schäffer-G salt mixture, such a mixture was titrated at ordinary temperatures at four acid concentrations, viz., 10N, 6N, 4N and 2N, using starch iodide paper to detect the end point. It was found that in 2N acid solution, the bromination was decidedly slow; 4N, the reaction was rather slow at the end point; 6N and 10N, the bromination proceeded rapidly, giving a sharp end point. It was therefore decided to use 6N sulphuric acid in all titrations in which Schäffer or R salt was to be estimated.

Potentiometric titration of Schäffer and R salts alone in 6N sulphuric acid solution gave the same results as titration with starch iodide paper as indicator. When mixtures of each of these two salts with G salt/

with G salt were titrated under the same conditions, a definite potential rise corresponding to the Schäffer or R salt content appeared. In attempting to determine the Schäffer salt content in a Schäffer-Crocein salt mixture with a 6N acid concentration, a curve of the "flat" type was obtained, but, on increasing the concentration to 10N, a curve with a vertical portion resulted.

This last observation suggested that a complete investigation of the effect of acid concentration on the type of curve obtained in titrating single salts and mixtures was necessary and a large number of titrations were carried out with this purpose in view. From the curves obtained, it was concluded that, provided that R salt and Crocein salt were not present in the same mixture, a sulphuric acid concentration of 10N was necessary to cover all possibilities. If pure R or Schäffer salt were to be estimated quantitatively alone, then the acid concentration need not be above about 4N. Mixtures of R and Crocein salts provided a difficulty. After many trials, it was discovered, that, if the titration were carried out at 40° in 10N sulphuric acid solution, a definite rise was obtained corresponding to the R salt content, although the curve, being of the "flat" type, left something to be desired. Later, it was discovered that the addition of potassium bromide to the solution (i.e. increasing the bromide concentration) before titrating with/

titrating with the bromide-bromate solution, led to an improvement in the graph. The sulphuric acid concentration had still to be maintained at 10N and the temperature was preferably kept between 20° and 30°. The titration of other mixtures was not affected by these new conditions.

Finally, potassium bromide was added to the 10N sulphuric acid solution of the sulphonates, which was then titrated with a standard solution containing potassium bromate alone. By employing this method, Schäffer or/and R salt could be estimated in the presence of Crocein or/and G salt with an accuracy of 1 per cent.

Turning now to "totals", it was discovered that G salt and mixtures of it with Schäffer or/and R salt could be determined in hydrochloric acid solution potentiometrically, if the temperature were about 50°. A study of the effect of acidity on such titrations showed that the best conditions for estimating quantitatively mixtures of Schäffer or/and R salt and G salt were 50° and 0.91N hydrochloric acid solution; but, for mixtures of Schäffer or/and R salt with Crocein salt, a temperature of 40° and 1.67N hydrochloric acid concentration were required. The two methods could not be combined since Crocein salt dibrominates slowly at temperatures above 40°, and G salt brominates slowly at 40°. It seems that a fundamentally different method is required to carry out titrations of mixtures/

of mixtures containing G and Crocein salts together.

The above short summary of the work done and conclusions arrived at has been given in order that the description of the experimental work may be more intelligible, since it is mainly a catalogue of graphs of potentiometric titrations carried out under varying conditions.

EXPERIMENTAL.

PREPARATION of PURE SPECIMENS of the SALTS of the SULPHONIC ACIDS.

PREPARATION of SCHAFFER and CROCEIN ACIDS.

The proportions used were those given in G.P. 33,857; the quantities, 0.5 lb. of sublimed beta-naphthol to 1 lb. concentrated (96%) sulphuric acid. The method consisted in adding small portions of the naphthol to the acid in the cold with constant stirring and keeping the mixture at room temperature for some days. Now since 1 mol beta-naphthol requires only 1 mol sulphuric acid for complete monosulphonation, it was thought that the use of these proportions would reduce the possibility of disulphonation; but when the experiment was tried, it was found that, before the necessary amount of beta-naphthol had been added, the mass became very thick and impossible to stir. On adding sufficient acid to bring the proportions up to 2 mols acid to one of naphthol, the rest of the naphthol could be added but the mass became stiff and could not be stirred. Finally, the remainder of the 1 lb. of acid was added and the mixture was stirred to obtain a homogeneous mass. In a few hours time, the mass had set hard; but after standing for 4 days at room temperature, it became sufficiently fluid to be stirred. After 10 days, the sulphonation mass was poured into water and limed out in the usual way. The mixed calcium salts were extracted by boiling water from/

water from the calcium sulphate and converted to the corresponding sodium salts by double decomposition with sodium carbonate. On concentrating the solution containing the sodium salts, the monosodium salt of Schäffer acid crystallised out first; after filtering off this first crop of crystals, the filtrate was further evaporated and a second crop was obtained. These two crops of crystals were kept separate and recrystallised four times. The filtrate was evaporated to dryness; the residue consisted of Crocein salt containing a quantity of Schäffer salt. A purification was attempted by boiling up the dry residue with 96% alcohol, in which Schäffer salt is much less soluble than Crocein salt. The undissolved solid was filtered off and the filtrate allowed to cool. It was found that the solubility was not very great and that no separation of solid took place on cooling. Crystals were only obtained after concentrating the alcoholic solution to about one quarter of its volume. The solid gave with concentrated nitric acid the red colour characteristic of Schäffer acid, proving that the separation had not been complete.

Claus and Volz (39) had prepared a disodium salt of Crocein acid, which they stated was soluble in alcohol and was obtained in the form of deliquescent crystals. Following up this observation, the partially purified salt was boiled up with 96% alcohol, to which had been added flake sodium hydroxide. The hot liquid/

hot liquid was filtered at the pump and allowed to cool; crystals separated, which gave a deep yellow colour with concentrated nitric acid, showing that little, if any, Schäffer salt was present; the salt was again crystallised from alcohol. The crystals were very deliquescent and, for this reason, were kept in a vacuum desiccator containing calcium chloride.

PREPARATION of SCHAFFER and R ACIDS.

A mixture of Schäffer and R acids was prepared by the method given in Fierz-David's "Dye Chemistry." 0.5 lb. sublimed beta-naphthol was added to 0.696 lb. of 100% sulphuric acid with constant stirring; (these quantities are in the proportions of 1 mol naphthol to 2 mols sulphuric acid). The mass was heated to 100° and kept at that temperature for 3 hours. After the elapse of this interval, the mass was diluted, limed out and the acids converted to the sodium salts in the usual way. The solution of the sodium salts was concentrated and allowed to crystallise. A crop of crystals of Schäffer salt was obtained and the filtrate further concentrated, when a second crop came down. Salt was then added in sufficient quantity to make a 10% solution and a third crop appeared. Each crop was separately recrystallised four times. The final filtrate was acidified and the acid sodium salt of R acid precipitated out but this was not worked up further.

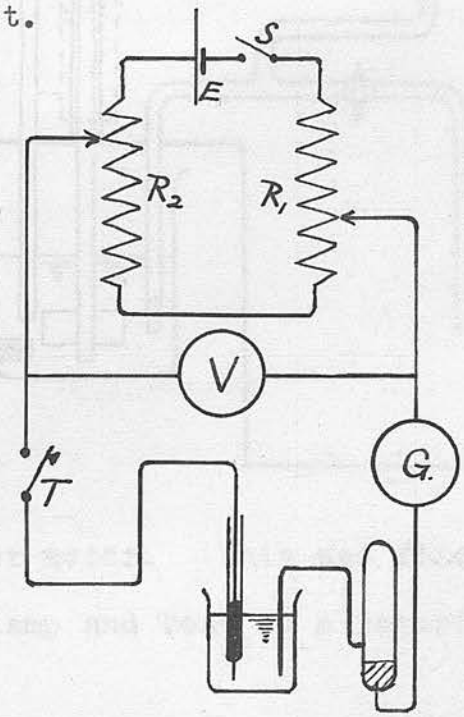
PREPARATION of R and G ACIDS.

In accordance with G.P. 36,491, 0.5 lb. sublimed beta-naphthol was added in small quantities to 2 lb. 100% sulphuric acid, the mixture being well stirred and kept cool during the addition; the quantities used were in the proportion of 1 mol naphthol to 6 mols acid. After all the solid had been added, the mixture was heated to 60°, and kept at this temperature for 36 hours with continual stirring. The mass was then diluted, limed out and the mixed sodium salts prepared in the usual way. Both the sodium salts are very soluble, but the R salt is the less soluble and so separated out first. Two crops were obtained and were recrystallised four times. On adding potassium chloride to the filtrate, the sparingly soluble potassium salt of G acid separated and was recrystallised four times. Difficulty was found in purifying the R salt due to its fairly large solubility.

Of the salts prepared, Schäffer, Crocein and G salts were found, by experiment, to be pure, whereas the R salt was found to contain some G salt. An R salt and a G salt, supplied by the B.D.H., which were found to be pure specimens, were used in all titrations of R and G salts. The G salt of the B.D.H. was used in preference to the potassium salt owing to its greater solubility.

APPARATUS USED in POTENTIOMETRIC TITRATIONS.

Before describing the experiments proper, a description of the apparatus used and the routine adopted in carrying out the potentiometric titrations will be given. The Hildebrand modification was employed, the circuit diagram of which is repeated below. The actual components used are given in the accompanying list.



(1) Electrical Circuit.

E - Siemens' dry cell, T type,

S - 5 amp. tumbler switch,

R_1 - Ostwald resistance box, permanent connections being made at 0 and 100 ohm pins (tappings variable in steps of 10 ohms),

R_2 - Zenith variable resistance, 18 ohms (infinitely variable),

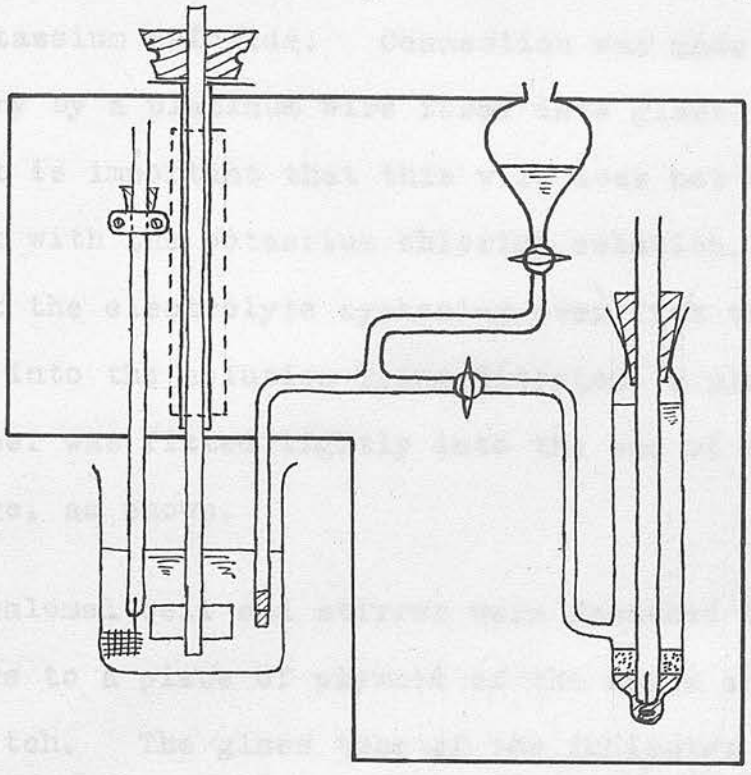
V - Weston voltmeter, reading up to 1.2 volts, 0.02v. divisions readable to 0.002v.,

G - Paul unipivot galvanometer,

T - Simple tapping key.

(2) Titration Stand.

A sketch of this piece of apparatus is given below. The stand was made up of four distinct parts:-



(a) Small water motor. This was fixed, in the usual way, by clamp and boss to a retort stand with a heavy base.

(b) Stirrer. Small glass paddles were fused on at one end of a length of glass rod; this was supported in the usual way by a length of glass tube of bore just greater than the diameter of the rod. A piece of sheet aluminium acted as bearing and a large cork provided with a groove as pulley.

(c) Indicator electrode. A piece of platinum gauze about 1 cm. square was welded to a platinum wire fused into a length of glass tube, connection being made by a copper wire and a small quantity of mercury in the usual way. In some of the earlier experiments, a platinum/

a platinum wire served as indicator electrode.

(d) Calomel Cell. Calomel prepared electrolytically was used, the electrolyte in the cell being normal potassium chloride. Connection was made to the mercury by a platinum wire fused into glass tubing. (It is important that this wire does not come in contact with the potassium chloride solution.) To prevent the electrolyte syphoning over from the half-cell into the solution being titrated, a plug of filter paper was fitted tightly into the end of the salt bridge, as shown.

The calomel cell and stirrer were fastened by copper wire to a piece of plywood of the shape shown in the sketch. The glass tube of the indicator electrode fitted tightly into a hole bored in a cork fastened to the board. Immediately behind the stirrer, in the position indicated by the dotted lines, in the sketch, was screwed to the back of the board a length of wood about 1 inch square, which served as a means of fixing, by clamp and boss, the whole to the retort stand to which the water motor was fixed. By arranging, in this way, that the stirrer and water motor were fixed to the same stand, vibration, such as takes place when they are mounted on separate stands, was eliminated.

A 100 c.c. Pyrex beaker was found to be a suitable vessel, in which to carry out the titration.

ROUTINE ADOPTED in POTENTIOMETRIC TITRATIONS.

Accurately weighed quantities of the salts were dissolved in standard flasks of 250 c.c. or 500 c.c. capacity; the concentrations were so chosen that 25 c.c. of the solution required about 10 c.c. of the bromide-bromate solution for titration. It was found preferable to make up these small quantities of solution as required, since it was noticed early in the investigation that the titre of an R salt solution changed on standing.

For the titration of a single salt, 25 c.c. of the solution and 25 c.c. of water were placed in a 100 c.c. Pyrex beaker and then the requisite quantity of acid added; in the case of mixtures of two salts, 25 c.c. of each of the corresponding solutions were placed in the beaker and the acid added. For mixtures of three salts, equal quantities of the solutions of two of them were mixed and 25 c.c. of the resulting solution used along with 25 c.c. of the remaining salt solution; in the case of mixtures of all four salts, two such mixed solutions were made up and 25 c.c. of each used. Except in one series of experiments, the Schäffer or/and R salt content of a mixture was approximately equal to the Grocein or/and G salt content (expressed in molecular quantities). The total volume before adding acid was always 50 c.c.

To save endless repetition, the following table is given/

is given to show the acidity of the solution after adding acid to 50 c.c. of the sulphonate solution. The values express, therefore, the acidity of the solution prior to titration and are calculated on the assumption that concentrated hydrochloric acid is 10N and concentrated sulphuric acid is 36N. The values are, of course, only approximate, since the acid was measured in all cases in a 25 c.c. graduated cylinder.

Hydrochloric Acid		Sulphuric Acid	
Volume	Acidity	Volume	Acidity
20 c.c.	2.86 N	25 c.c.	12 N
		20 c.c.	10 N
10 c.c.	1.67 N	15 c.c.	8 N
		10 c.c.	6 N
5 c.c.	0.91 N	6 c.c.	4 N
		3 c.c.	2 N

On adding the concentrated sulphuric acid to the solution, heat was evolved, so that it was necessary to cool the acid solution in many cases before commencing a titration.

When the titration was carried out at a temperature other than room temperature, a nichrome wire resistance mat, working off 230v. A.C. was employed as the source of heat. The mat was placed on a piece of asbestos tile and was covered with asbestos paper, on which stood the beaker. This arrangement provided a convenient means of heating, since, when the temperature had reached the required value, the current was switched off and when the temperature had fallen slightly/

fallen slightly, the current was switched on again. In this way, the temperature could be maintained at a predetermined value with a maximum variation of $\pm 2^{\circ}$. A thermometer in the solution recorded the temperature.

The routine method of carrying out a titration proper may be shortly described as follows. The beaker containing the acidified solution was raised to make contact with the calomel cell via the salt bridge, and the position of the indicator adjusted until it was completely covered by solution. The stirrer was started and, if necessary, the solution was heated to the requisite temperature. After stirring for a short time, the potential of the indicator electrode relative to the calomel cell was determined by the method already described (p.32). The bromide-bromate solution was then added slowly as a series of drops; usually about 5 c.c. were added as the first increment, then 3 c.c., 1 c.c. and so on, gradually diminishing in volume, until in the near region of the end point increments of one or of two drops were added. After the addition of each increment, the solution was allowed to stir for <u>one</u> minute (the interval recommended by Pamfilov and Kisselva), before taking a reading. The table given below will give an idea of the amounts added at the various stages of the titrations. The titration was stopped when the potential approached constancy after the rise of potential/

rise of potential. In certain titrations the solution was stirred after the completion of the reaction, to see if the potential fell with time; these will be noticed in their proper place.

The curve showing the variation of potential with volume of bromide-bromate solution added was drawn for each titration, since such a curve gives more information than a table of readings; hence, curves are given in this paper in preference to tables of readings. The curve for the whole titration need not be drawn, since one is only interested in the rise of potential which indicates the completion of the reaction and the appearance of excess of the titrating agent; hence, that portion of the curve in the region of the end point is given in each case.

Each titration proper required from one half to three quarters of an hour for its completion. The greater part of the time was consumed in obtaining readings in the region of the end point; a titration yielding a sloping portion required a longer time, since a larger number of increments had to be added before a constant potential was reached. For example (see next page for readings and graphs), in the titration of Schäffer salt at 6N sulphuric acid concentration, only three increments were required after the large jump in potential, i.e. an interval of 5 minutes at the most, whereas, in the titration of Schäffer salt in presence of Crocein salt at the same acid concentration, about/

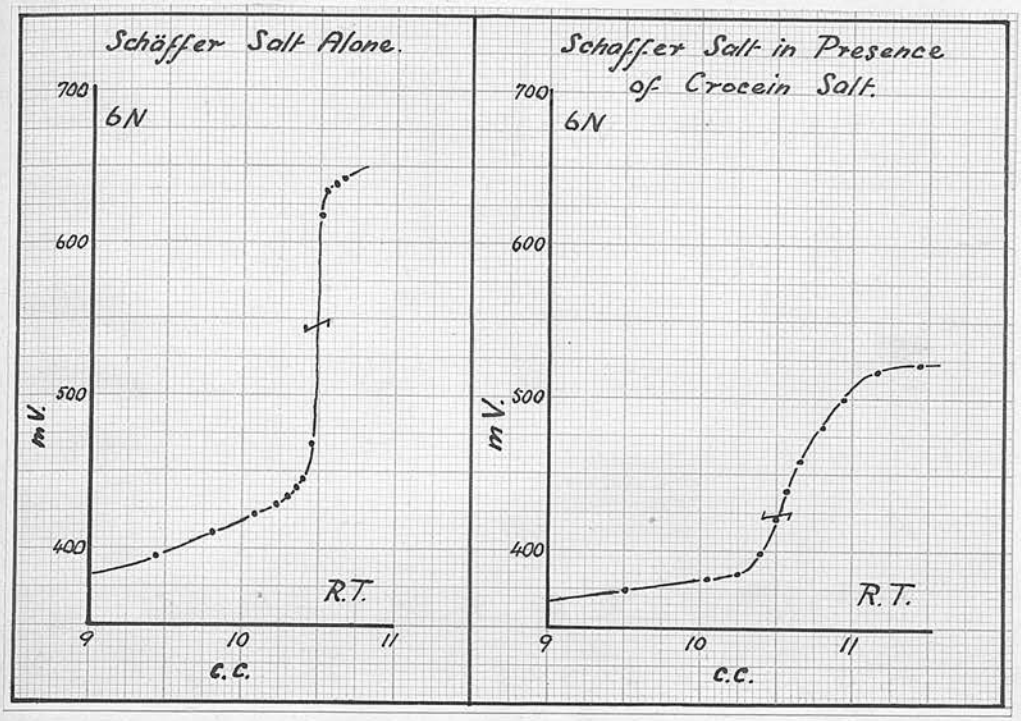
concentration, about eight increments were required or about 12 minutes in one instance. Hence, in finding out conditions for securing that the potential-volume curve shall have a vertical portion instead of a gently sloping one, one secured two advantages at once, viz., easier detection of the end point (point of inflexion) and reduction in the time required to carry out the titration.

REPRESENTATIVE TITRATIONS.

The following table gives the complete readings obtained in a titration of Schäffer salt in 6N sulphuric acid, and in one of Schäffer salt in presence of Crocein salt at the same acid concentration; the corresponding graphs are also given.

Schäffer Salt in 6N Acid		Schäffer Salt in presence of Crocein Salt in 6N Acid	
25 c.c. solution, 25 c.c. water, 10 c.c. conc. acid.		25 c.c. Sch. salt soln. 25 c.c. Cro. salt soln. 10 c.c. conc. acid.	
Vol.	mV.	Vol.	mV.
0	416	0	340
5.14	346	3.99	342
8.31	360	6.02	344
9.44	394	8.06	356
9.87	410	9.52	374
10.10	422	10.05	382
10.24	428	10.25	386
10.32	434	10.39	400
10.37	440	10.50	422
10.41	444	10.57	440
10.46	468	10.67	458
10.52	618	10.82	482
10.56	634	10.94	500
10.62	638	11.17	518
10.66	642	11.45	522

The curves are given on the next page.



