STUDIES ON THE NEPHELOMETRIC ENDPOINT
OF ATOMIC WEIGHT TITRATIONS

THE ATOMIC WEIGHT OF SODIUM
The Ratio of Sodium Bromide to Silver

by

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SENSITIVITY OF THE ENDPOINT IN
THE NEPHELOMETRIC TITRATION OF
SILVER CHLORIDE

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THE ENDPOINT IN NEPHELOMETRIC
TITRATIONS OF SILVER BROMIDE
SENSITIVITY OF THE ENDPOINT OF SILVER CHLORIDE TITRATIONS

Introduction

Since the invention of the nephelometer by Richards in 1898 it has served in the best known method for the determination of atomic weights. The pure chloride or bromide of the element under consideration is titrated with pure silver nitrate, and the endpoint is determined by comparing the turbidity of two equal test portions of the supernatant liquid. One of these carefully prepared test solutions contains an added excess of silver, and the other an equivalent excess of halide. At the stoichiometrical point the concentrations of silver and halide in the analytical solution are equal, and it is assumed that under these conditions the two test portions will contain equal amounts of suspended silver halide and will be equally turbid. The nephelometer is an instrument by which the turbidities of the test suspensions may be quantitatively compared. Appropriate additions of dilute standard solutions of silver or halide are made to the analytical solutions until the ratio of the turbidities in the two test portions is unity.

Hurley (1) has considered the errors which might be involved in the determination of the endpoint. The basic principle that a solution of silver chloride at the stoichiometrical point will give equivalent turbidities, i.e. "equal opalescence," under the test conditions given above was established at room temperature by Richards (2), and has since been confirmed by several investigators. At zero degrees centigrade,
however, both Hurley and Johnson (3, 4) found an apparent excess of chloride in solutions of pure silver chloride. Cooling the analytical solutions in an ice bath to diminish the solubility of the silver halide and thereby increase the sensitivity of the nephelometric measurements is a procedure which has often been used in atomic-weight work. It appears that at least in the case of the chloride the correct endpoint is not one of equal opalescence at zero degrees. No such tests of the validity of the equal opalescence endpoint have been performed on solutions of silver bromide. One suggested explanation of the inconsistent behavior of silver chloride is based upon its decreased solubility at lower temperatures. It has been established that the solubility of silver chloride or bromide is first decreased and later increased by the addition of an excess of the halide ion to a saturated solution (1). This would cause the amount of silver halide suspended in the excess halide test solution to be less than that in the excess silver solution. This difference is insignificant relative to the total turbidity at room temperature, but becomes appreciable if the analytical solutions are cooled in ice before the test solutions are removed. Extending this reasoning to silver bromide leads to the prediction that a saturated solution of silver bromide might not exhibit equal opalescence, even at room temperature, since its solubility is roughly only one-fourteenth that of silver chloride. An investigation of this possibility seemed desirable.

The sensitivity of the nephelometric tests to an excess of silver or halide has been studied for the chloride by several investigators with rather conflicting conclusions. Richards
and Wells (2) in their pioneer experiments concluded that an opalescence ratio of 1.25 represented "an excess or deficiency of 0.15 mg. of silver per liter of solution and other amounts in proportion." From this they estimated the endpoint to be determined to within 0.02 mg. of silver assuming a final volume of one liter and the average of many nephelometer readings to be accurate to two percent. Weatherill (5) found that 0.2 mg. of silver or its equivalent of chloride produces a definite change from one side of the equilibrium to the other when near the endpoint, and estimated that the actual limits of uncertainty were within 0.1 mg. of silver. He did not, however, report the volume of the analytical solutions on which the tests were made.