These two titrations are chosen to show the two types of curves obtained, viz., one with a large vertical portion and one of the "flat" type. The end point can easily be detected in the former, but, in the case of the latter, it is found that the end point corresponds to a point near to where the graph begins to rise. To avoid this ambiguity, conditions were always sought for, which would give rise to a curve having a more or less vertical portion. There were many variations between the two types of curves obtained during the course of the investigation.

The graphs also show the standard method of setting out the curves. The horizontal scale is 2 cms. equal 1 c.c.; and the vertical, 2 cms. to 100 mV. The acidity used is given at the top left hand corner and the temperature at the bottom right hand corner/

hand corner (R.T. stands for room temperature). Where no temperature is given, it may be assumed that the titration was carried out at room temperature. The point taken as the end point (point of inflexion) is indicated by the small mark on the curve, and an arrow head shows (where it is given) the point which would be taken as the end point, if starch iodide paper were used as indicator, i.e. where a definite blue stain was recognisable.

CARE of INDICATOR ELECTRODES.

When the indicator electrodes were not in use, they were kept in concentrated hydrochloric acid. Previous to a titration they were ignited in a blow pipe flame. It was found that they were apt to be "poisoned" after a few titrations especially in sulphuric acid solution, but ignition rendered them sensitive again.

FIRST TITRATIONS.

The three crops of Schäffer salt from the Schäffer-R preparation were analysed using Callan and Henderson's method, and were found to contain respectively 86.1, 85.9 and 86.0% monosodium salt. The determination of the sodium content as sodium sulphate gave similar results. The three crops were, therefore, identical in composition; they were mixed together and the bulk so obtained formed the stock, used in carrying out the subsequent titrations involving Schäffer salt.

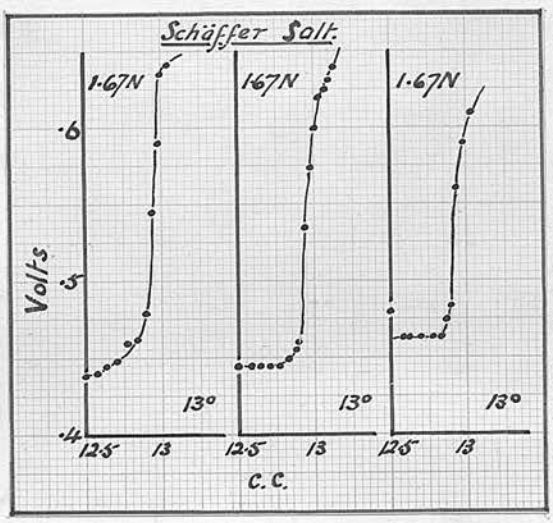
The quantitative bromination of G salt (using the potassium salt prepared) was next tried at the temperature recommended by Vaubel (65^{o}-70^{o}). Great difficulty was experienced in getting an end point at this temperature. If, at a certain point, the test drop were transferred to the starch iodide paper at an ordinary rate, no colour developed; but if the drop were transferred rapidly, a decided colour appeared. It was realised that a titration could not be carried out conveniently under these circumstances and it was at this point that the potentiometric method was turned to, in the hope that the difficulties encountered in the use of starch iodide paper might be avoided.

TRIAL of POTENTIOMETRIC METHOD.

After a few preliminary experiments, a series of titrations of the three salts - Schäffer, R and G - was carried out, with the smaller volume of solution (50 c.c.), to which was added 10 c.c. concentrated hydrochloric acid, the indicator electrode being a length of platinum wire of about 3 cms. The brominating solution contained 5.547 gm. Merck's pure potassium bromate and 30 gm. potassium bromide (free from bromate) per litre; the proportions were practically the same as those recommended by Redman, Weith and Brock, but the solution had twice the normality.

The following titrations were carried out and gave rise to the curves shown.

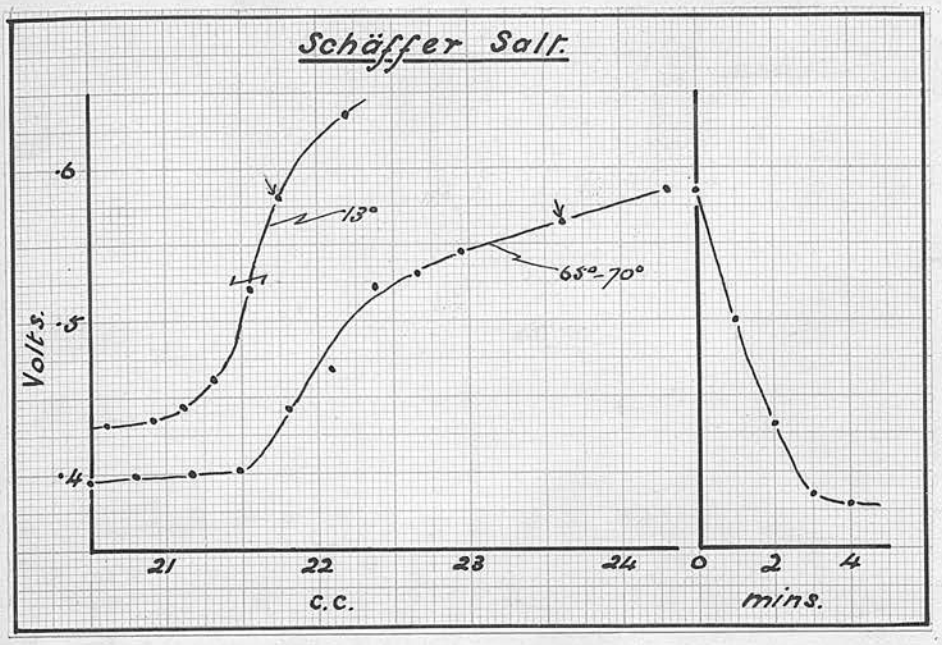
(1) Three consecutive titrations of a Schäffer salt solution.



These curves show that reproducible results were obtainable with this method.

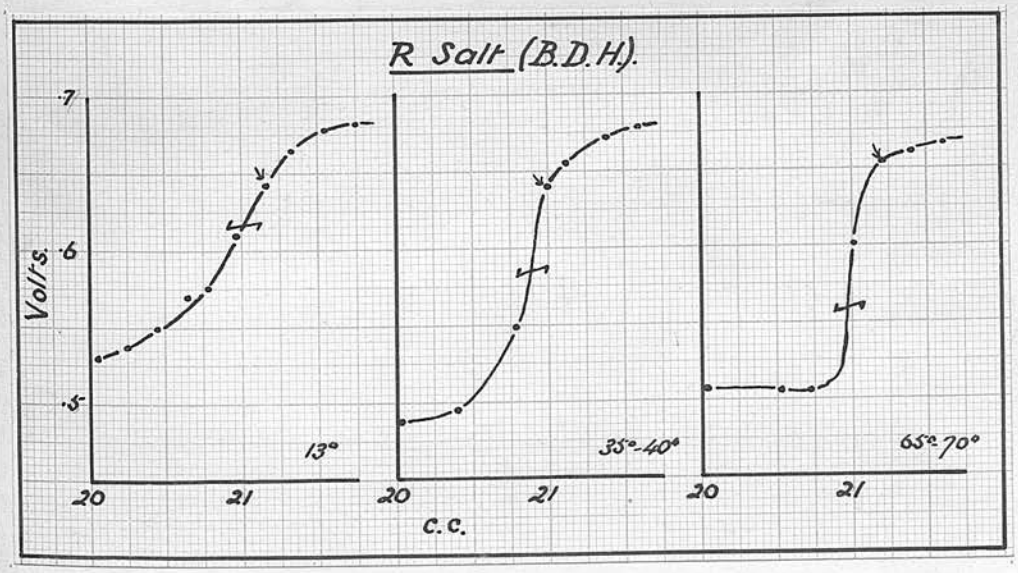
(2) A Schäffer salt solution at 13° and at 65 -70°.

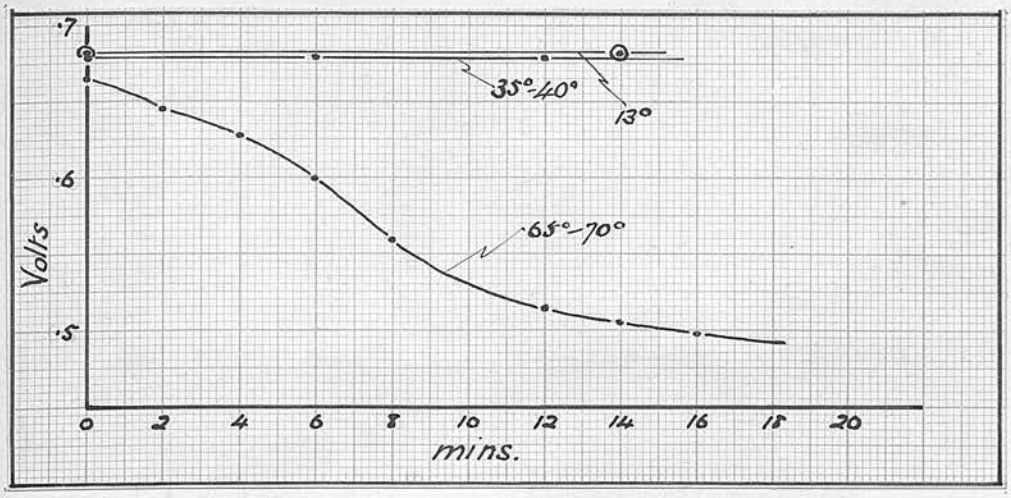
(Curves on next page).



The higher temperature led to a "flatter" curve, on which the end point could not be detected with any degree of accuracy. The fall of potential with time after the completion of the titration is also plotted, for the higher temperature. Since a blank titration at 65°-70° did not show this fall with time, it was concluded that it was due to dibromination of the sulphonate present.

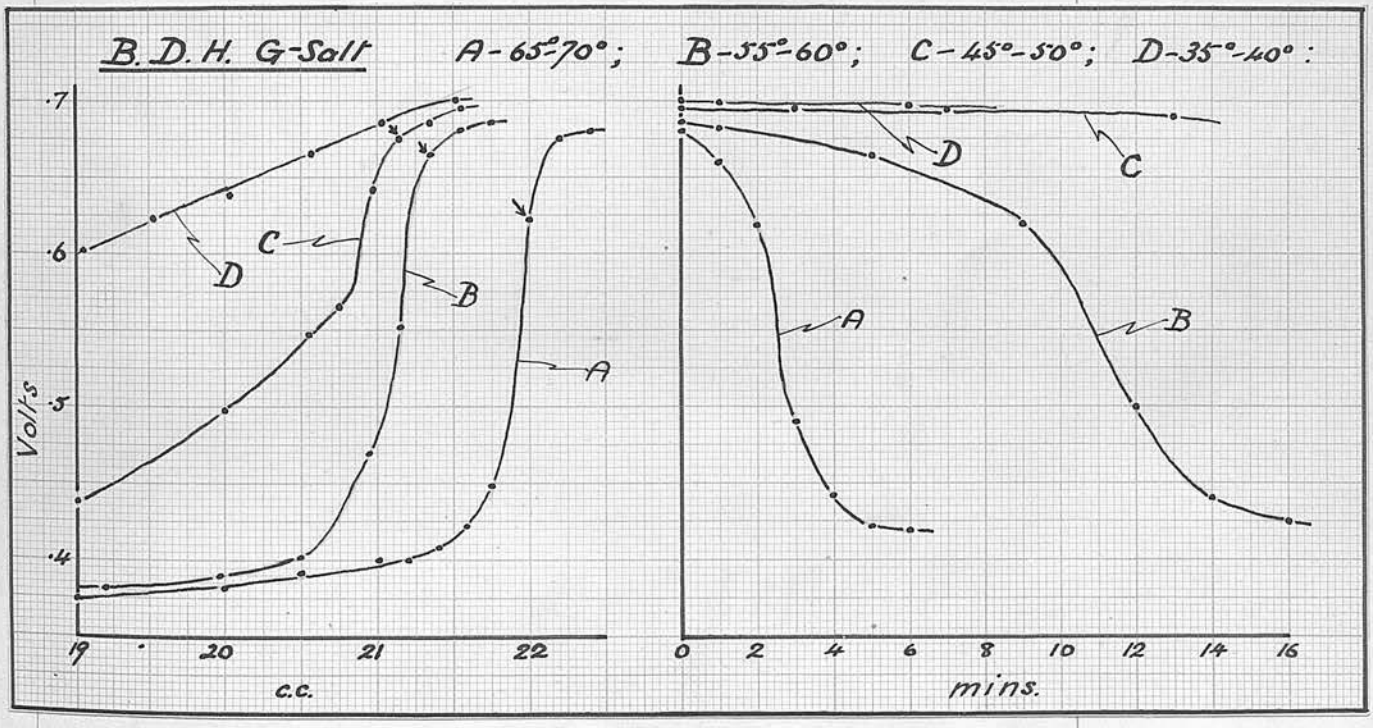
(3) An R salt (B.D.H.) solution at 13°, 35°-40° and 65°-70°.





From the three curves given, it appeared that 35°-40° was the best range at which to carry out the titration of R salt. The potential-time curves show that the salt was brominating slowly at the high temperature.

(4) A G salt (B.D.H.) solution at four ranges of temperature.

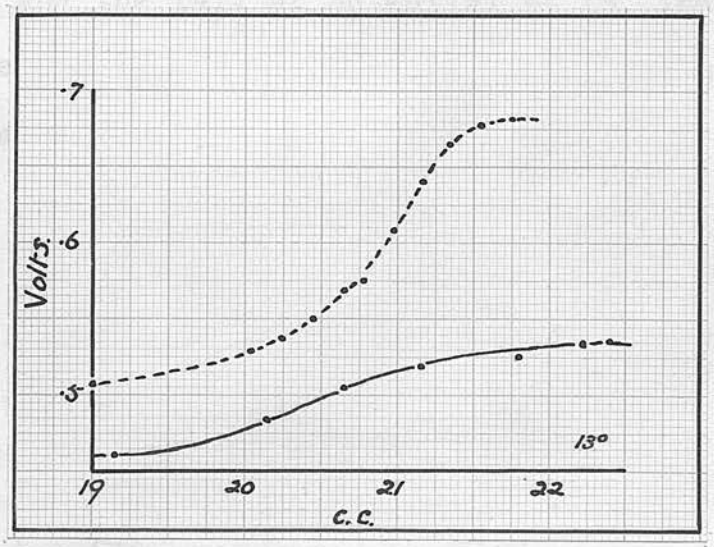


Each range of temperature gave a different end point. The potential-time curves show that 50° was sufficiently elevated/

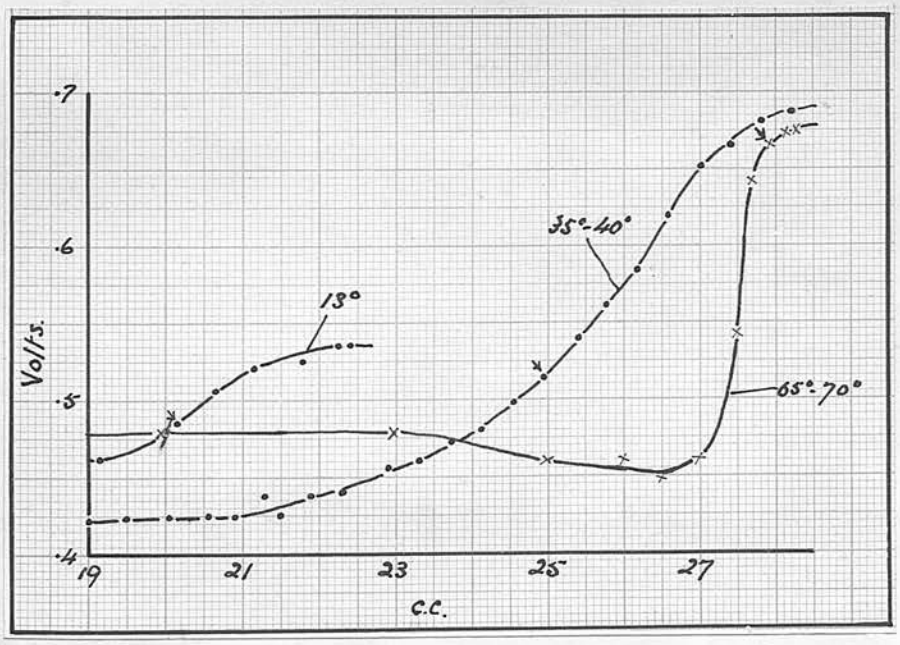
sufficiently elevated for the bromination of G salt. 35° was too low, a blue stain being given on starch iodide paper long before the end point.

The potassium G salt gave exactly similar curves; these are not given.

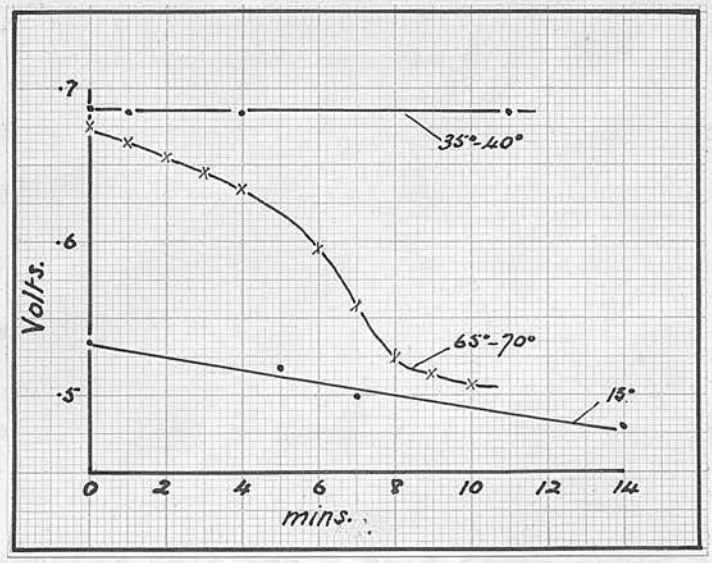
(5) R salt in presence of G salt.



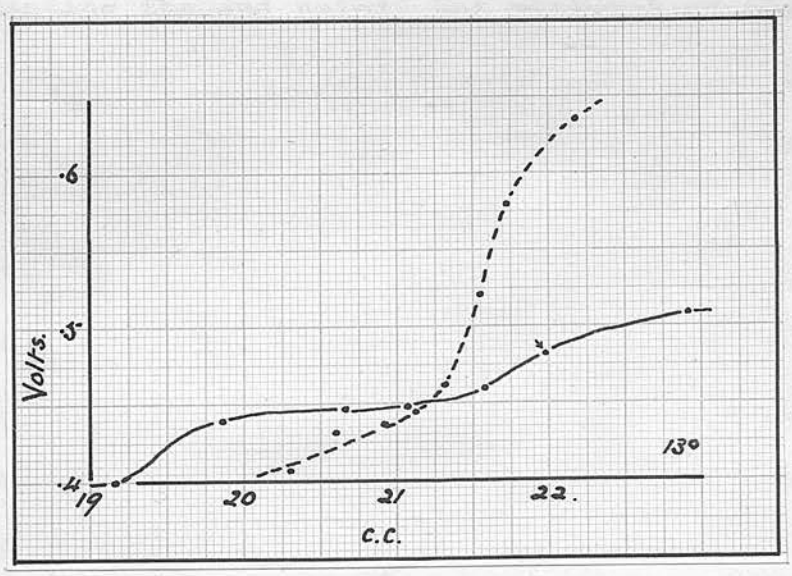
The curve of the titration at room temperature showed no useful rise of potential, which would indicate the end point corresponding to the R salt content. For comparison, the curve obtained with R salt alone (dotted curve) is given.



The curve for the titration at 35°-40° (the range found suitable for R salt alone) was useless, since it gave neither the R salt content nor the total sulphonate present; titration at 65°-70° gave a rise corresponding to the "total". The potential-time curves show that the high temperature led to dibromination and the fall of potential at 13° indicated that the G salt was brominating slowly at that temperature in hydrochloric acid solution.

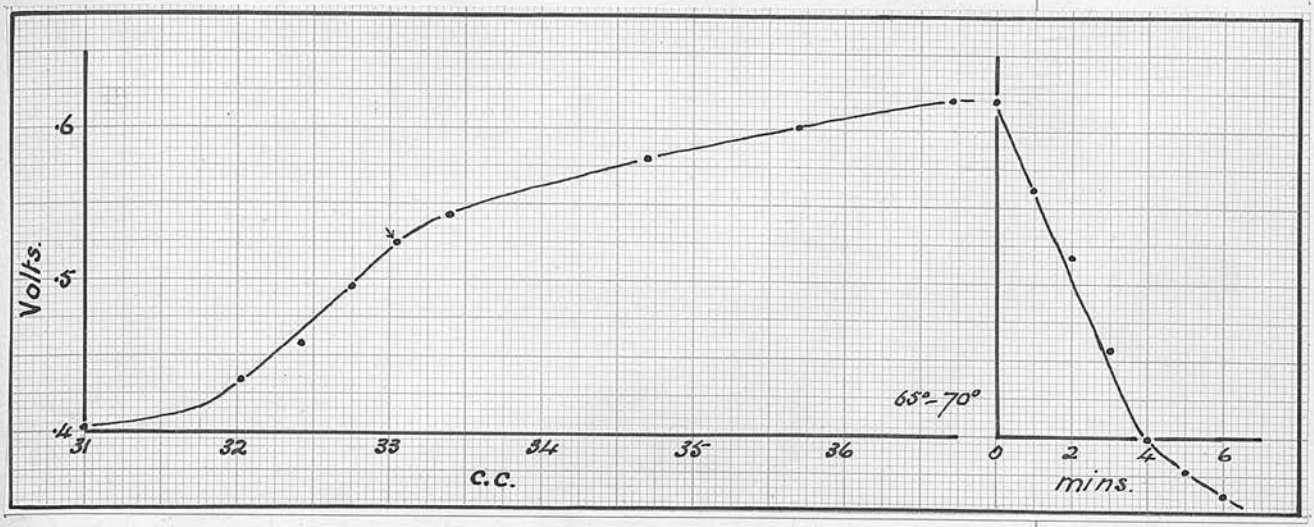


(6) Schäffer salt in presence of G salt.