Johnson (3) was apparently the first to perform experiments designed especially for determining the sensitivity of nephelometric tests. He states that when the measurements on silver chloride are conducted at room temperature there exists an uncertainty of 0.57 mg. of silver or its chloride equivalent per liter of solution. He selected two analytical solutions which had been shown to contain equivalent amounts of chloride and silver ions by his standard solution method at zero degrees, and allowed them to saturate at room temperature. He then titrated away from the endpoint with dilute standard solutions of silver nitrate and sodium chloride. There was no definite deviation from equal opalescence until the excess concentrations reached 0.36 mg. of silver and the chloride equivalent of 0.21 mg. of silver. At these points there was apparently a sharp break. The experiments were not extended
beyond these concentrations, and presumably they were not repeated despite their surprising results. His data are summarized in Table I, where the opalescence ratio given is the mean of all measurements at the corresponding concentration, usually about four. A positive ratio indicates an apparent excess of chloride over silver in the test solution, and a negative ratio indicates an apparent excess of silver.

Table I

<table>
<thead>
<tr>
<th>Excess Silver (mg. / liter)</th>
<th>Opalescence Ratio</th>
<th>Excess Chloride (as mg. Ag/liter)</th>
<th>Opalescence Ratio</th>
</tr>
</thead>
<tbody>
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<td>.00</td>
<td>1.01</td>
<td>0.00</td>
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</tr>
<tr>
<td>.45</td>
<td>-1.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is important to note that before any additions were made his two solutions gave ratios which differ by an amount appreciably greater than the variations among the check measurements at any one concentration. In testing the sensitivity at room temperature the solutions selected should show an initial ratio of unity, since it has been established that pure silver chloride has this property under usual analytical conditions.

At about the same time Briscoe (6) reported that a titration involving five to ten grams of silver in a final volume of four to six liters results in an uncertainty of 0.2 to 0.5 mg. of silver. This volume, however, is two to three times
larger than that used by most atomic-weight workers. Briscoe discarded the nephelometer altogether, and determined the endpoint by concentrating the decanted supernatant liquid of his analytical solutions to about twenty ml. by an elaborate evaporating system. He always assured an excess of two to three mg. of silver in the precipitation, and the exact excess was determined by titrating the concentrate with standard potassium thiocyanate using ferric alum as indicator. The practical difficulties encountered in this method are obvious.

Baxter and Alter (7) repeated Johnson's experiments using only one analytical solution to which they added both standard sodium chloride and standard silver nitrate. During the course of the experiment they reversed from one side of the equilibrium to the other four times. They found that near the endpoint a difference of 0.1 mg. of silver per liter altered the nephelometric ratio about ten percent. Although they made only a few determinations their data show a fairly consistent linear relationship between opalescence ratio and concentration of the excess ion.

None of these estimations of the sensitivity was complete enough to establish definite conclusions, and since their results disagree so widely a more thorough investigation of this problem was undertaken in order to furnish a more dependable basis for calculation of the precision of atomic-weight ratios established by the titration method.
EXPERIMENTAL STUDY OF THE SENSITIVITY
OF THE SILVER CHLORIDE ENDPOINT

Reagents.

The reagents used in the following experiments were all of the high state of purity demanded for atomic-weight research. Unless otherwise stated, the methods of purification and the precautions observed were the same as those described in detail by Hurley (8).

Preparation of the nephelometric test suspensions.

For each measurement of the opalescence ratio of a solution, two equal twenty ml. portions were withdrawn by a pipet and transferred to "uniform" precipitating vessels described by Scott and Hurley (9). Suspensions of silver chloride were formed by adding a two ml. portion of silver nitrate to one sample and an equal amount of equivalent sodium chloride to the other. The precipitants contained 1.0 mg. of silver per liter or the chloride equivalent. Use of these vessels allows simultaneous addition of the reagents to the nephelometer tubes and assures complete mixing. One hour was allowed for development of maximum turbidity before comparisons were made. Reproducibility of this method was shown to be satisfactory by Scott and Hurley.

Sensitivity of the equal opalescence endpoint for silver chloride titrations.

It was pointed out in the introduction to this paper that the meagre data so far obtained on the sensitivity of the equal opalescence endpoint for silver chloride titrations are both
confusing and incomplete. A series of three experiments was performed which were designed to clarify this situation. Several theories have been advanced regarding the behavior of silver chloride suspensions, and will be considered in the discussion of the results of these experiments.