The same results are noticed in the case of this mixture/

this mixture, when the titration was carried out at room temperature (13°). When the determination was



carried out at 65°-70°, an extremely flat rise corresponding to the total sulphonate content was obtained. This was to be expected, since Schäffer salt alone gave a flat curve at this range of temperature (see (2) above).

The conclusions drawn from these experiments were:-

(a) Schäffer salt and R salt alone could be determined bromometrically using the potentiometric method of detecting the end point, but mixtures of them with G salt could not be titrated to determine the Schäffer or R salt content, in hydrochloric acid solution at 13°.

(b) The temperature recommended by Vaubel for the bromination of G salt quantitatively (65°-70°) was too high and gave rise to a certain amount of dibromination. In all probability, 50° was sufficiently elevated for the bromination of G salt.

RETURN to STARCH IODIDE PAPER as INDICATOR.

Seeing that these first attempts gave no definite results, a return was made to the ordinary method of detecting the end point by means of starch iodide paper. The same conditions were used as in the potentiometric method, viz., 50 c.c. of solution and 10 c.c. concentrated hydrochloric acid. The bromide-bromate was slowly run in with constant stirring, until a persistent excess of bromine was noticeable. The results are summarised as follows.

0.6068 gm. of Schäffer salt required 21.33 c.c. (mean of two determinations) at 15° and 21.42 c.c. at 45°-50°, allowing for blanks.

0.8854 gm. of G salt required 20.92 c.c. at 45°-50°; bromination at this temperature proceeded quite smoothly and the end point was easily detected.

0.8434 gm. of R salt required 20.25 c.c. at 15°; the reaction towards the end point appeared to be slow but the end point could be detected nevertheless. At 45°, 20.34 c.c. were required.

In each case, the stain given by a test drop at the end point after 5 minutes' stirring had the same intensity as the one after 1 minutes' stirring.

The titration of mixtures of Schäffer and G salts and R and G salts were attempted both in the cold (15°) and in the hot (45°-50°). The end point at the first temperature was inclined to be indefinite, the stain after two or three minutes' stirring being much fainter than that after one minute's stirring; the fading/

the fading still took place several drops after the end point corresponding to the Schäffer or R salt content. The end point at 45°-50° corresponding to the "total" was also indefinite. This fading made it difficult to detect the end point with any degree of certainty.

TRIALS with SULPHURIC ACID.

At this point, sulphuric acid was substituted for hydrochloric acid in the titration of a Schäffer-G mixture, the volume being 50 c.c. as before and the titrating agent bromide-bromate solution. It has been already explained (p.41) that 6N sulphuric acid was decided on as the acid concentration at which to carry out the titrations. So far as could be ascertained by employing starch iodide paper as indicator, G salt did not brominate at 15°, 45°, or 60° in sulphuric acid at any of the concentrations 10N, 6N, 2N, 0.5N and 0.26N, although it brominated readily in hydrochloric acid solution at 40°. A return was made to the potentiometric method to see if the use of sulphuric acid would lead to the possibility of the titration of Schäffer or/and R salt in presence of G salt with bromide-bromate solution, using this method of detecting the end point.

POTENTIOMETRIC TITRATIONS involving the USE of SULPHURIC ACID.

The following solutions were made up and used in these titrations:-

Schaffer salt - 3.001 gm. in 250 c.c.

R salt - 3.930 gm. in 250 c.c.

G salt - 4.109 gm. in 250 c.c.

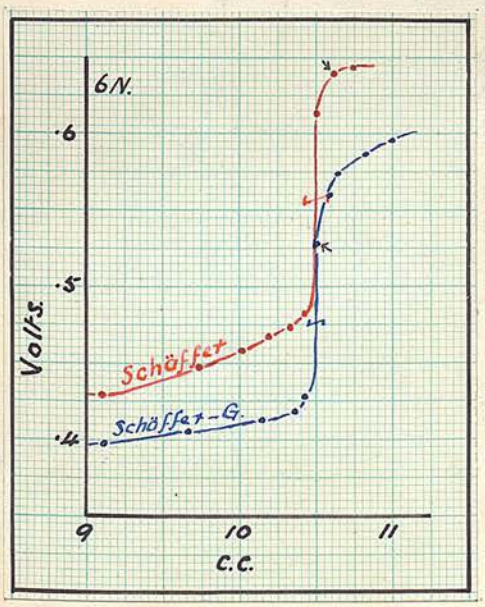
The routine previously described (p.52) was adopted in these titrations.

A platinum wire gauze, about 1 cm. square, was used as indicator electrode for these and all subsequent titrations; this electrode appeared to be more sensitive than the wire electrode, probably due to its greater surface and, therefore, its greater capacity. The titrations carried out are set forth, as usual, in the form of their potential-volume curves in the region of the end point.

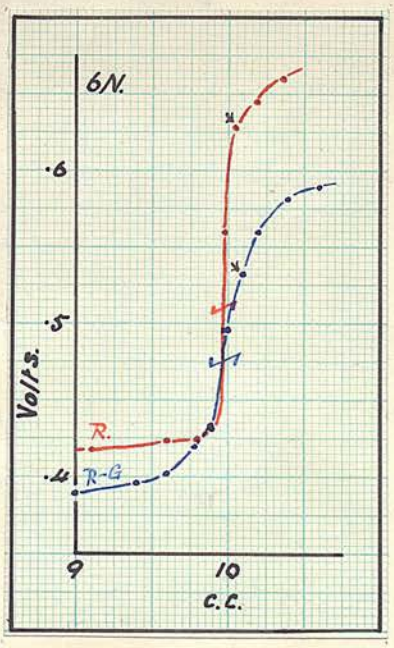
(1) Schäffer salt alone and in presence of G salt.

(2) R salt alone and in presence of G salt.

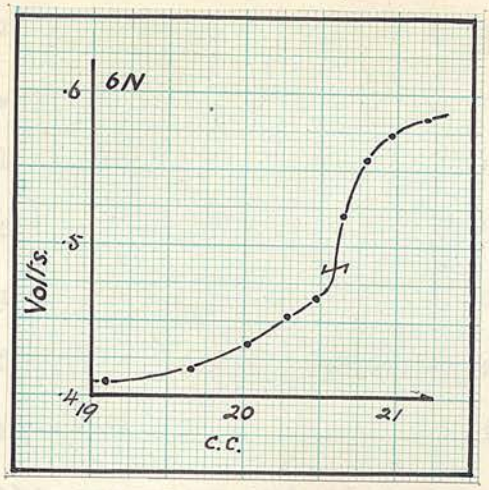
(1)



(2)

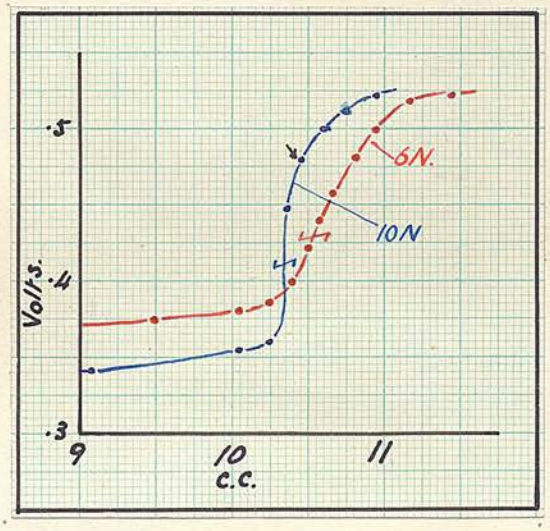


(3) Schäffer and R salts in presence of G salt.



The curves for mixtures were totally different from those, which were obtained in the earlier experiments involving the use of the potentiometric method (see p.63). They showed conclusively that Schäffer or/and R salt could be determined in the presence of G salt with an accuracy of at least 1 per cent, if sulphuric acid were used to liberate the bromine.

(4) Schäffer salt in presence of Crocein salt.



The last two curves should be specially noticed. In 6N sulphuric acid solution, Schäffer salt in presence of/

presence of Crocein salt gave a gradual rise of potential after the end point. By increasing the acidity to 10N, a vertical portion was obtained and such a curve allowed one to identify the end point with greater accuracy and certainty. This last observation suggested the desirability of carrying out a series of titrations of the pure salts and mixtures of them at various acid concentrations. This involved the carrying out of a large number of experiments, but many interesting results were obtained from the large number of graphs collected.

EFFECT of CONCENTRATION of SULPHURIC ACID on SHAPE of CURVES.

In this series of titrations, the following solutions of the salts were used:-

Schäffer salt - 6.000 gm. in 500 c.c.

R salt - 9.000 gm. in 500 c.c.

G salt - 9.000 gm. in 500 c.c.

Crocein salt - 7.0 (approx.) gm. in 500 c.c.

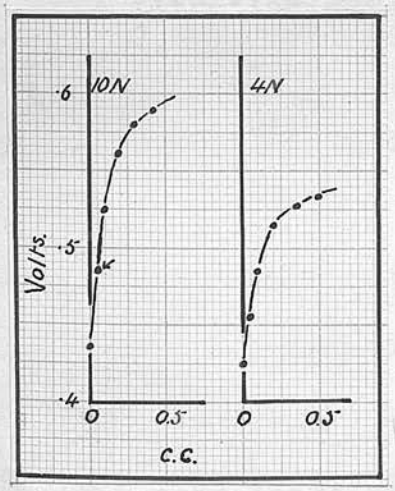
The bromide-bromate solution contained 5.567 gm. Merck's pure potassium bromate and 30 gm. potassium bromide (free from bromate) per litre. The results obtained are summarised below.

(1) Acid alone.

Acidity	Potl. of indicator electrode.	Potl. of indicator electrode after adding 1 drop bromide-bromate.
10N	474 mV.	776 mV.
6N	472 mV.	854 mV.
4N	484 mV.	844 mV.
2N	484 mV.	844 mV.

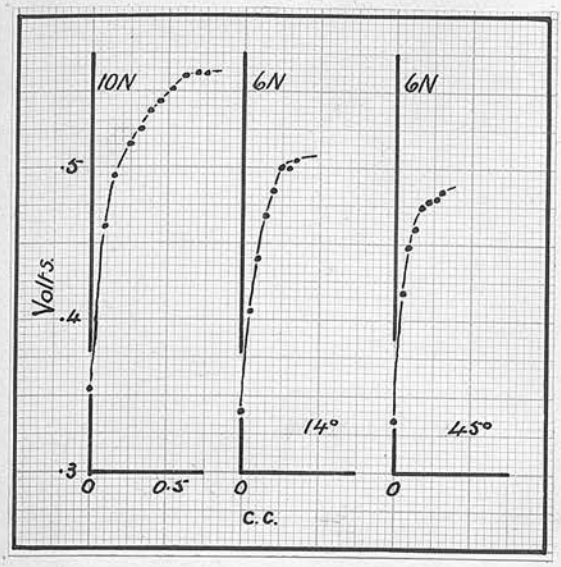
A second drop caused very little change.

(2) G salt alone.



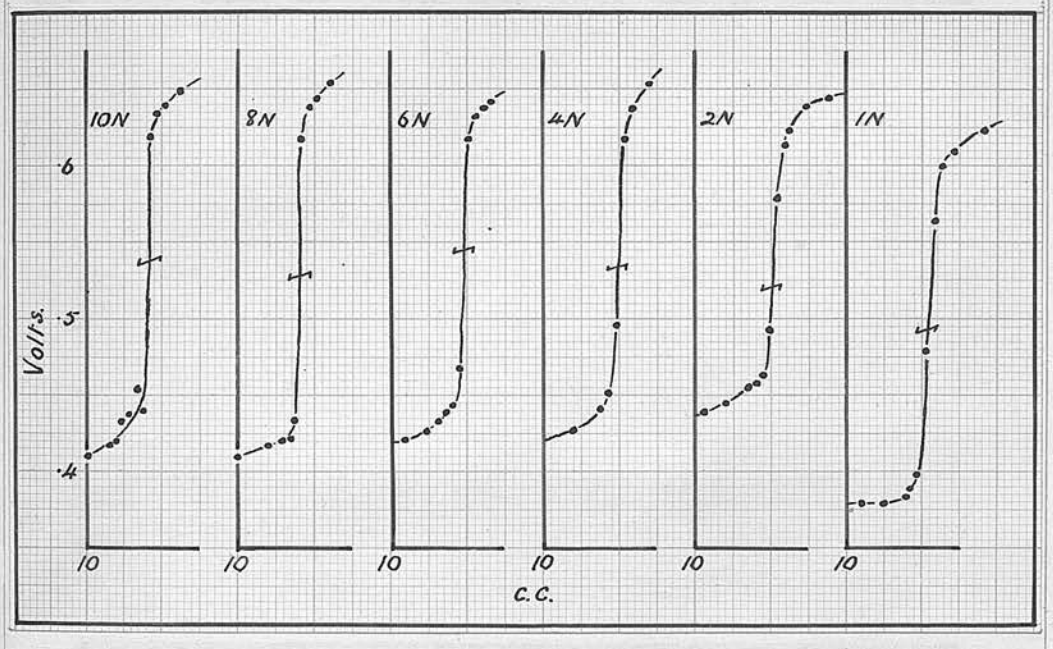
An immediate rise was given, but the total rise at 4N was not so great as at 10N. The potentials tended to rise further with time. This showed that G salt did not brominate in sulphuric acid solution.

(3) Crocein salt alone.



Similar results were given in this case. The potential at 10N had not changed after stirring for 30 minutes.

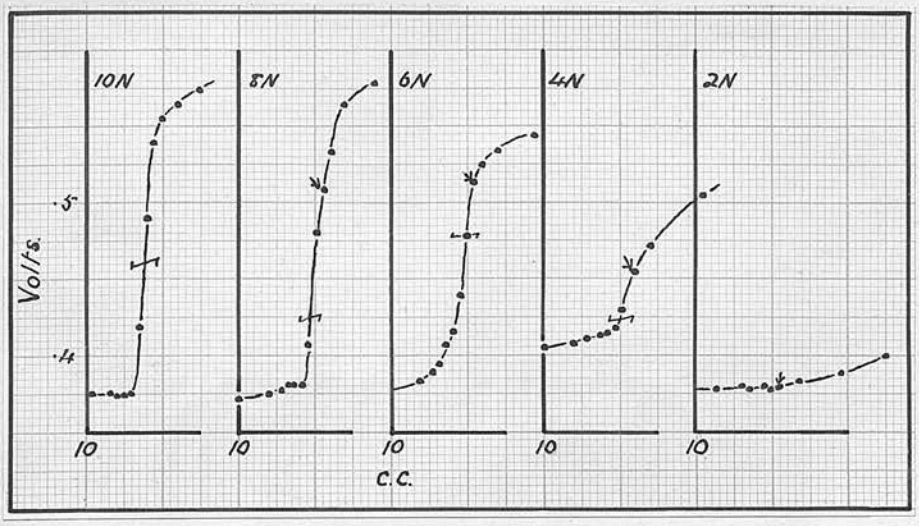
(4) Schäffer salt alone.



A titration was also tried at 0.5N acid concentration, but no rise of potential was obtained. The potential remained constant at 444 mV. between 10.00 c.c. and 11.08 c.c. At 10.47 c.c. a blue stain appeared slowly on starch iodide paper.

Acid concentration above 0.5N has little effect on the shape of the graphs except that the rise becomes less vertical with decreasing acid concentration.

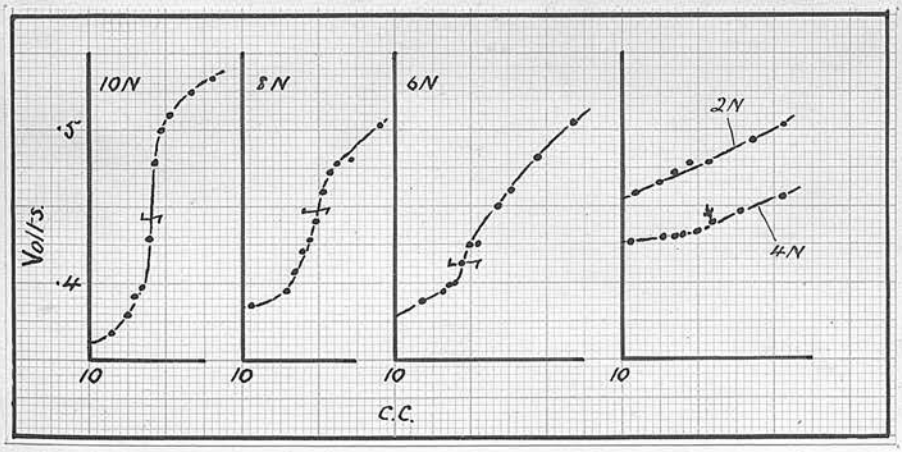
(5) Schäffer salt in presence of G salt.



The titrations at 4N and 2N were repeated and the same type of curve was obtained in both cases. Although the end point could not be detected potentiometrically at 2N acid concentration, starch iodide paper gave a good indication of the end point.

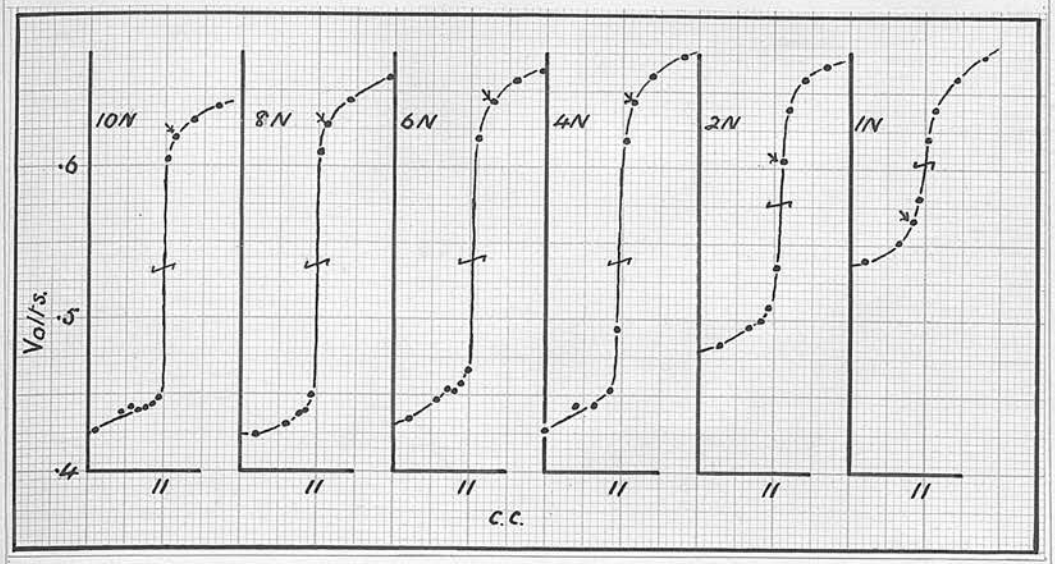
The potentials tended to rise with time; thus after the completion of the titration at 4N acid concentration, the solution was stirred for 9 minutes and the potential had then risen to 558 mV.

(6) Schäffer salt in presence of Crocein salt.



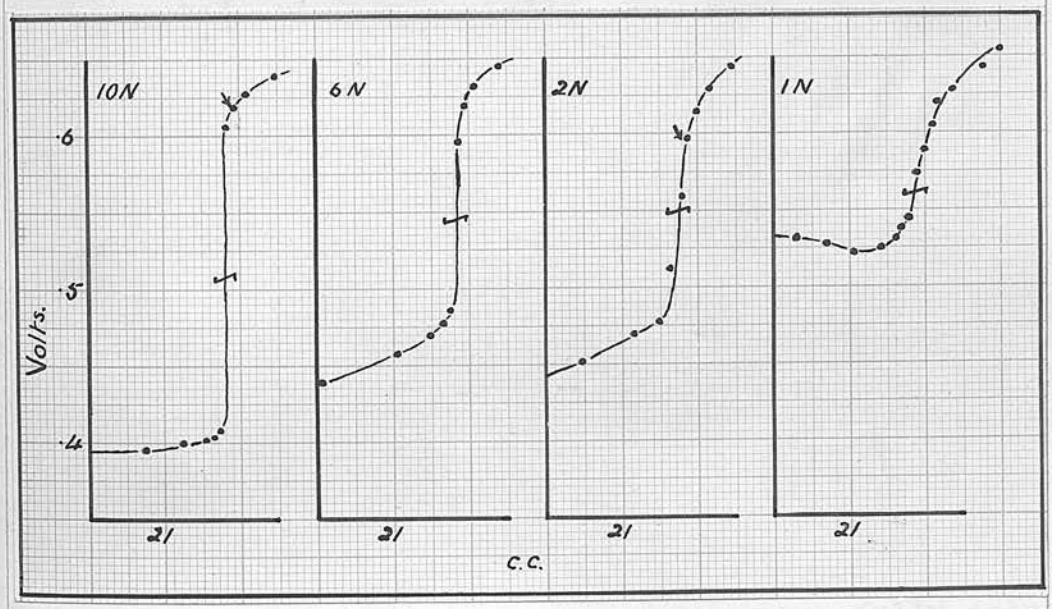
Similar results were obtained in this case.