The first measurements of the sensitivity of the nephelometric tests were made on solutions of silver chloride which as nearly as possible duplicated usual analytical conditions. One-fortieth of a mol of silver chloride was precipitated by adding 0.1 m silver nitrate very slowly from a buret to 0.1 M sodium chloride in a five hundred ml. tincture bottle. Both solutions were also 0.16 M with respect to nitric acid, and were kept well mixed during the precipitation. The silver nitrate was prepared from the C. P. salt which was twice recrystallized from pure nitric acid. The crystals were centrifuged with washing and dried over fused sodium hydroxide before weighing. The sodium chloride was taken from a sample which had been purified for atomic-weight analysis. Ten such precipitates were made, and washed six times with distilled water. This was followed by three washings with 0.16 M nitric acid. The wash solution was removed by suction through a glass tube which was connected to an aspirator through a trap bottle. By this method the liquid may be almost entirely removed without disturbing the precipitate, while washing by decantation usually results in some loss of the granular solid. The amount of precipitate per unit volume was equivalent to a typical analytical solution. Pure 0.16 M nitric acid was then added to
the five hundred ml mark, and the solutions saturated by frequent shaking for four or five days. After ascertaining that the opalescence ratio of each solution was unity within two percent, standard silver nitrate containing 0.1 mg. of silver per liter was added to solutions I to V in amounts equal to 0.1, 0.2, 0.3, 0.4, and 0.5 mg. of silver per liter of solution. Equivalent amounts of sodium chloride were added to solutions VI to X. After allowing at least four days for establishment of equilibrium, the opalescence ratio of each solution was measured. The solutions were shaken after each measurement, and usually five or six tests were made extending over a period of fifteen to twenty days. The liquid was then removed by suction, and the precipitates were again washed six times with water and three times with nitric acid as previously described. After saturation in 0.16 M nitric acid the opalescence ratio was checked to be unity within two percent. Additions of standard silver chloride or sodium nitrate were again made, extending the concentrations of the excess ions to 1.0 mg. of silver per liter of solution. Silver was added to the same solutions which had contained excess silver in the first additions (see Table II). These solutions were vigorously shaken twice a day for three or four days and then remained undisturbed for three and one-half months before measurements were made. The opalescence ratio of each solution was measured in the same manner as described for the previous experiment. Results of both experiments are given in Table II, and are shown graphically in figure 1. The ratio given is the mean of all measurements taken on each solution. The significance of the sign of the
ratio is the same as in Table I, and will be used throughout this paper.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Excess ion (mg. Ag/liter)</th>
<th>Number of measurements</th>
<th>Mean opelescence ratio</th>
<th>Average deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.1</td>
<td>4</td>
<td>-1.05</td>
<td>.01</td>
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<td>5</td>
<td>-1.21</td>
<td>.05</td>
</tr>
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<td>5</td>
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<td>.02</td>
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<td>4</td>
<td>-1.32</td>
<td>.08</td>
</tr>
<tr>
<td>III</td>
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<td>5</td>
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<td>.01</td>
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<td>.02</td>
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<td>.02</td>
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<td>VI</td>
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<td>1.05</td>
<td>.00</td>
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<tr>
<td></td>
<td>0.6</td>
<td>6</td>
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<td>6</td>
<td>1.09</td>
<td>.02</td>
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<td></td>
<td>0.7</td>
<td>5</td>
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<td>.02</td>
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<tr>
<td></td>
<td>0.8</td>
<td>4</td>
<td>1.26</td>
<td>.02</td>
</tr>
<tr>
<td>IX</td>
<td>0.4</td>
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<td></td>
<td>1.0</td>
<td>6</td>
<td>1.31</td>
<td>.07</td>
</tr>
</tbody>
</table>
Figure 1

Excess Chloride

Excess Silver

Concentration of Excess Ion (mg Ag per liter)

Opalescence Ratio
Figure 1 shows a rather regular increase in turbidity with increasing concentrations of either ion in excess. Beyond 0.5 mg. of silver per liter the turbidity in the presence of excess chloride seems to increase more slowly than in the presence of excess silver. This is in agreement with the previously mentioned discovery that the solubility of silver chloride is increased by the addition of an excess of chloride ion. There is no sharp break such as Johnson found at 0.36 mg. excess of silver per liter and the chloride equivalent of 0.21 mg. of silver per liter. Agreement with Baxter and Alter is much better. Both experiments show a linear relationship between turbidity and concentration of the excess ion, and both extrapolate to equal opalescence at the stoichiometrical point. They found that an excess of 0.1 mg. of silver per liter altered the nephelometric ratio about ten percent, which is twice the change in turbidity observed for that concentration in these experiments. Neither observation, however, failed to detect this excess, and it appears that 0.1 mg. of silver per liter is a safe lower limit for the sensitivity of the tests.

The assumption that an analytical solution of silver chloride which is not at the stoichiometrical point will not show an opalescence ratio of unity presupposes that the ion in excess predominates in the liquid. If this excess were effectively removed from the solution by preferential adsorption on the precipitated silver chloride, it would not be detected by the nephelometric tests until the excess had exceeded that amount necessary to satisfy the surface forces of
the precipitate. At this point a sharp break would be expected—such as that found by Johnson. It is well known that sols of the silver halides adsorb halide or silver ions (10). It is therefore conceivable that the presence of a granular precipitate might effect the endpoint of a silver halide titration. To examine this possibility the above experiment was repeated with solutions containing fused silver chloride which offers only a relatively small surface, and again with solutions which had been filtered through Munroe crucibles, and thus contained no solid salt.

The experiments with the solutions of fused silver chloride were carried out in the same manner as those of Baxter and Johnson. Only two solutions were used, and were titrated away from the endpoint by the addition of 0.1 M silver nitrate or sodium chloride from calibrated burets. The amount of surface exposed in the two solutions was roughly equal. One solution contained eleven grams of silver chloride in one piece, and the other contained seven grams in three approximately equal pieces. One month was allowed for saturation in 0.16 M nitric acid, with frequent shakings during this interval. The initial volume of each solution was two liters, and the opalescence ratio was checked at unity within two percent before additions were begun. Several measurements of the opalescence ratio were made after each addition. The solutions were well shaken after each measurement. The investigations were carried only to concentrations of the excess ion equivalent to 0.5 mg. of silver per liter. The results are summarized in
Table III and are shown in figure 2. They agree well with those of the previous experiment; the variation of turbidity with concentration of excess ion is again linear. The precision of measurements near the endpoint is not so good, and the ratio at concentrations beyond 0.5 mg. of silver is slightly greater.

Table III

<table>
<thead>
<tr>
<th>Excess Ion (mg. Ag/liter)</th>
<th>Number of Measurements</th>
<th>Opalescence</th>
<th>Ratio</th>
<th>Deviation</th>
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<tbody>
<tr>
<td>0.0</td>
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<td>0.00</td>
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<td>0.1</td>
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<td>1.00</td>
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<tr>
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<td>0.01</td>
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<tr>
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<td>0.01</td>
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</tr>
<tr>
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<td>0.00</td>
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</tr>
<tr>
<td>0.5</td>
<td>3</td>
<td>1.27</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

For the experiments on solutions from which all non-colloidal silver chloride had been removed, saturated silver chloride in 0.16 M nitric acid was filtered through Munroe crucibles into five hundred ml. tincture bottles like those used in the first experiment herein described. Equal opalescence was checked before any additions were made. Ten such solutions
Figure 2

Concentration of Excess Ion (mg Ag/liter)

Figure 3

Concentration of Excess Ion (mg Ag/liter)
were prepared, and additions of 0.1 M silver nitrate or sodium chloride were made from burets. Studies were made at each 0.1 mg. of silver per liter or its chloride equivalent up to 0.5 mg. The solutions were then frozen solid in a carbon dioxide-alcohol freezing mixture, and their opalescence ratios again measured. In every case there was little or no change, and the slight alterations which did appear had no definite sign. The solutions were then discarded, the bottles well washed, and the experiment repeated. Concentrations of the excess ion were chosen at intervals midway between those studied in the first measurements. The results of both series of measurements are given in Table IV, and are shown graphically in figure 3.