(7) R salt alone.



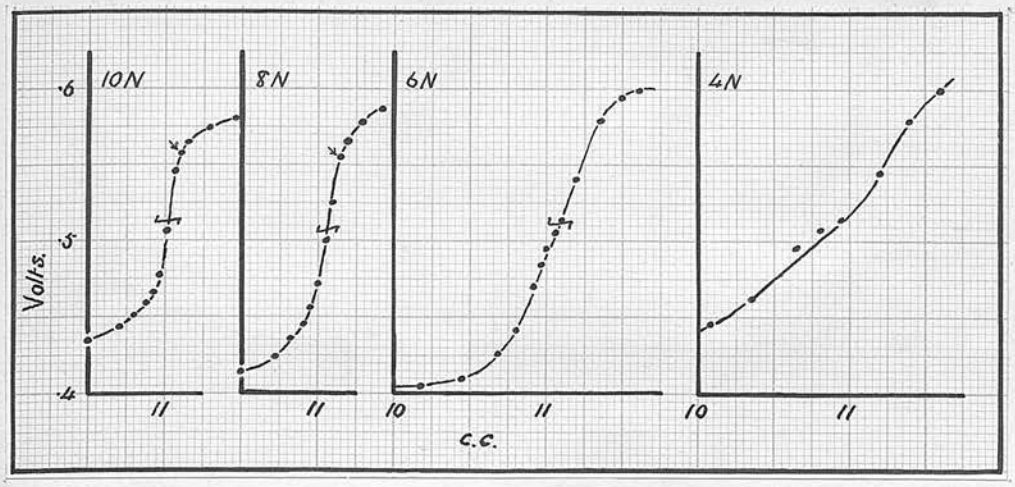
The rise became less vertical with decreasing acid concentration, and the amount of the rise at the two lowest concentrations decreased due to the potentials before the end point being higher.

(8) Schäffer and R salt together.



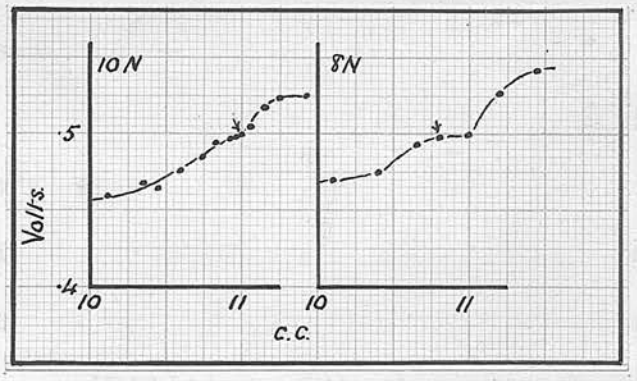
The curves were similar to those obtained with the salts separately, but the characteristics of the titration of R salt predominated, e.g. titration at 1N acid concentration.

(9) R salt in presence of G salt.



The presence of G salt modified the curves considerably, so that the curve at 6N acid concentration was too "flat" for the accurate determination of the end point.

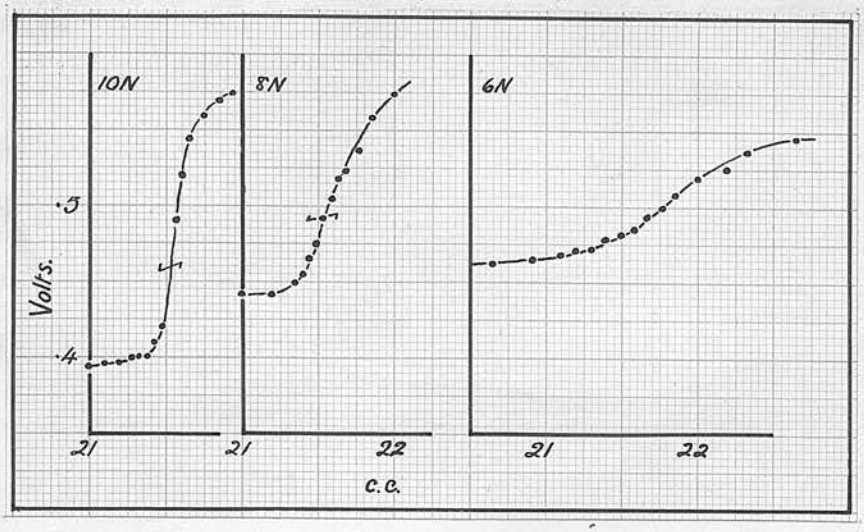
(10) R salt in presence of Crocein salt.



The curves obtained were practically useless, although a slight indication of an end point was given at about 11 c.c., but the evidence was too slight to be of practical use. The titration of this particular mixture is discussed more fully later.

(11) Schäffer and R salts together in presence of G salt.

(Curves on next page.)



In this case, a practically flat curve appeared at an acid concentration of 6N. It was thought unnecessary to carry out titrations atlower acid concentrations.

. . . . .

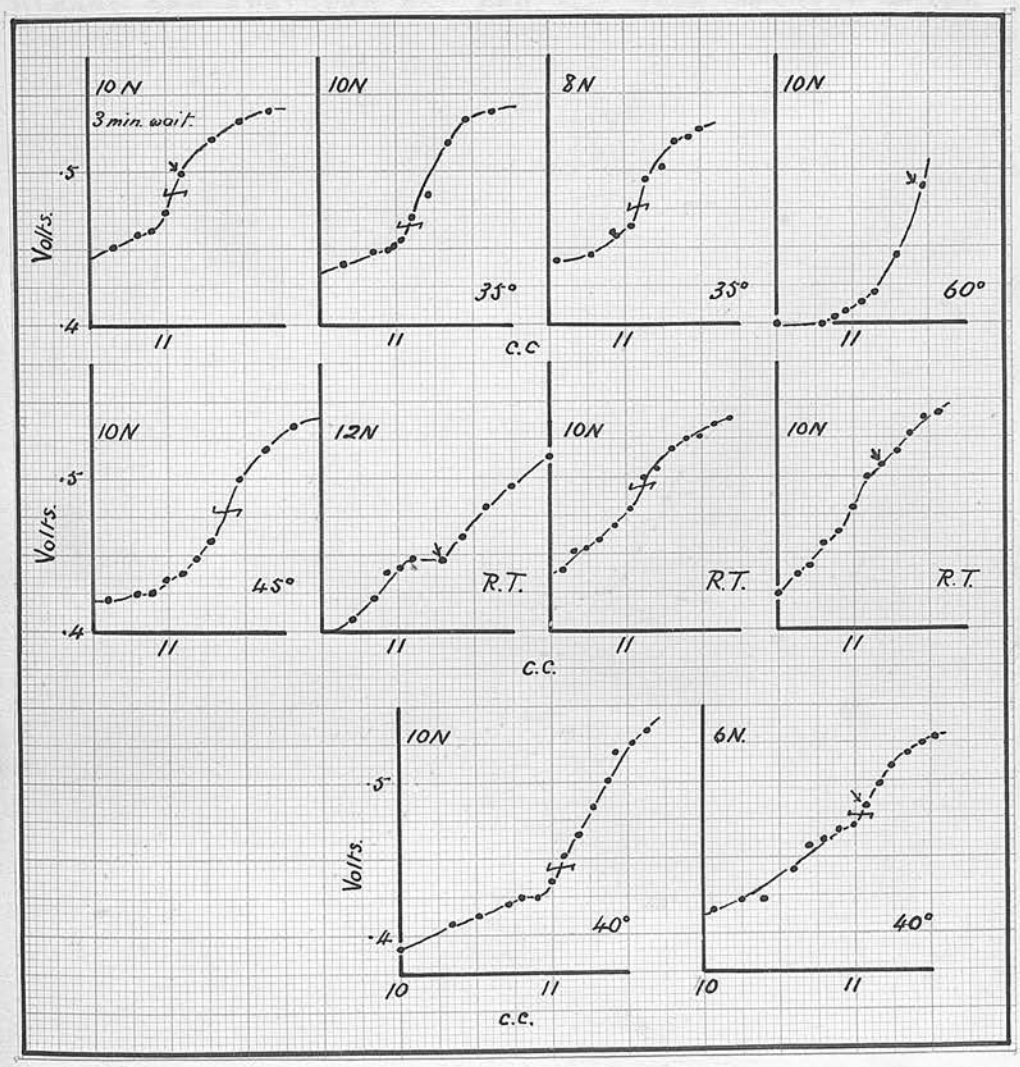
A study of the above series of graphs will lead to the observation that if a pure Schäffer or R salt sample is to be titrated, an acid concentration of 4N need not be exceeded (even N acid solution gives quite good results), but if either G or Crocein salt is present then a normality of 10 must be used to cover all possibilities with the exception of mixtures containing R and Crocein salts together, if a curve with a more or less vertical portion is to be obtained.

The R-Crocein mixture provided a difficulty, and attempts made to improve the curves obtained on titrating such a mixture are described in the next section of the paper.

The TITRATION of R SALT in PRESENCE of CROCEIN SALT.

The curves obtained in the titration of R salt in presence of Crocein salt were unlike any obtained with other mixtures and were useless, since they showed no definite sudden rise in potential. In 8N acid concentration, free bromine could be detected (by starch iodide paper) at 10.66 c.c. after stirring for one minute, proving that the bromination of R salt was being hindered by the presence of Crocein salt.

The following series of graphs indicates the

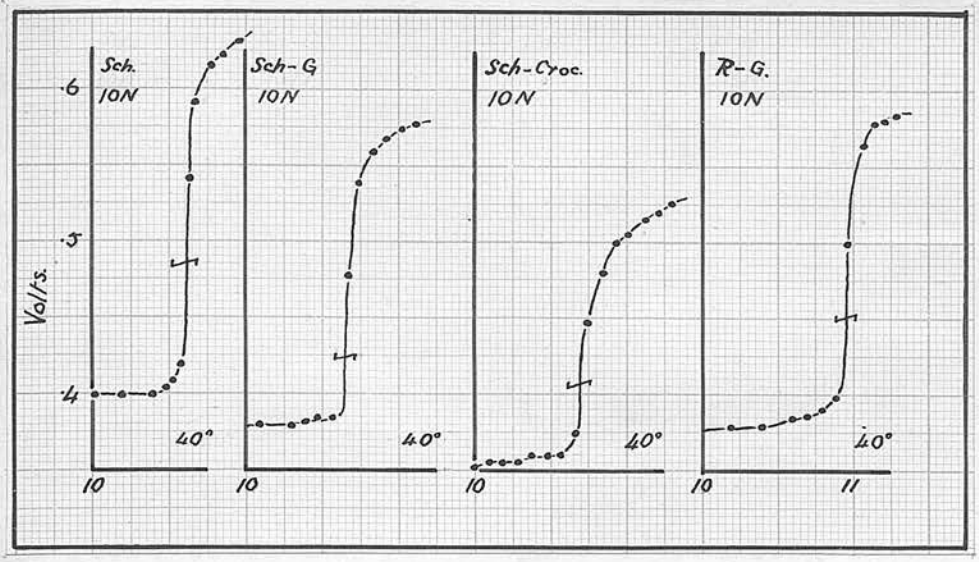


variations of the method tried, in order to find conditions leading/

conditions leading to the production of more useful curves. When the solution was allowed to stir for three minutes after the addition of bromide-bromate solution before taking a reading, an improved graph was obtained, but the time of titration became exceedingly lengthy. Increasing the acid concentration to 12N led to no useful result; a repeat titration gave an exactly similar curve. Increasing the temperature appeared to be the most hopeful variation, titration in 10N acid at 35° giving a quite useful curve, the end point being within 1 per cent. The higher temperatures 45° and 60° gave results which were too high.

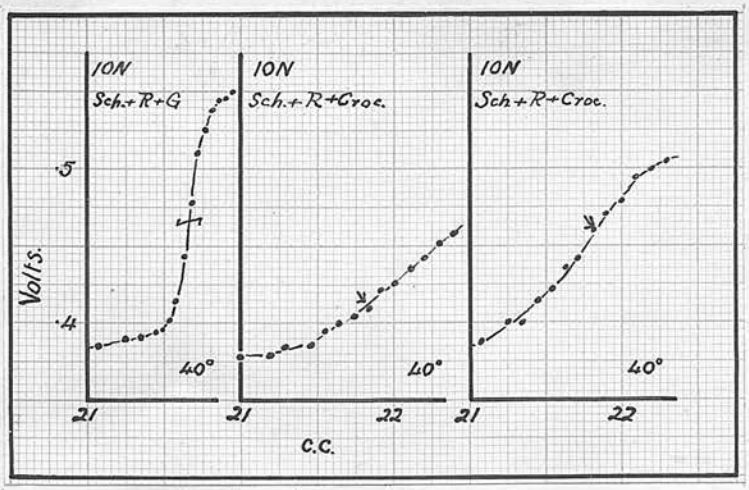
When the titration of this mixture was taken up later, it was again found that the curve obtained when using 10N acid solution and room temperature showed a straight line rise in the region of the end point. By increasing the temperature to 40°, the curve obtained appeared to be quite serviceable but left something to be desired. 6N acid concentration did not give such a good curve at the same temperature.

The discovery of these new conditions rendered it necessary to repeat the titrations of mixtures other than the R-Crocein mixture under the new conditions; the curves are given on the next page. The higher temperature gave, in certain cases (e.g. R-G and Schäffer-Crocein mixtures), a better curve than the one obtained previously at room temperature, by reducing/

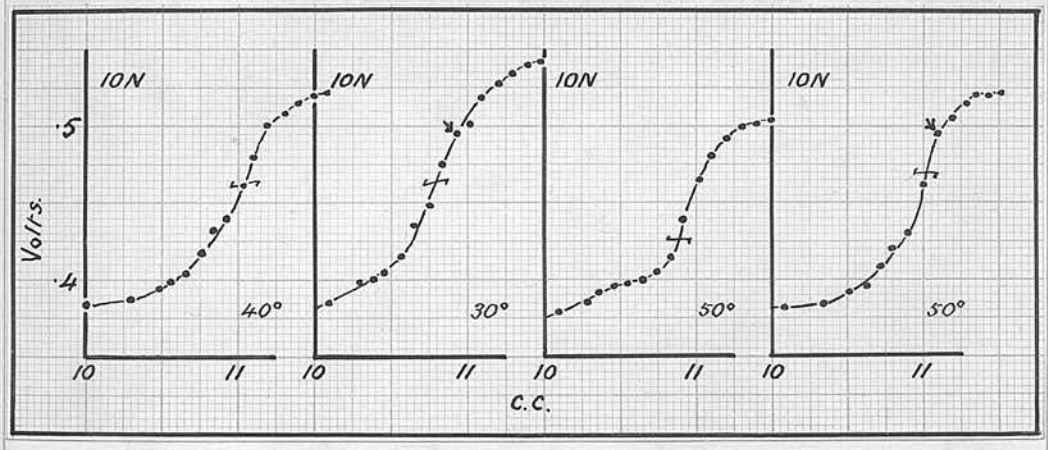


by reducing the potentials just before the end point and so making the potential rise more prominent and more vertical.

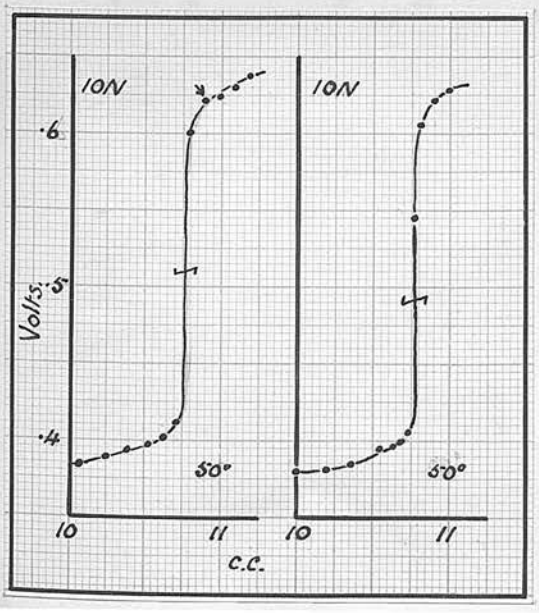
Attention was next turned to the titration of mixtures of Schaffer and R salt in presence of G and Crocein salts under the new conditions (10N acid and 40°). 25 c.c. of each of the standard Schäffer and R salt solutions were mixed with 50 c.c. of the standard G salt solution and 40 c.c. of concentrated sulphuric acid added. The whole was titrated at 40°. The curve obtained is given below; the end point indicated is within 0.5 per cent. A similar mixture of Schaffer, R and Crocein salt was made up and titrated. The curves in this case showed a straight



line rise, which showed no end point. In order to make the titration comparable with those previously carried out, equal volumes of the standard Schäffer and R salt solutions were mixed and 25 c.c. of this mixture used along with 25 c.c. of the Crocein salt solution. Unsatisfactory curves were obtained, being all too flat to give reliable results. Titration at three temperatures was tried, and although the first titration at 50° gave a promising curve, a different and unsatisfactory was obtained on repeating the titration. The end points indicated on the graphs were all too high, some being as much as 3 per cent out.



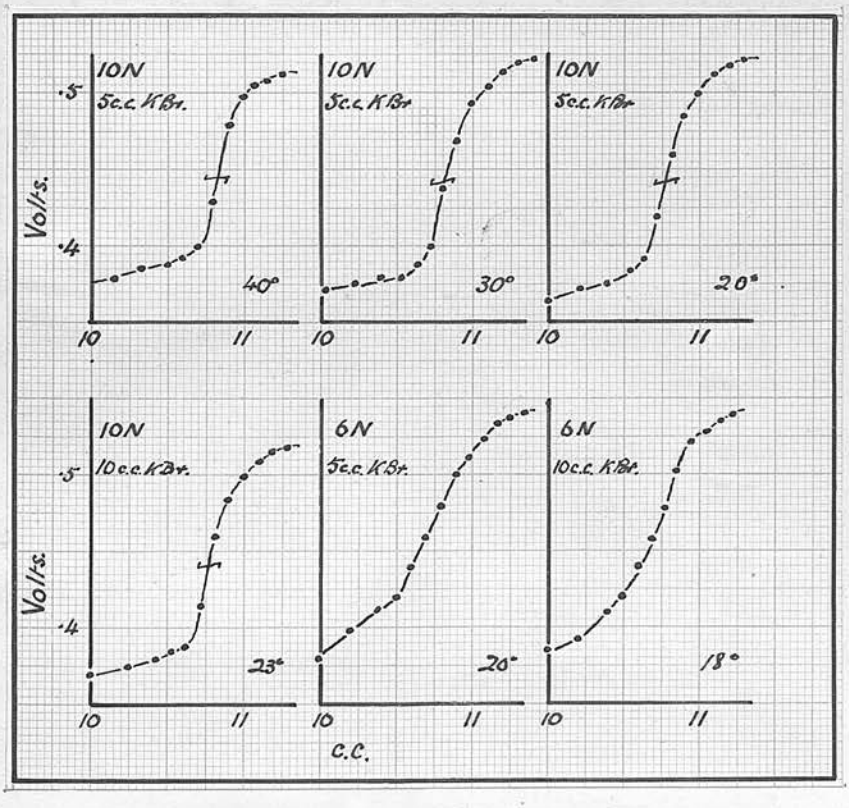
The Schäffer-R salt mixture alone gave normal curves at 10N acid concentration and 50°.



A means of getting over the difficulty of the flat type of curve is given in the next section of the paper.

EFFECT of ADDITION of POTASSIUM BROMIDE on SHAPE of CURVES.

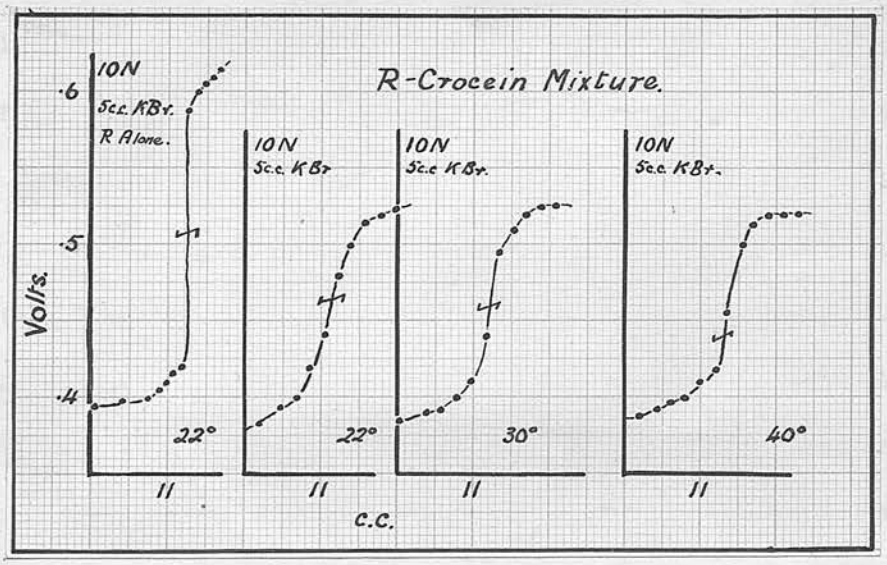
The effect of adding potassium bromide to the solution before commencing the titration was investigated. The extra amount of bromide improved the graphs of the Schäffer-R-Crocein mixture by reducing, in some way, the voltages before the end point; this effect resulted in the potential jump becoming more apparent and more vertical. The first titration tried was one of such a mixture at 10N acid concentration and 40° (i.e. under standard conditions) with the addition of 5 c.c. of a 20% solution of potassium bromide. Then followed others at lower temperatures, 30° and 20°, one with a larger volume of potassium bromide solution (10 c.c.) and two at a lower acid concentration (6N). It was seen from the graphs



that there/

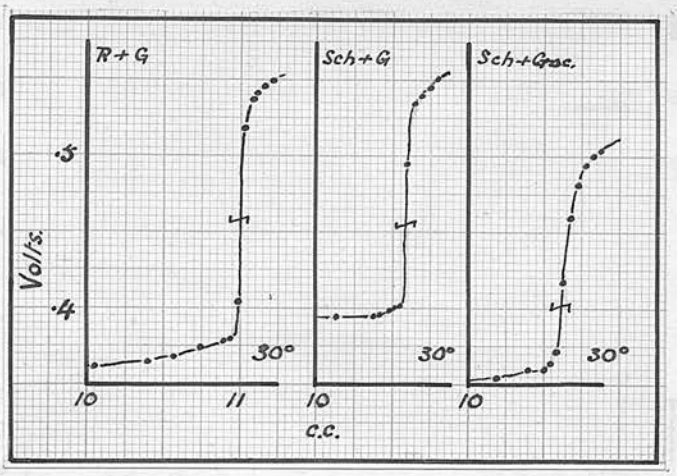
that there was no advantage in using the higher temperature for the estimation of Schäffer plus R salt in presence of Crocein salt, that 5 c.c. of the bromide solution was just as efficient as 10 c.c., and that the acidity must be maintained at 10N, if reliable curves were to be obtained.

The next obvious step was to apply this observation to the titration of R-Crocein salt mixtures. This was done and the curves showed that a temperature of not less than 30° appeared to be necessary for this mixture. This might be expected, since the proportion of R salt is greater than in mixtures containing



Schäffer, R and Crocein salts.

Other mixtures were tried at this temperature with the addition of 5 c.c. of potassium bromide solution. The curves (given on next page) showed that the addition of the bromide had no disturbing influence on the titration of other mixtures.

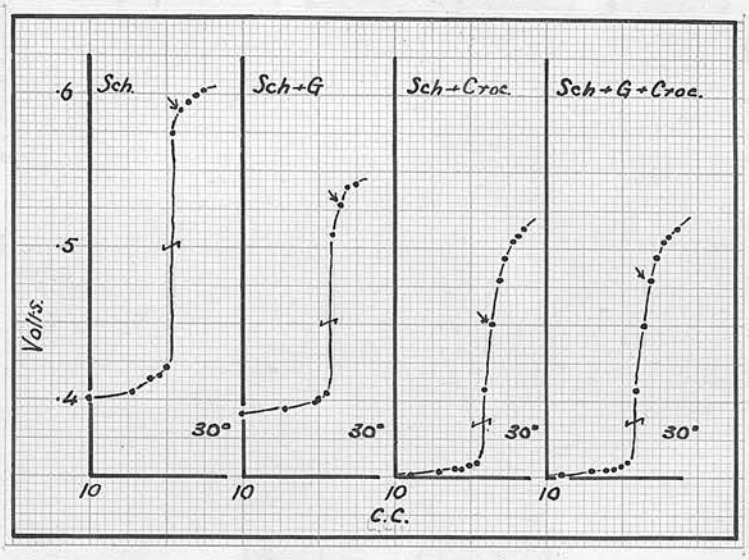


Finally, to complete this series, the titration of every possible mixture of the four salts in sulphuric acid solution was carried out using the method of Callan and Henderson suitably modified to conform with the results discovered in the present investigation. The sulphuric acid concentration was 10N and the temperature 30°, except in two cases; the potassium bromide was added in the form of a 20% solution, 10 c.c. being used for each titration; the titrating agent was a solution of potassium bromate containing 5.567 gm. Merck's pure salt per litre. Approximately equimolecular quantities of brominating and non-brominating salts were present in each mixture; the method of making up the mixtures has been given previously (p.52). Single drops were added in the region of the end point, except in one case.

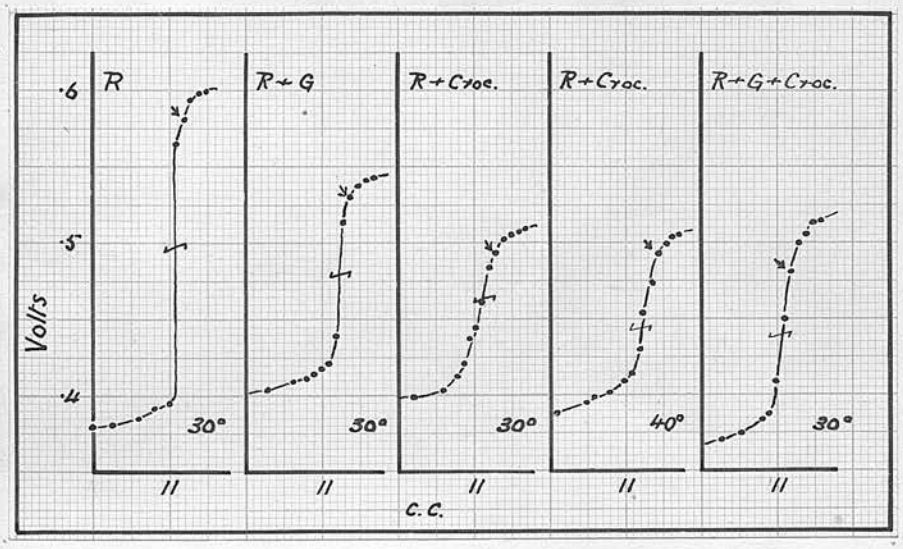
All the curves (see next page) were satisfactory with the exception, again, of R-Crocein and Schäffer-R-Crocein mixtures. In the case of the former mixture, a better/

a better curve was obtained by raising the temperature to 40°, and in the case of the latter a better curve was obtained when increments of two drops were added in the region of the end point.

(a) Mixtures containing Schäffer salt.

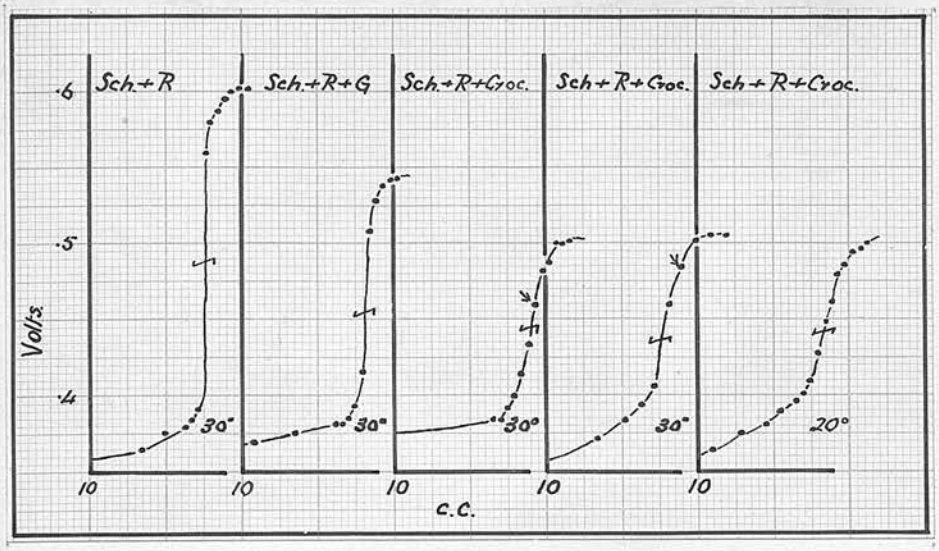


(b) Mixtures containing R salt.

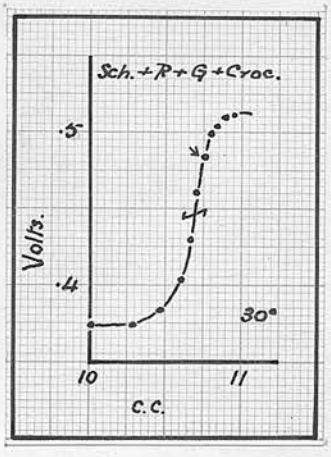


(c) Mixtures containing Schäffer and R salts.

(See next page.)



(d) All four together.



Below is given a table showing the results of these titrations.

Schäffer salt alone	10.54 c.c.
Schäffer-G salt mixture	10.59 c.c.
Schäffer-Crocein mixture	10.56 c.c.
Schäffer-G-Crocein mixt.	10.57 c.c.
R salt alone	11.02 c.c.
R-G salt mixture	11.13 c.c.
R-Crocein mixture	11.08, 11.12 c.c.
R-G-Crocein mixture	11.03 c.c.

Schäffer-R mixture/

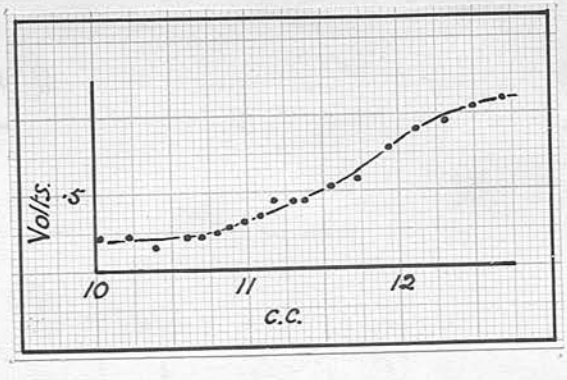
Schäffer-R-mixture	10.75 c.c.	(theor. 10.78 c.c.)
Schäffer-R-G mixture	10.83 c.c.	
Schäffer-R-Crocein mixt.	10.90, 10.75, 10.83 c.c.	
Schäffer-R-G-Crocein mixt.	10.68 c.c.	

The results are all within 0.1 c.c. (or 1 per cent) of the correct values.

The TITRATION of MIXTURES containing SMALL PROPORTIONS of SCHAFFER and R SALTS.

In all the mixtures discussed above, the brominating salt or salts and the non-brominating salt or salts have been present in approximately equal molecular quantities. Hence the conditions found most suitable for such mixtures will also be suitable for all mixtures containing up to 50 per cent of the non-brominating salt or salts. But would these conditions be suitable in cases where the brominating salt was present to the extent of only 10 per cent? This point was looked into.

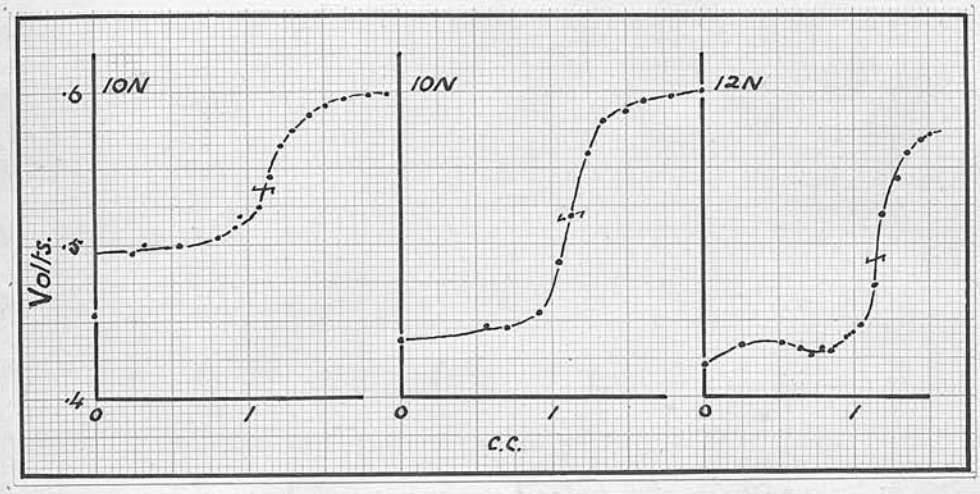
The R salt solution used previously (9 gms. per 500 c.c.) was diluted 10 times and 25 c.c. of this diluted solution used for each titration; the bromide-bromate solution was diluted to a similar extent. The titration of the diluted R salt alone in 6N sulphuric acid solution gave the normal curve, but when an R-G salt mixture was tried at 10N acid concentration, a curve of the type obtained previously in the case of R-Crocein mixtures resulted. It was



thought that the reason of the flatness of the curve was that/

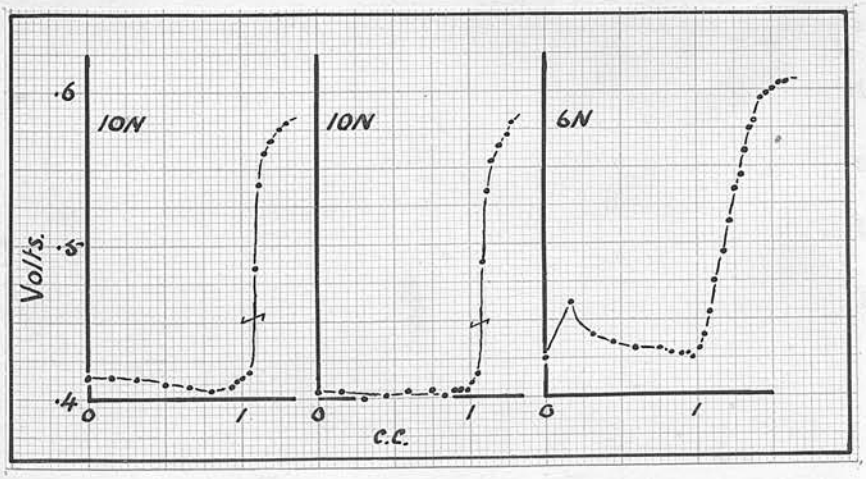
was that the G salt was brominating very slowly but at a rate comparable with that at which the bromine was being added in the form of the diluted bromide-bromate solution.

A return was therefore made to the use of the undiluted brominating solution. A burette was improvised from a 2 c.c. graduated pipette reading to 0.02 c.c. The titrations were more successful, 10N



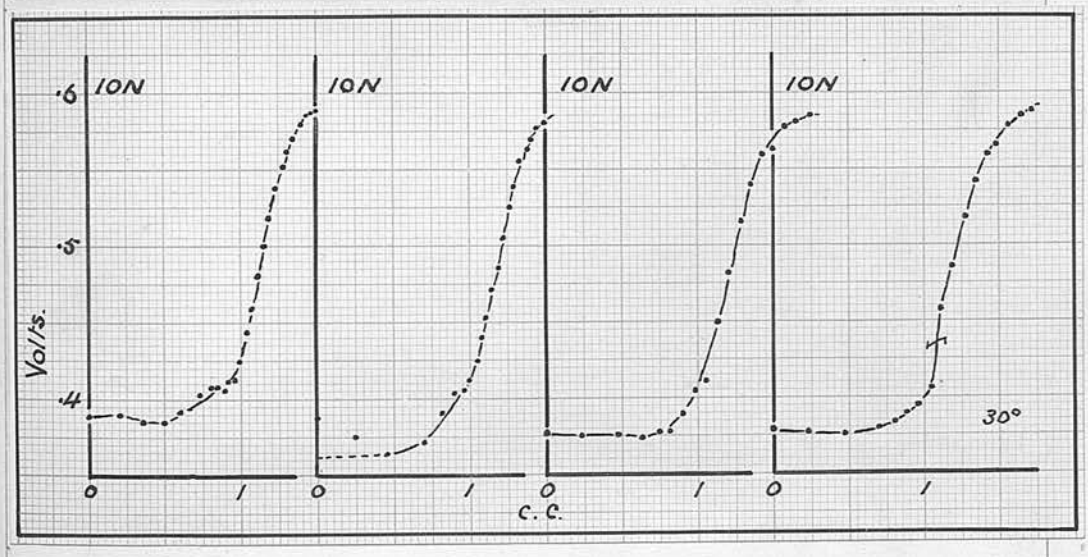
acid giving the best results, i.e. with an error of 2 - 3 per cent; 6N acid did not give good curves except at 50°, when the end point given was too high (curves not given). Since titrations of mixtures including G salt always gave results which were slightly too high, the error is quite reasonable.

Continuing the series, a corresponding mixture



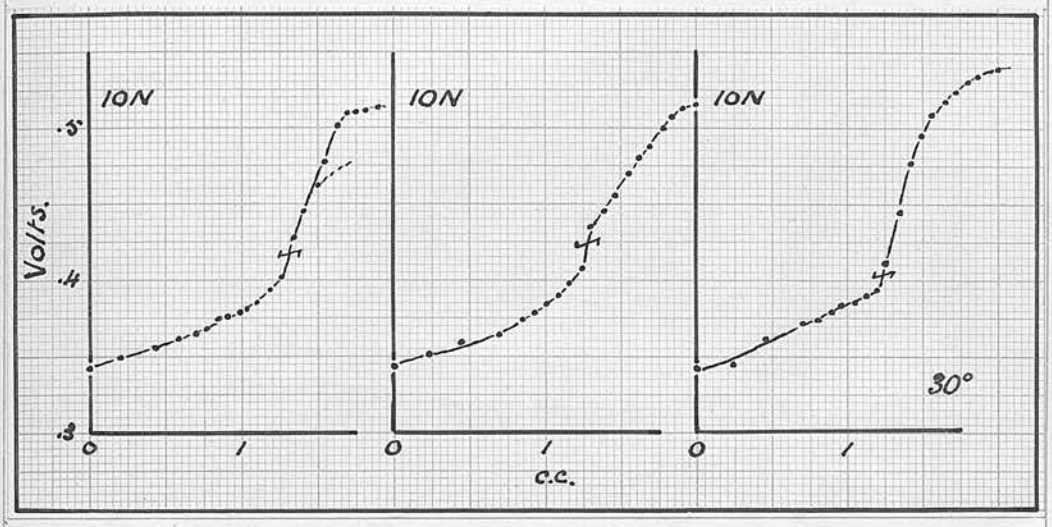
of Schäffer and G salts was titrated with the undiluted bromide-bromate solution. Results similar to the above were obtained except that the curves (see previous page) at 10N acid concentration had, perhaps, a better form.

A mixture of Schäffer and R salts was made up by placing 25 c.c. of each of the standard salt solutions in a 500 c.c. graduated flask and diluting to the mark. 25 c.c. of this diluted solution were added to 25 c.c. of the standard G salt solution and then titrated in 10N sulphuric acid solution. At ordinary temperatures, the curves were not too satisfactory and the end points were too high, but at 30° a good curve and result were obtained.



The titration of Schäffer-Crocein mixtures, the Crocein being present in the greater quantity, did not yield satisfactory results. The best curve was obtained at a temperature of 30°, but the results it gave was 20 percent too high. When Crocein salt was titrated/

was titrated alone in 1ON sulphuric acid solution, the potential rose at once (see p.72) and although the titration of Schäffer-Crocein mixtures containing equal quantities of the salts gave a value 0.06 c.c. too high, this difference was not sufficient to account for the large error in the above titrations. The curves are given below.



When these experiments were carried out, no satisfactory conditions had been found for the titration of R salt in presence of Crocein salt, and so the titration of R salt in presence of a large quantity of Crocein salt was not attempted. The effect of adding potassium bromide had not been discovered at this time.

POTENTIOMETRIC TITRATIONS involving the USE of HYDROCHLORIC ACID.

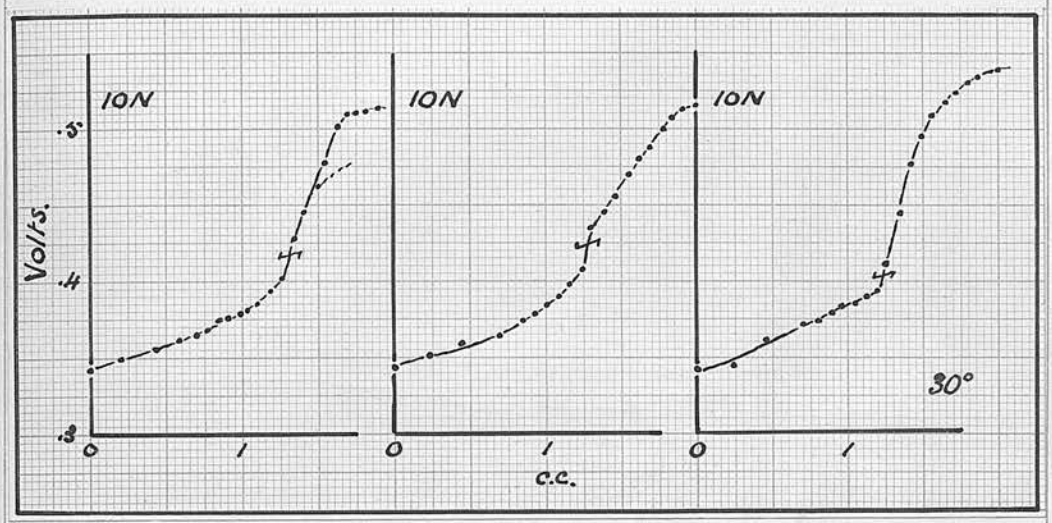
DETERMINATION of G SALT.