Table IV

<table>
<thead>
<tr>
<th>Excess ion (mg. Ag/liter)</th>
<th>Number of Measurements</th>
<th>Opalescence Ratio</th>
<th>Average Deviation</th>
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<td>Silver Chloride Measurements</td>
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<td>0.2</td>
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Table IV cont'd

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<td>Silver Chloride</td>
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<tr>
<td>.45</td>
<td>2</td>
<td>1.18</td>
<td>.01</td>
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</tbody>
</table>

Discussion of results.

Johnson (3) suggested that his observation of the failure of the equal opalescence method to detect additions of silver and chloride ions might be caused by adsorption of the added ions by the silver chloride precipitate. Even if the test portions were filtered through Munroe crucibles, an appreciable amount of silver chloride might remain suspended in the colloidal form. Hurley (1) concluded that the precipitate played little or no part in the non-equal opalescence observed at zero degrees. If the concentration of chloride is actually greater than that of silver it could result from preferential adsorption of silver by the precipitate on cooling the solution, or from the precipitation of more silver than chloride by formation of a complex ion such as AgCl₂. Hurley tested the endpoint in the absence of any precipitate by preparing standard solutions of silver chloride covering a wide range—including concentrations less than that of a saturated solution. He
found that the most dilute solutions showed an apparent excess of chloride, and this excess diminished regularly with increasing concentrations until it disappeared entirely at concentrations approaching the solubility of silver chloride at room temperature. The opalescence ratio of his standard solution corresponding to the concentration of silver chloride at zero degrees agreed very well with results on solutions at this temperature which contain precipitated silver chloride. He attributes the non-equal opalescence at low concentrations to failure of the fundamental postulate that turbidity is strictly proportional to the concentration of the ion precipitated.

The curves of figures 1, 2, and 5 are very similar, and show that the presence of a precipitate has no significant effect on the opalescence ratio of silver chloride solutions at room temperature. They follow the simple proportionality between turbidity and concentration of the excess ion which is the basis of nephelometric analysis. The sensitivity of the method is also independent of the presence of a precipitate. It is safe to estimate the lowest concentration of excess ion which can be detected with certainty to be 0.1 mg. of silver or its chloride equivalent per liter of solution. This conflicts with the findings of Johnson and Briscoe, but is in rather good agreement with the results of Baxter and Alter. It has been pointed out that the conclusions of all of these investigators were drawn from only a few measurements. These experiments justify the wide acceptance of the nephelometric titration of chlorides with silver in the determination of
atomic weights, and lend support to the claims of high accuracy by investigators using this method.
Following the early success of the nephelometer in determining the endpoint of silver chloride titrations, the method was extended to include the titration of bromides with silver. The validity of this step seems never to have been tested, although many atomic-weight investigations have been based upon it. It has been pointed out that although a saturated solution of silver chloride at room temperature exhibits equal opalescence, it does not follow that silver bromide necessarily possesses this property. The solubility of silver bromide is much less than that of silver chloride, and the turbidities of the test solutions will be correspondingly less. Because of this it has been assumed that the sensitivity of the nephelometric tests is greater than in the case of the chloride. However, any small difference in the solubility of silver bromide in an excess of silver or bromide would probably not be completely masked as in the case of the chloride at room temperature.