Observations already made on the subject of the titration of G salt may be summarised as follows:-

G salt, although it does not brominate in sulphuric acid solution by the method already given, does so readily in hydrochloric acid solution especially at higher temperatures. Vaubel's original method required the use of a temperature between 65° and 70°, but sulphuric acid was used to liberate the bromine. When such a temperature was tried, difficulties were experienced with the "spotting test" on starch iodide paper (see p.59). The first trials of the potentiometric method led to varying results at different temperatures (p.62), but the curves showed that G salt brominated quite well at 50°, and that this temperature was sufficiently high since, at higher temperatures, slight dibromination was taking place as shown by the fall in potential with time after the completion of the titration. At 50°, the potential fell very slowly with time. On returning to the titration of the various salts with starch iodide paper as external indicator, it was found that the end point could be detected fairly well when the temperature lay between 45° and 50°.

When the potentiometric method was taken up again, the/

was titrated alone in 1ON sulphuric acid solution, the potential rose at once (see p.72) and although the titration of Schäffer-Crocein mixtures containing equal quantities of the salts gave a value 0.06 c.c. too high, this difference was not sufficient to account for the large error in the above titrations. The curves are given below.



When these experiments were carried out, no satisfactory conditions had been found for the titration of R salt in presence of Crocein salt, and so the titration of R salt in presence of a large quantity of Crocein salt was not attempted. The effect of adding potassium bromide had not been discovered at this time.

POTENTIOMETRIC TITRATIONS involving the USE of HYDROCHLORIC ACID.

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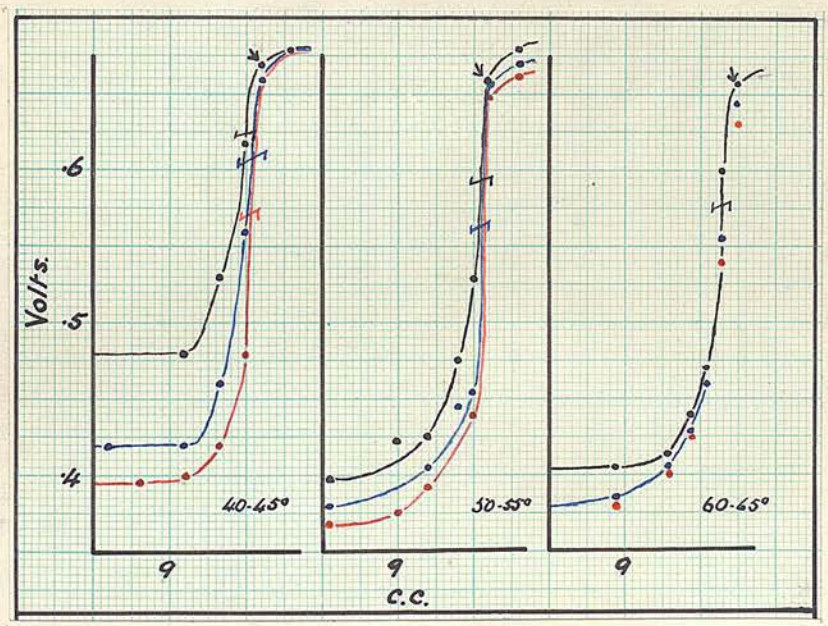
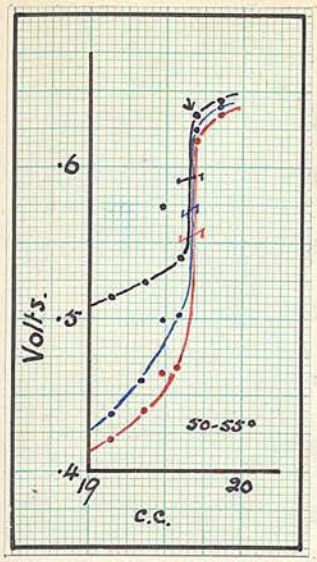
When the potentiometric method was taken up again, the/

again, the bromination of G salt was tried at three ranges of temperature, viz., 40°-45°, 50°-55°, and 60°-65°. 25 c.c. of a G salt solution (containing 0.3914 gm.) were diluted with 25 c,c. water and 10 c.c. concentrated hydrochloric acid added; during the titrations, readingswere taken 1 (black), 2 (blue), 3 (red) and 4 minutes after the addition of the bromide-bromate solution; (the points on the "4-minute" curve lay practically on the "3-minute" (red) curve). The potential remained constant during half an hour after the completion of the titration at 40°-45°; it had fallen 210 millivolts after 16 minutes in the titration at 50°-55°; and 180 millivolts in four minutes in the titration at 60°-65°. The graphs showed little divergence amongst themselves, but showed that, for the one minute wait, the lowest range of temperature was rather low. It was there-

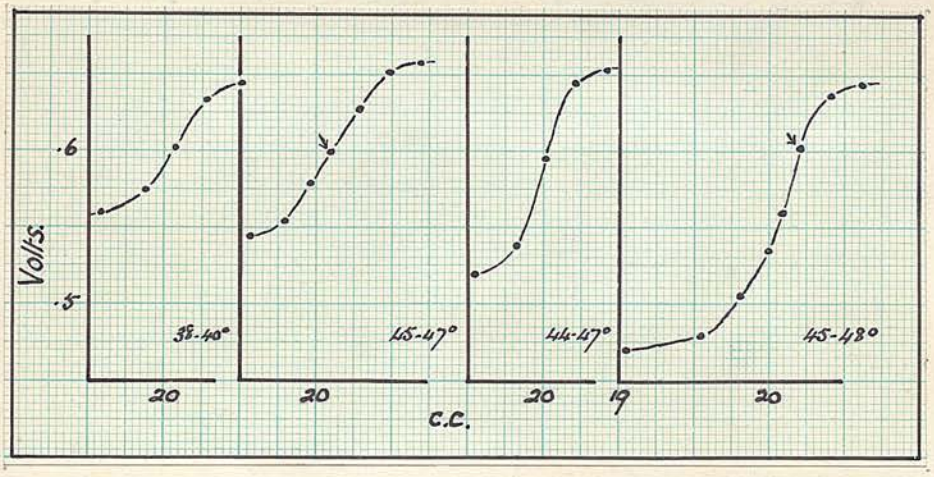


fore decided to choose 50° as the temperature at which to carry out titrations of mixtures containing G salt.

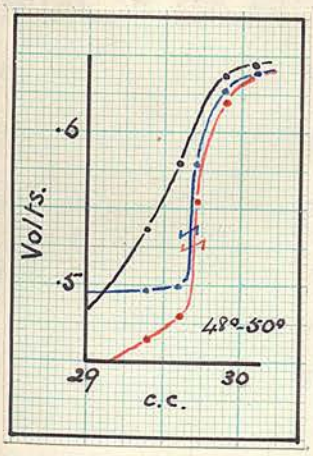


The titration of a solution containing R and G salts was carried out at 50° at the same acidity and gave the curves shown. The colours have the same significance as above. The end point was 0.2 c.c. or 1% too high.

The following four graphs were obtained in the titration of a Schäffer-G salt mixture at the temperatures given. None of them were



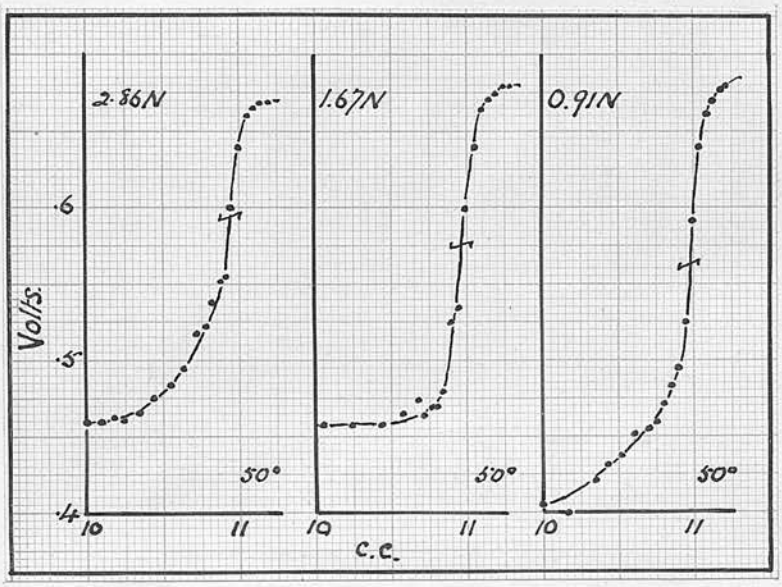
satisfactory.



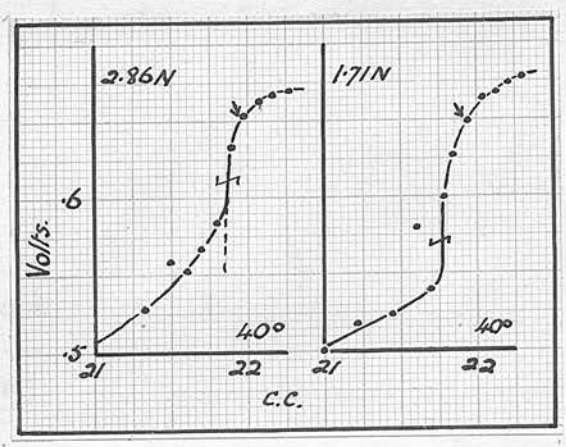
The accompanying graph was obtained in the titration of a mixture containing Schäffer, R and G salts. The graph for a two-minute wait was satisfactory.

EFFECT of HYDROCHLORIC ACID CONCENTRATION on SHAPE of CURVES.

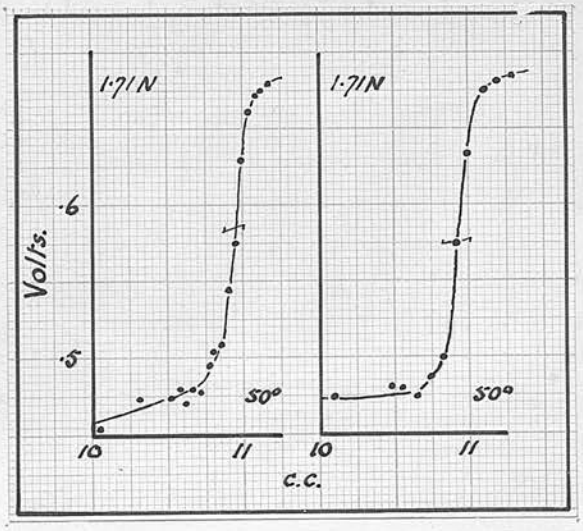
After the effect of concentration of sulphuric acid on the curves of the titration of mixtures had been investigated, a few experiments were carried out to ascertain if the concentration of hydrochloric acid had any effect on the titration of G salt at 50°. The following three graphs show the effect of three



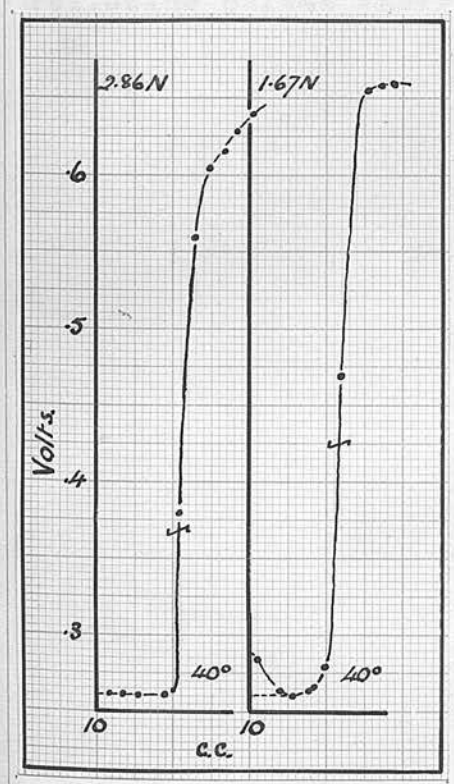
acid concentrations. The three graphs gave practically the same end point; the long rise before the end point in the curve of the titration at 2.86N acid concentration seemed to be characteristic of the titration of G salt at this acidity; it appeared again in the titration of R-G mixtures. The curves obtained in the titration of double quantities at two



acid concentrations at 40° are given; the shapesof the curves were similar to those obtained at the higher temperature. The characteristic rise before the end point at 2.86N acid concentration was shown more markedly. Finally, two curves show the titration of duplicates in 1.71N acid solution at 50°, in one of which increments of one drop were added in the region of the end point and in the other increments of two drops were used. Both curves were of the



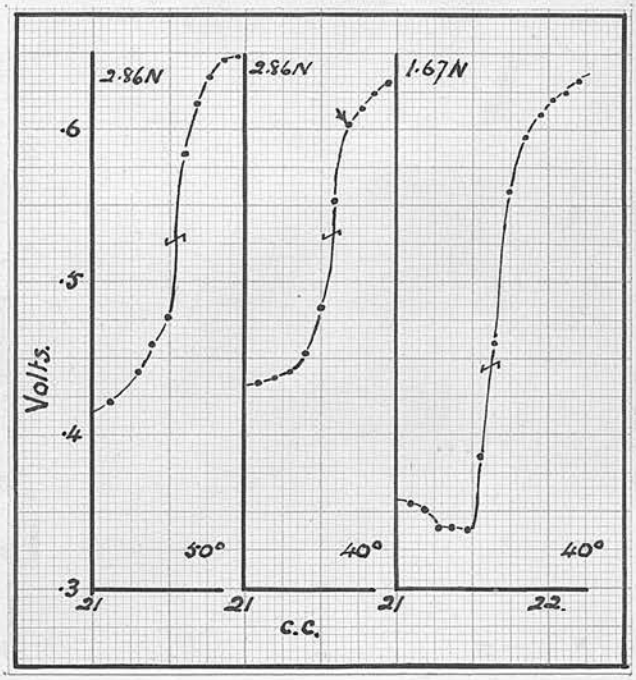
same shape and gave practically the same end point.



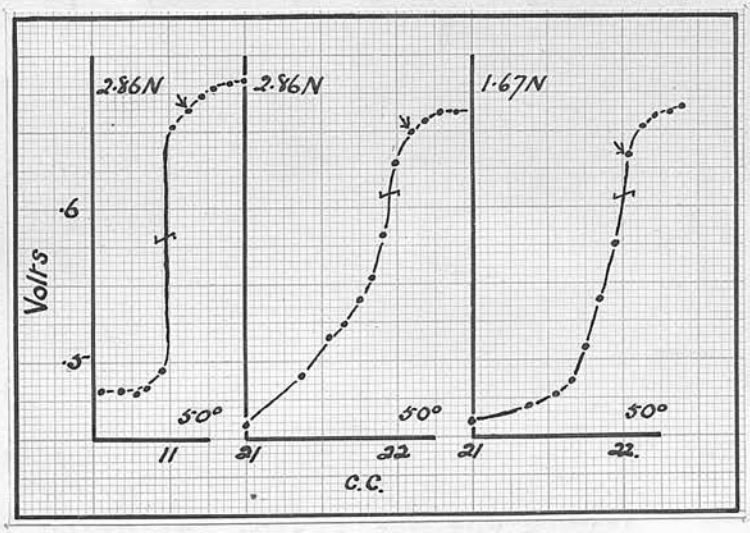
(In the above and subsequent titrations, the standard salt solutions given on p.71 were used.)

The accompanying graph shows the titration of Schäffer at two acid concentrations. Extremely large potential rises were given by this salt under the conditions of the titrations.

The titration of the two salts - Schäffer and G - together gave rise to curves, which gave the total sulphonate present. The end pointsobtained were within 0.5 c.c. of the correct value, i.e. the sum of the volumes required by the salts separately.

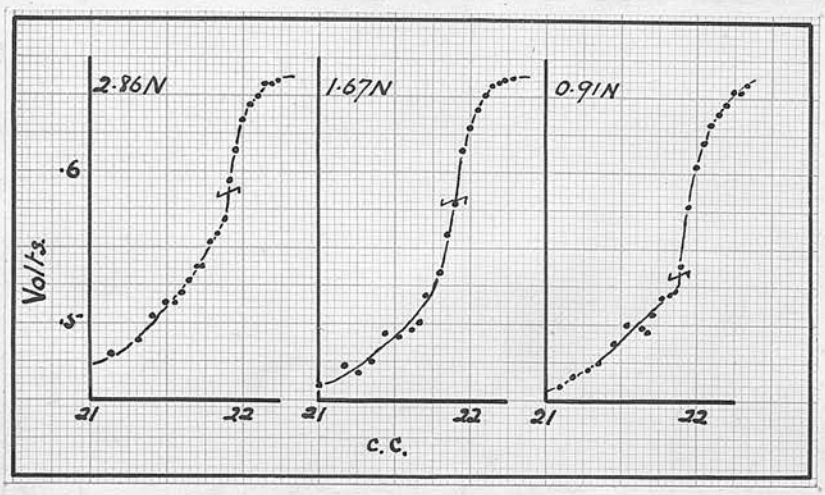


The titration of mixtures containing R and G salts was next investigated. The first of the three following curves shows the result of the titration of



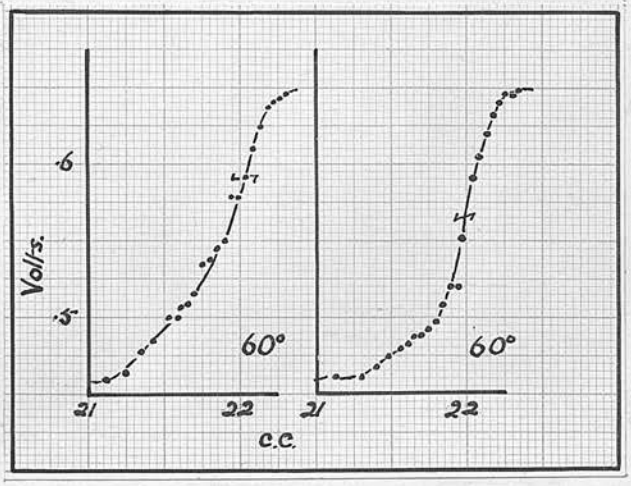
R salt alone, the other two being the curves obtained in the titration of the mixture at two acid concentrations when/

tions, when increments of two drops were added in the region of the end point. Another series was carried out, in which increments of one drop were added in the region of the end point. The most satisfactory



curve was given by the titration in 0.91N acid solution; a lower concentration (0.5N) gave unsatisfactory curves (not given).

Two titrations of the R-G mixture were done at 60°, but the curves were not satisfactory.

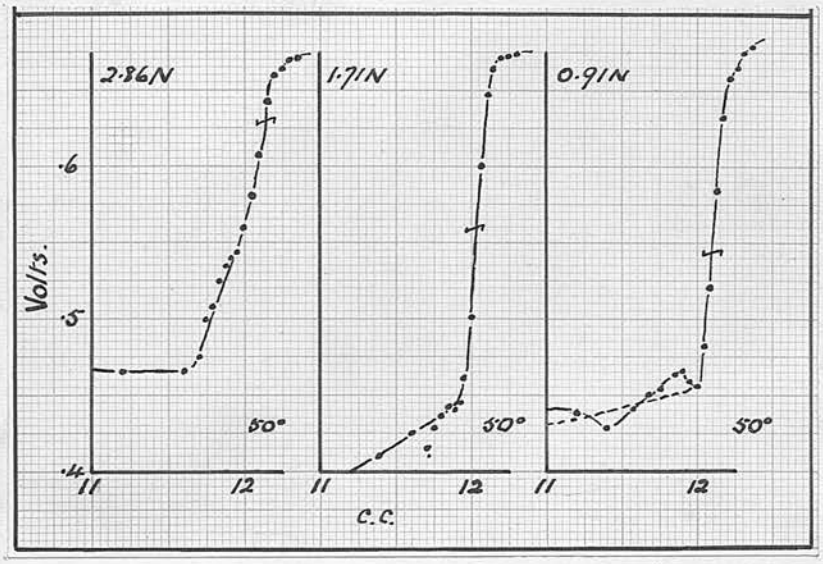


It will be noticed that all the graphs of titrations in 2.86N acid concentration showed the long rise of potential before the end point. The potential fell slowly with time, after the completion of the titrations at 50°, and very quickly at 60°.

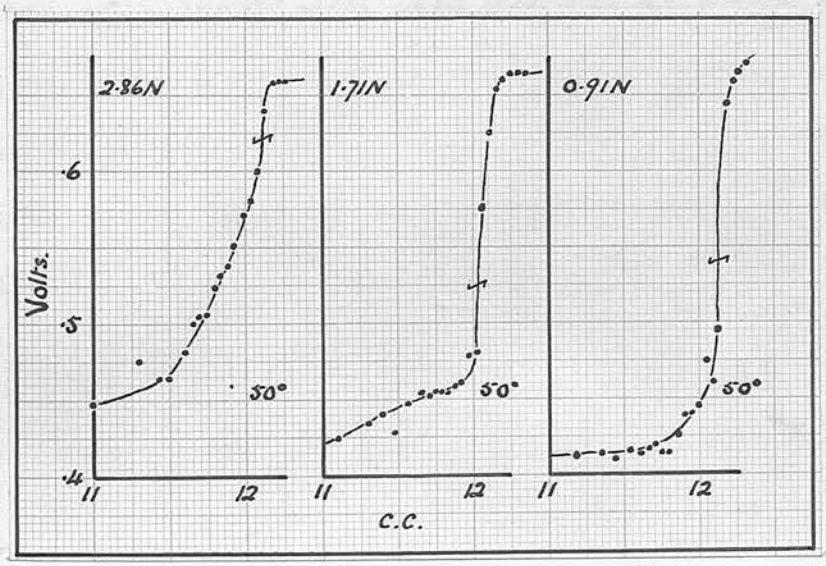
The TITRATION of MIXTURES containing SMALL PROPORTIONS of SCHAFFER and R SALTS.

At the time when the titration of such mixtures was being carried out in sulphuric acid solution, the total sulphonate content was also determined. The following graphs were obtained:-

(a) "Total" of R-G mixtures.

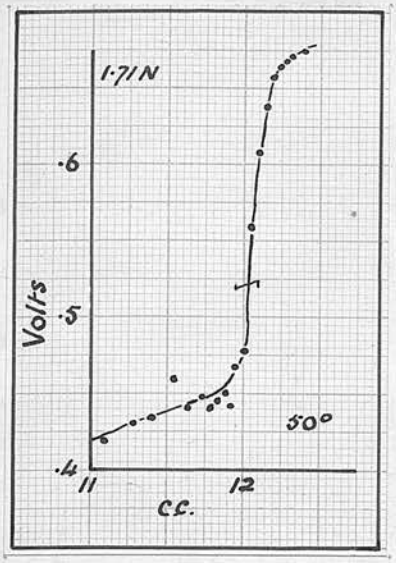


(b) "Total" of Schäffer-G mixture.



(c) "Total" of Schäffer-R-G mixture.

(See next page).



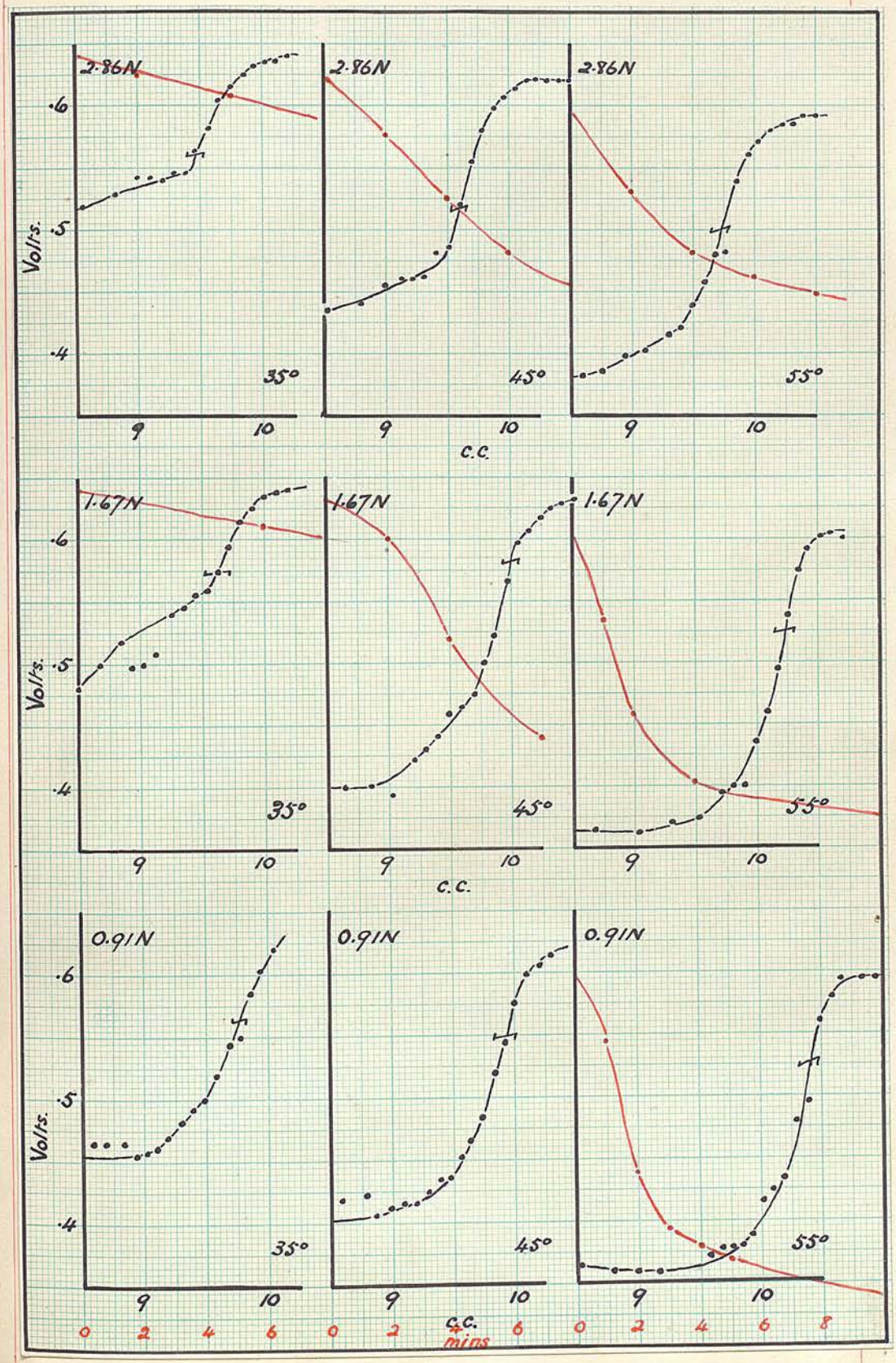
The mixtures were made up in the same way as in the previous experiments (see p. 87).

The curves of titrations at 2.86N acid concentration were unsuitable for the detection of the end point with any degree of accuracy. An acid concentration of 1.7N gave the most accurate results (0.5 c.c. too high); Schäffer salt always gave too high results alone and in mixtures when the acid concentration was 0.91N.

Hence it appears that the most suitable concentration of hydrochloric acid for the determination of mixtures containing Schäffer or/and R salt and G salt is 1.67N (10 c.c. concentrated (10N) acid to 50 c.c. solution): the temperature of the solution should be 50° during the titration.

DETERMINATION of CROCEIN SALT.

When Crocein salt was titrated in 1.67N hydrochloric acid solution at 40°-45° with starch iodide paper as indicator, no distinct end point was discernable. Therefore, it was decided to submit the

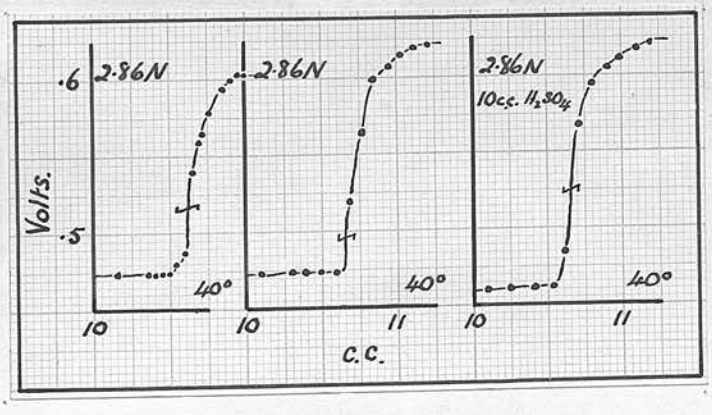


Crocein salt to potentiometric titration under varying conditions of acidity and temperature. The solution used contained 7.000 gms. of the salt in 500 c.c.; the various solutions were made up as described previously.

The curves obtained under the various conditions are given on the previous page. The curves in red show the rate of fall of potential with time after the completion of the titration. In 0.91N and 1.67N acid solutions, the end points increased with rise in temperature, but at 2.86N acid concentration the end points were much the same - 9.45, 9.6, 9.7 c.c. It was therefore decided to take this last concentration and 40° as the best conditions for the titration of Crocein salt.

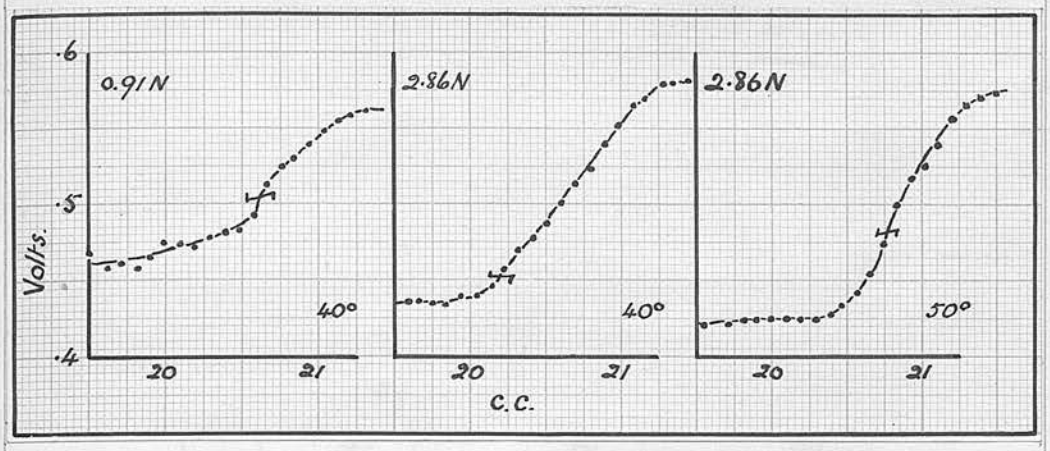
Using these conditions, a number of titrations of single salts and mixtures were carried out, the curves for which are given below.

(a) Schäffer salt alone.



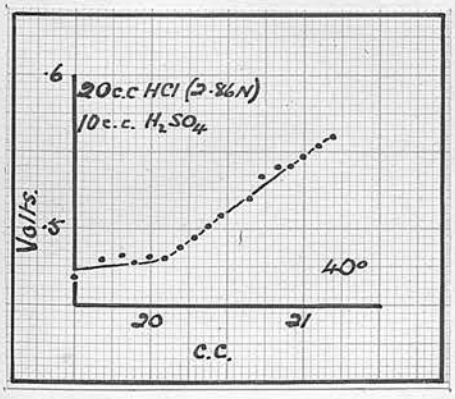
All the curves give practically the same end point.

(b) "Total" of Schäffer-Crocein mixture.

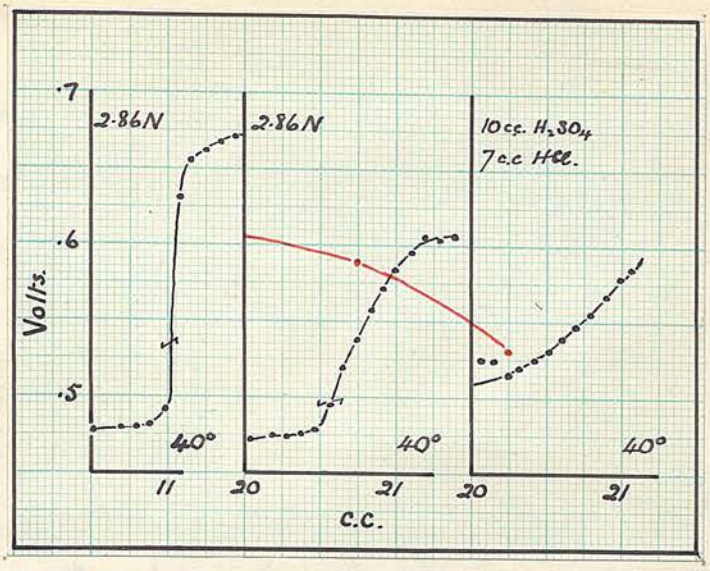


The end point indicated on the curve of the titration at 2.86N acid concentration and 40° was practically correct (0.05 c.c. too high), but the end points given by the other two graphs were much too high.

Since, sulphuric acid was found to prevent the bromination of Crocein salt, it was thought that a mixture of hydrochloric and sulphuric acids might lead to better results, the latter preventing the second bromine atom entering the molecule readily. But the curve obtained was less useful than the one obtained with hydrochloric acid alone under the same conditions. The curve obtained on titrating Schäffer salt alone with the same acid mixture is given under (a) on the previous page. It was quite normal.



(c) "Total" of R-Crocein mixture.



The titration under the standard conditions chosen for Crocein salt gave the correct end point. Titration in a hydrochloric-sulphuric acid mixture gave a useless curve.

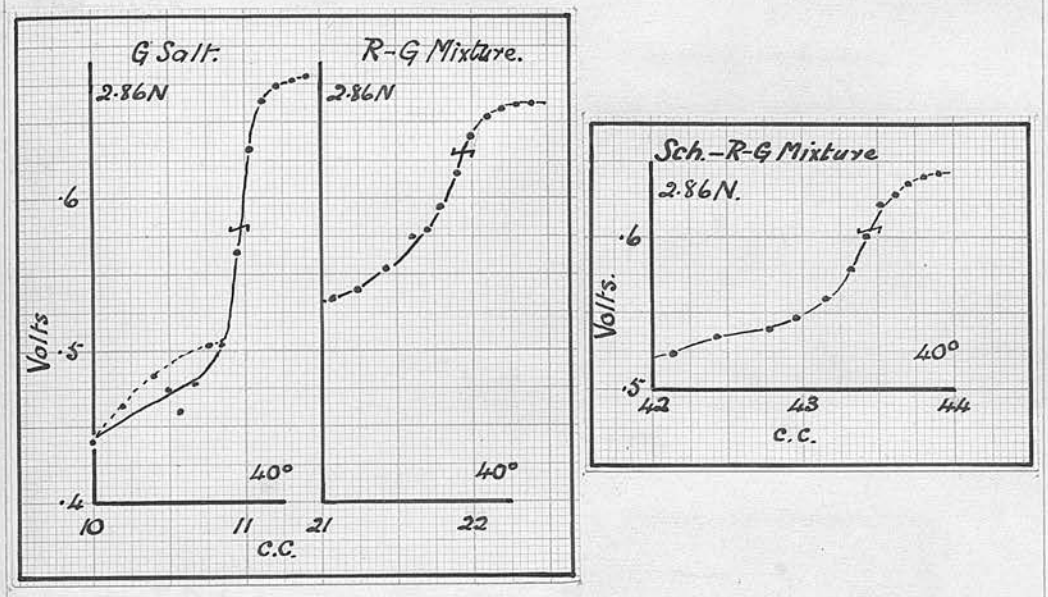
Now that conditions (2.86N acid and 40°) had been established for the titration of certain Crocein salt mixtures, it appeared necessary to carry out titrations of G salt mixtures under the same conditions to see if the same conditions would be suitable for both cases. Already they had been found suitable for the Schäffer-G salt mixture (p.96), but when the "total" of an R-G salt mixture was ascertained, the curve, as would be expected, was not too good, although the end point given was correct. Even G salt alone gave irregular readings before the large rise in potential. This showed that either

(1) the temperature was just on the low side for the minute wait, or conversely,

(2) the minute/

(2) the minute wait was not long enough for the lower temperature.

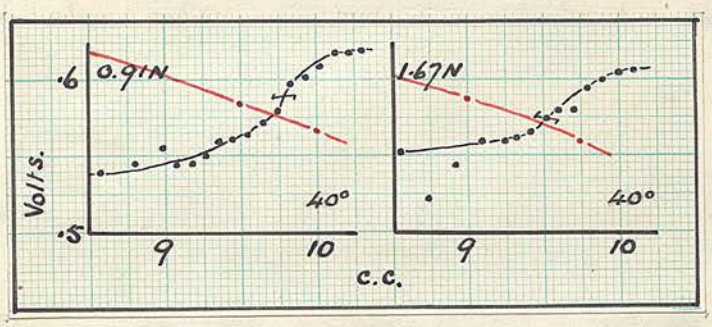
Proceeding, a mixture containing 25 c.c. each of Schäffer and R salt solutions and 50 c.c. G salt solution was made up and titrated at 40° after adding 40 c.c. concentrated hydrochloric acid. A curve



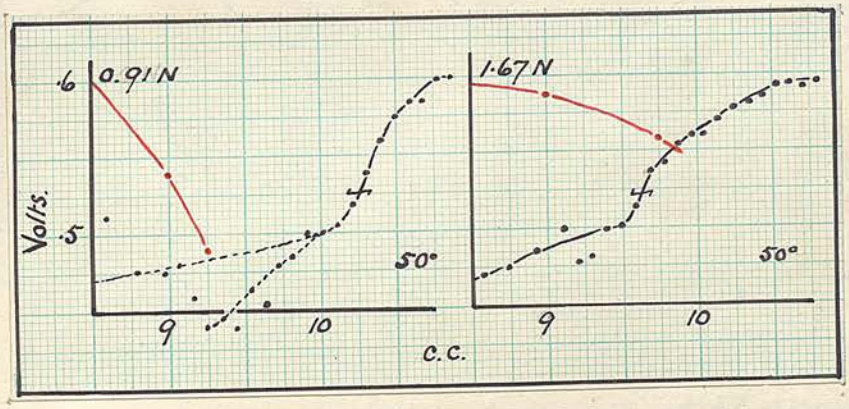
very similar to those obtained in the case of the R-G mixture appeared, but the end point was in close agreement with the theoretical, viz., the sum of the separate end point volumes.

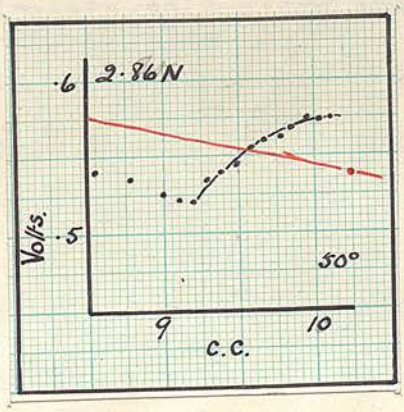
After completing the experiments on the effect of the addition of potassium bromide on the titrations in sulphuric acid solution, the effect on Crocein salt titrations was looked into. Vaubel's original method of adding acid and bromide to the solution and titrating with bromate solution was first tried at 40° under different acidities. 10 c.c. of a 20% solution of potassium bromide were added in each experiment. It was found that Crocein salt brominated much/

ated much more slowly under these conditions than when the solution was titrated with bromide-bromate solution. After adding about 2 c.c. of the bromate solution, the potential of the indicator electrode rose to about 550 mV. and remained at that value until the end point was reached when a slight rise was shown. The curves obtained were unsatisfactory.



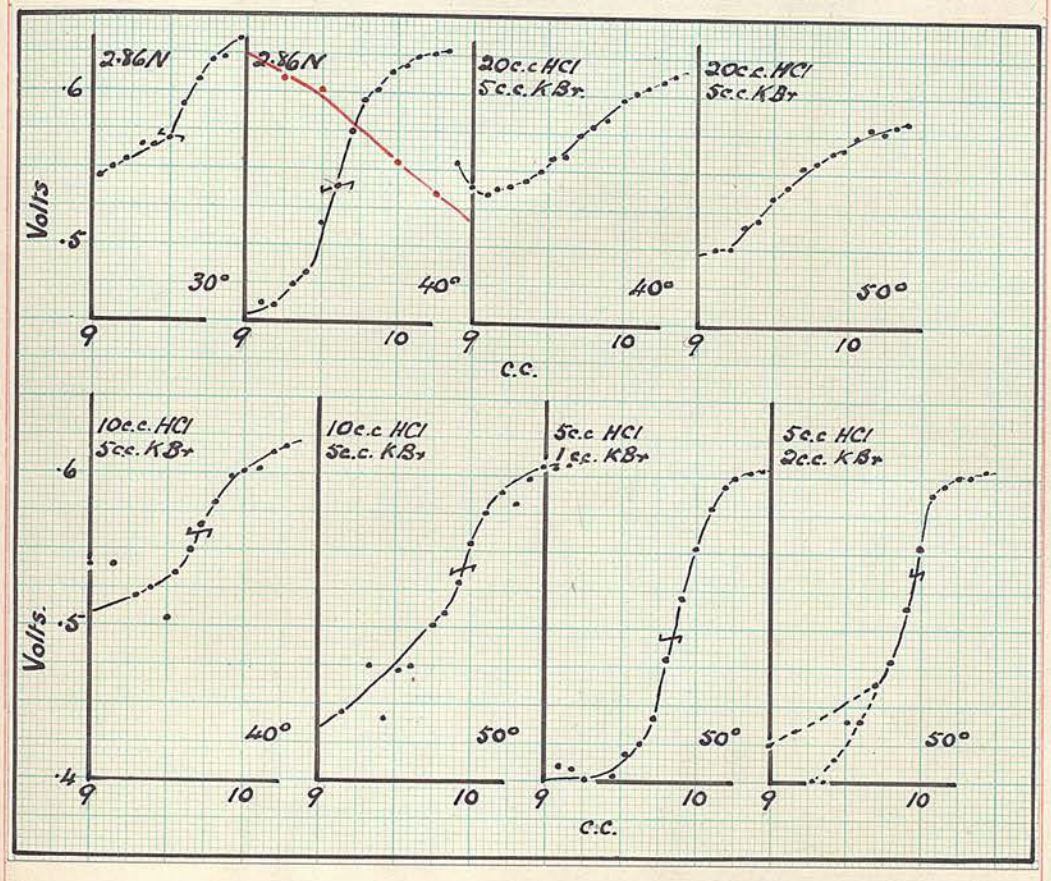
Three titrations at 50° were carried out using the same method, but the curves were unsatisfactory.





Spotting on starch iodide paper gave a blue stain all through the titrations at 40°, but no end point was detectable at 50°.

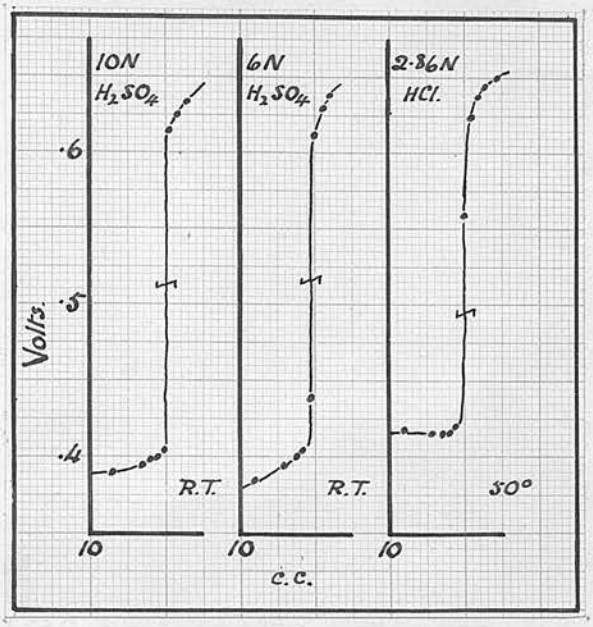
Lastly, a series of titrations of Crocein salt alone with bromide-bromate solution was carried out under different conditions with the addition of potassium bromide before the commencement of the titration. No improvement was noticed in the graphs.



The graphs given show that the quantitative estimation of Crocein salt alone and of mixtures containing it is still unsatisfactory and that the presence of excess potassium bromide retards the bromination of the salt.

Finally, it was noticed that the amount of bromide-bromate solution required for the titration of Schäffer salt alone varied from 10.40 c.c. to 10.65 c.c. Three consecutive titrations were carried out with the same Schäffer salt solution under different conditions/

different conditions. The curves obtained showed



that the variation was due to the stock of Schäffer salt not being uniform and not to the various methods tried.

GENERAL NOTES on CURVES obtained in TITRATIONS in SULPHURIC ACID SOLUTION.

When "spotting" on starch iodide paper was carried out in parallel with the potentiometric titration, no colour developed on testing immediately after the potential rise; a blue spot was however obtained after the next drop had been added. This proved that the platinum indicator electrode was a much more sensitive indicator than starch iodide paper in these titrations. This observation is one common to all potentiometric titrations, which can also be carried out by using coloured indicators.

One exception to the above was provided by R salt, when being titrated in N sulphuric acid solution (see p.74). At 10.92 c.c. (i.e. about two drops before the end point) a distinct spot was obtained indicating the presence of free bromine, and yet a potential jump took place at the proper point. An explanation of this phenomenon may be that, at this particular acid concentration, the bromine was being liberated rather slowly and the R salt was not able to take it up sufficiently quickly (within the minute interval), so that free bromine was present in the solution. Now if the higher potential of the indicator electrode is due to the equilibrium between the adsorbed bromine and the bromide ion in the solution, this equilibrium will not be established as long as there is unbrominated R salt present, since the adsorbed bromine/

adsorbed bromine may be expected to be more active and, therefore, the equilibrium at the electrode will be disturbed by bromination at it. This appears to be the only explanation for the fact that free bromine can be detected in the solution, but the indicator electrode is not showing its high potential. When all the R salt has been brominated, this brominating effect is not present and a true equilibrium between bromine and bromide ion is established.

Another peculiarity is shown by most of the curves. When a mixture is being brominated, the potentials before the rise are characteristic of the salt giving the highest potential, when it is being brominated alone under the same conditions. This may be better explained by an example. When Schäffer salt was brominated in N sulphuric acid concentration, the potentials before the rise were roughly 380 mV., while the corresponding readings for R salt under the same conditions were about 540 mV. When a mixture of the two was brominated under the same conditions, the potentials in the region considered were about 530 mV. (i.e. the higher value). The exact reverse holds in the case of the potentials obtained after the end point; these potentials are characteristic of the salt giving the lowest potential under the same conditions. For example, if G salt is "brominated" in 10N sulphuric acid solution, the maximum potential obtained is rather less than 600 mV., while/

600 mV., while Schäffer or R salt singly gives a maximum potential approaching 650 mV. Crocein salt shows this peculiarity to a more marked extent; when it is brominated in 10N sulphuric acid solution, the maximum potential is about 560 mV., and, in titrations of mixtures having Crocein salt as a component, the maximum potential never exceeds 550 mV.

The above observations may be explained in the following way. It has been mentioned that R salt brominates more slowly than Schäffer salt under the same conditions. Now, it is reasonable to expect that, in a mixture of these two, the Schäffer salt present will be fully brominated before the end point is reached, and hence the curve in the region of the end point will be more or less characteristic of R salt. Again, in the case of, say, a Schäffer-Crocein mixture, the titration is one of Schäffer salt up to the end point and the curve may be expected to be one characteristic of Schäffer salt up to the end point; but, after the end point, it is the equilibrium between bromine and Crocein salt that predominates and hence the curve after the end point will resemble that characteristic of the bromination of Crocein salt under the same conditions.

INDIRECT TITRATION of the SALTS and MIXTURES of THEM.

At the point in the investigation where the titration of R-Crocein mixtures was giving difficulty, the indirect method was turned to in the hope that it might lead to better results. The method of procedure was similar to that adopted by Redman, Weith and Brock in their thorough study of the determination of phenol by this method. The first salt to be tried was R salt.

For each titration, 25 c.c. of the standard R salt solution (9 gm. in 500 c.c.) were placed in an ordinary reagent bottle of 250 c.c. capacity with a close fitting glass stopper. 25 c.c. dilute (4N) sulphuric acid were added, followed by the bromide-bromate solution from a burette. An amount approximately 2 c.c. in excess of that required was run in and during its addition the bottle was gently rotated. After the addition of the brominating solution, the bottle was stoppered at once and shaken by hand for the time indicated in table I. The stopper was then removed, 20 per cent potassium iodide aolution added quickly and the stopper replaced. After shaking for the requisite time, the stopper was removed, washed down with distilled water, and the free iodine titrated with N/20 sodium thiosulphate solution, using a few drops of 1 per cent starch solution when the colour of the iodine had nearly disappeared.

The equivalency, in terms of the bromide-bromate solution, of/

solution, of the thiosulphate solution was determined in the following way. 20.00 c.c. of the bromide-bromate solution were diluted to 100 c.c. in a standard flask. 25 c.c. of this solution were pipetted out into a bottle, 2 c.c. of a 20% potassium iodide solution added and then 25 c.c. dilute sulphuric acid. The bottle was stoppered, shaken for two minutes and the free iodine titrated with the thiosulphate solution. From the figures obtained, the volume of bromide-bromate solution equivalent to 1 c.c. of the thiosulphate solution could be calculated. With this conversion factor, the volume of bromide-bromate solution equivalent to the volume of thiosulphate used in the back titration of the R salt was calculated and hence the volume of brominating solution absorbed by the R salt present. Practically all the titration were done in duplicate.

The conditions chosen for the first titrations were -

(1) time of bromination - 5 minutes,

(2) volume of 20% potassium iodide soln. added - 2 c.c.

(3) time for liberation of iodine - 3 minutes.

By progressively reducing these values, it was found that (1) could be reduced to 1 minute, (2) to 0.5 c.c. and (3) to 1 minute, without in any way affecting the results. Times less than one minute were not tried. Table I (on the next page) gives the results of the experiments with R salt alone.

TABLE I. - TITRATION of R SALT.

Expt. No.	Br_2 soln. added	Time	Vol. KI	Time	Thio.	Equi. Thio.	Br_2 abs.
	c.c.	min.	c.c.	min.	c.c.	c.c.	c.c.
1	13.00	5	2	3	8.00	1.99	11.01
2	12.99	5	2	3	8.11	2.02	10.97
3	13.02	2	2	3	8.15	2.03	10.99
4	12.98	2	2	3	7.95	1.98	11.00
5	12.97	2	2	3	7.96	1.98	10.99
6	13.01	2	2	3	8.00	1.99	11.02
7	12.99	2	2	2	8.03	2.00	10.99
8	12.99	2	2	1	7.86	1.96	11.03
9	13.01	2	2	1	8.06	2.01	11.00
10	12.99	1	1	1	7.94	1.98	11.01
11	12.99	1	1	1	7.92	1.97	11.02
12	12.98	1	1	2	8.04	2.00	10.98
13	13.00	1	1	2	7.90	1.97	11.03
14	12.98	1	0.5	1	7.92	1.97	11.01
15	13.00	1	0.5	1	9.60	2.39	10.61
16	12.97	3	0.5	1	7.98	1.99	10.98
17	12.00	1	0.5	1	3.93	0.98	11.02
18	15.10	1	1	1	16.46	4.10	11.00

Four miscellaneous titrations are given at the foot of the table. Experiments 15 and 16 were carried out in N acid solution, 12.5 c.c. dilute acid and 12.5 c.c. water being added to the 25 c.c. of R salt solution; they show that the bromination is not complete in one minute in N acid solution, but is complete in three. Experiments were carried out to see if the excess of brominating solution added had any effect on the results, but no variation was shown. This last point was found to be important in the case of mixtures.

A few trials were sufficient to show that the same conditions were suitable for the determination of Schäffer salt alone. The results are given in table II (see next page). Increasing the time of bromination, however, to 5 minutes caused a slightly higher result/

TABLE II. - TITRATION of SCHAFFER SALT.

Expt. No.	Br_2 soln. added	Time	Vol. KI	Time	Thio.	Equi. Thio.	Br_2 soln. abs.
	c.c.	min.	c.c.	min.	c.c.	c.c.	c.c.
19	12.54	1	0.5	1	8.23	2.05	10.49
20	12.56	1	0.5	1	8.26	2.06	10.50
21	12.60	5	0.5	1	8.03	2.00	10.60
22	12.63	5	0.5	1	7.92	1.97	10.66
23	12.69	5	0.5	6	8.37	2.09	10.60

higher result, proving that Schäffer salt was slowly dibrominating under such conditions and the extra bromine did not react with potassium iodide (Expt. 5).

In continuation, 25 c.c. of the standard G salt solution were added in place of the dilute acid and 6 c.c. of an 18N solution of sulphuric acid poured in to supply the necessary acid. In order that the acidity should be the same as before - 2N - and also that the total volume should be similar, 3 c.c. of concentrated (36N) sulphuric acid were necessary; but if such an amount were added, there would be a slight evolution of heat. To prevent this, the concentrated acid was diluted with its own volume of water and 6 c.c. of the diluted acid used in each case.

Table III (see next page) shows the extent of the variations tried. The employment of the conditions already proved suitable for the titration of R salt led to fairly good results. An increase of the time of bromination caused the results to be too high - 5 minutes, 1.5%; 10 minutes 3% - showing that the G salt was absorbing bromine slowly. An increase of acidity to 6N had no effect on the results. In

one titration/

TABLE III. - TITRATION of R SALT in PRESENCE of G SALT.

Expt. No.	Br_2 soln. added	Time	Vol. KI	Time	Thio.	Equi. Thio.	Br_2 soln. abs.
	c.c.	min.	c.c.	min.	c.c.	c.c.	c.c.
24	13.05	1	0.5	1	8.05	2.00	11.05
25	13.03	1	0.5	1	8.10	2.02	11.01
26	13.05	5	0.5	1	7.50	1.87	11.18
27	13.01	5	0.5	1	7.55	1.88	11.13
28[x]	13.02	5	0.5	1	7.45	1.86	11.16
29[x]	12.99	1	0.5	1	7.70	1.92	11.07
30	12.99	1	0.5	1	7.85	1.96	11.03
31	13.02	10	0.5	1	6.86	1.71	11.31
32	12.10	1	0.5	1	4.73	1.18	10.92
33	12.00	1	0.5	1	4.32	1.08	10.92
34	12.02	1	0.5	1	4.80	1.20	10.82
35	15.11	1	2.0	1	16.44	4.10	11.01
36	15.07	1	2.0	1	16.10	4.01	11.06

[x] - The acidity was 6N in these experiments.

one titration (expt. 32), 12 c.c. of bromide-bromate solution were added in mistake for 13 c.c. and a low result was obtained. A repeat titration confirmed the observation. A larger excess (4 c.c.) did not affect the results (expts. 35 and 36). Hence the conditions found suitable for the titration of R salt could be used for R-G salt mixtures provided that the excess of bromide-bromate solution added was not less than 2 c.c. Since longer times caused the G salt to brominate, it was thought advisable to select 1 minute as the standard period of bromination.

A few titrations (see table IV on next page) of the Schäffer-G salt mixture were sufficient to establish that, under similar conditions, Schäffer salt could be estimated in presence of G salt with an accuracy of about 0.5%. However, in this case, an excess of 1 c.c. was sufficient to lead to accurate results.

TABLE IV. - TITRATION of SCHAFFER SALT in PRESENCE of G SALT.

Expt. No.	Br_2 soln. added	Time	Vol. KI	Time	Thio.	Equi. Thio.	Br_2 soln. abs.
	c.c.	min.	c.c.	min.	c.c.	c.c.	c.c.
37	12.40	1	0.5	1	7.34	1.83	10.57
38	12.60	1	0.5	1	8.34	2.08	10.52
39	11.50	1	0.5	1	3.83	0.96	10.55
40	11.54	1	0.5	1	4.11	1.03	10.52
41	14.46	1	2.0	1	15.42	3.84	10.62
42	14.59	1	2.0	1	16.20	4.03	10.56
43	12.71	5	0.5	1	8.12	2.02	10.69
44	12.51	5	0.5	1	7.32	1.82	10.69

The titration of R salt in presence of Crocein salt was next investigated. As in the other methods considered, this titration gave rise to a certain amount of difficulty. Table V, on the next page, sets out the variations made and the results obtained in each case. The conditions already found suitable led to low results. Increase of acidity brought them higher, likewise an increase in the amount of bromide-bromate solution in excess. A study of the table will show that, when 10 c.c. of the 18N acid and an excess of 4 c.c. of bromide-bromate solution were employed, accurate results were obtained. One might argue that the increase of the excess used would provide a better opportunity for the Crocein salt to brominate, but this does not seem to be so, since the amount of bromine absorbed was not a linear function of the excess added, but came to a more or less constant value when 4 c.c. or over were added in excess.

TABLE V. - TITRATION of R SALT IN PRESENCE of CROCEIN SALT.

Time of Bromination - 1 minute.

Time to liberate Iodine - 1 minute.

Expt. No.	Acid	Br_2 soln. added	Vol. KI	Thio.	Equi. Thio.	Br_2 soln. abs.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
45	6	13.15	0.5	11.45	2.84	10.31
46	6	13.23	0.5	12.15	3.01	10.22
47	6	14.21	1.0	13.90	3.44	10.77
48	6	14.16	1.0	13.70	3.39	10.77
49	6	15.49	1.5	18.09	4.48	11.01
50	6	15.28	1.5	17.34	4.30	10.98
51	6	16.06	2.0	20.45	5.06	11.00
52	6	17.39	2.0	25.45	6.31	11.08
53	6	17.34	2.0	25.34	6.26	11.08
54	10	13.13	0.5	9.32	2.31	10.82
55	10	13.28	0.5	10.05	2.49	10.79
56	10	13.08	0.5	9.86	2.46	10.62
57	10	13.05	0.5	9.81	2.44	10.62
58	10	13.24	0.5	10.32	2.57	10.67
59	10	14.12	1.0	12.94	3.22	10.90
60	10	14.14	1.0	12.54	3.12	11.02
61	10	14.21	1.0	13.45	3.34	10.87
62	10	14.11	0.5	12.87	3.20	10.91
63	10	15.37	1.0	17.71	4.41	10.96
64	10	15.24	1.0	17.00	4.23	11.01
65	10	15.43	1.0	17.67	4.40	11.03
66	10	15.38	1.0	17.71	4.41	10.97
68	10	16.16	1.5	20.36	5.06	11.10
69	10	16.17	1.5	20.70	5.15	11.02
70	10	17.23	1.5	24.90	6.19	11.04
71	10	17.07	1.5	24.08	5.99	11.08

Table VI. - TITRATION of SCHAFFER SALT in PRESENCE of CROCEIN SALT.

Time of bromination - 1 minute.

Time to liberate iodine - 1 minute.

Expt. No.	Acid	Br_2 soln. added	Vol. KI	Thio.	Equi. Thio.	Br_2 soln. abs.
	c.c.	c.c.c	c.c.	c.c.	c.c.	c.c.
72	10	12.71	0.5	8.58	2.14	10.57
73	10	12.78	0.5	8.61	2.15	10.63
74	10	12.73	0.5	8.63	2.15	10.58
75	10	12.67	0.5	8.24	2.05	10.62
76	10	14.88	1.0	17.23	4.29	10.59
77	10	14.78	1.0	16.61	4.14	10.64
78	10	16.79	1.5	24.60	6.13	10.66
79	10	16.93	1.5	25.34	6.30	10.63

Table VI shows the results obtained in the titration of Schäffer-Crocein mixtures, with various excesses of bromide-bromate solution. Experiments 72 and 73 record the result of titrating Schäffer salt alone.

Summarising, it may be said that, to cover all the above possibilities, an excess of 4 c.c. and 10 c.c. of 18N sulphuric acid are necessary if results within 1 per cent are to be obtained. A series carried out under such conditions is recorded in table VII.

TABLE VII. - TITRATION of MIXTURES and SALTS.

Time of bromination - 1 minute.

Time of liberation of iodine - 1 minute.

Expt. No.	Br_2 soln. added c.c.	Time min.	Vol. KI c.c.	Thio. c.c.	Equi. Thio. c.c.	Br_2 soln. abs. c.c.
Schäffer salt alone.						
80	14.61	1	1.1	16.23	4.04	10.57
81	15.23	1	1.0	18.72	4.66	10.57
Schäffer-Crocein						
82	15.07	1	1.0	17.90	4.45	10.62
83	15.07	1	1.0	18.05	4.49	10.58
Schäffer-G						
84	15.17	1	1.0	18.18	4.52	10.65
85	15.13	1	1.5	17.98	4.47	10.66
86	15.18	1	1.5	18.21	4.53	10.65
R salt alone						
87	15.68	1	1.0	18.80	4.68	11.00
88	15.60	1	1.0	18.44	4.59	11.01
R-G						
89	15.62	1	1.0	18.05	4.49	11.13
90	15.55	1	1.0	17.89	4.45	11.10
R-Crocein						
91	15.56	1	1.0	18.55	4.61	10.95
92	15.68	1	1.0	19.08	4.75	10.93
93	15.57	1	1.0	18.48	4.60	10.97
94	15.56	1	1.0	18.42	4.58	10.98

The results are all within 1 per cent.

INDIRECT METHOD using HYDROCHLORIC ACID to LIBERATE the BROMINE.

A number of miscellaneous titrations were carried out, using hydrochloric acid to liberate the bromine. These were more of theoretical interest than of practical value. The results may be summarised as follows.

The concentration of acid (between 0.91N and 2N) had no effect on the determination of Schäffer or R salt, but increase of the bromination period led to a slight amount of dibromination of Schäffer salt. When mixtures of either of these two salts with G salt were brominated, the amount of bromine absorbed was in excess of that required for the Schäffer or R salt alone; it was found that the more bromide-bromate solution added, the larger was the volume absorbed. The presence of sulphuric acid did not seem to influence the reaction very much. This observation showed that G salt was brominating quite readily at ordinary temperatures when an excess of bromine was present. This is interesting, since it explains why an end point could not be obtained when R salt was titrated in presence of G salt in hydrochloric acid solution by the direct method.

The determination of G salt by the indirect method was also tried, using higher temperatures, but was not very successful; the determination of Crocein salt was totally unsatisfactory.

COMPARISON of the INDIRECT METHOD with the DIRECT.

G salt brominated slowly in sulphuric acid solution, when the indirect method was used, necessitating a short bromination period, but this difficulty did not arise in the direct method, since at no period in the titration was there any great excess of bromine present, as in the case of the indirect method.

Where it can be used, the indirect method requires less time than the potentiometric method, a determination requiring about 6 minutes, compared with one half to three-quarters of an hour for a potentiometric determination. Further experiments may show that the wait of one minute is not necessary, and thus the time for a complete potentiometric titration may be reduced.

APPLICATION of SIMPLIFIED METHODS.

The application of a simplified method to the potentiometric titration of mixtures seems to be impossible, since the end point does not always occur at the same potential.

SUMMARY.

1. Crocein and G salts brominate extremely slowly in sulphuric acid solution, whereas Schäffer and R salts brominate readily.

2. The addition of a large excess of potassium bromide previous to titration with bromate solution decreases the rate of bromination of Crocein salt.

3. The temperature must not exceed 50°, when titrating in hydrochloric acid solution, owing to dibromination of all four salts to a slight extent above 50°.

4. Schäffer or/and R salt can be determined in the presence of Crocein or/and G salt by taking advantage of the different rates of bromination in sulphuric acid.

5. The total sulphonate content of mixtures containing Schäffer or/and R salts and G salt can be determined.

6. The total sulphonate content of mixtures containing Schäffer or R salt and Crocein salt can be determined (but not too satisfactorily).

7. The accuracy of the methods described is about one per cent.

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