It was discovered early in this work that the nephelometer tubes must be clear and free from surface scratches. Tubes which had become slightly etched by repeated steaming served very well for chloride measurements, but did not give reproducible results for silver bromide. The total turbidity of a saturated solution of silver bromide is relatively very small, and any contribution by a factor other than suspended silver bromide leads to an appreciable error. New tubes were made from carefully selected six inch soft glass test tubes, and were checked several times by measurement of a known solu-
tion of silver bromide before acceptance. Even with these precautions it was found impossible to reproduce quantitative comparisons of opalescence. However, a few experiments concerning the endpoint of silver bromide titrations were performed, and the opalescence ratios were recorded merely as "apparent excess of silver or bromide" or "apparent equal opalescence."

A precipitate of 0.08 moles of silver bromide was formed under analytical conditions by adding 0.1 M silver nitrate slowly from a buret to 0.1 M sodium bromide contained in a two liter glass-stoppered bottle. The sodium bromide had been partially purified for atomic-weight work, and the silver nitrate was the same as that used in the experiments on silver chloride. Both solutions were 0.16 M with respect to nitric acid. The precipitate was washed eight times with distilled water and five times with 0.16 M nitric acid, removing the wash liquid through a glass tube by means of an aspirator as previously described. It was then covered with fifteen hundred ml. of 0.16 M nitric acid and allowed to stand undisturbed for three and one-half months. Test suspensions were prepared in the same manner as those of the chloride experiments. The turbidities were compared after one hour, and showed an apparent excess of bromide. It was thought that this apparent excess might result from the low concentrations of silver and bromide ions in the saturated solution, and, analogous to the chloride, disappear at higher concentrations. Accordingly, six standard solutions of silver bromide were prepared from the same dilute standard solutions used for the previous ex-
periment. They contained silver bromide equivalent to 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 mg. of silver per liter. The concentration of a saturated solution of silver bromide at room temperature is equal to about 0.08 mg. of silver per liter. Opalescence measurements were made in the usual way and all solutions showed apparent excess of bromide with the exception of the weakest, which showed equal opalescence. The total turbidity in both tubes increased regularly with increasing concentration of silver bromide, but the difference in turbidities at each concentration was approximately constant except for the weakest solution. It was later discovered that this apparent excess of bromide diminishes with increasing time after formation of the test suspensions, and disappears entirely in four to six hours. This result was also obtained with saturated silver bromide. On re-examination of the solution containing only 0.05 mg. of silver per liter, it was found that it too exhibited an apparent excess of bromide immediately after preparation of the test suspensions, but diminished more rapidly than the stronger solutions and showed equal opalescence after forty-five minutes. After aging for several months the standard solutions of silver bromide containing more than 0.10 mg. of silver per liter diminished in total turbidity of the test suspensions, and approached that of a saturated solution. Examination of these solutions in a Tyndall cone of non-actinic light revealed very small crystals of silver bromide which settled out if the solution was not disturbed for twenty-four hours. For saturated silver bromide maximum turbidity is
developed in the tube containing silver nitrate, i.e. "excess silver" tube, in about twenty minutes, but the excess bromide tube is practically dark at first and reaches maximum turbidity only after four to six hours of gradual change. It made no difference in the time required for establishment of equal opalescence whether the test suspensions were prepared by the "uniform" method of Scott and Hurley, or by adding the precipitant from a pipet to the solution contained in the nephelometer tube, followed by stirring with a glass rod. The suspensions are very stable. They show very little settling out after forty-eight hours, which is in contrast to Hurley's observation that suspensions of silver chloride are appreciably less turbid after standing for twelve hours (1).

The sensitivity of the endpoint in silver bromide titrations was examined by making small additions of silver and bromide to four analytical solutions of silver bromide which were at the equal opalescence endpoint at room temperature. The standard silver and bromide solutions used for the additions had been prepared for atomic-weight work, and contained 0.10 mg. of silver per liter or the bromide equivalent. To two of the analytical solutions silver was added equal to 0.05 and 0.10 mg. of silver per liter. Bromide equivalent to these concentrations was added to the other solutions. Four days was allowed for the establishment of equilibrium with frequent shaking during this interval. Opalescence measurements detected the excess ion in all four solutions. It was, of course, necessary to wait for the development of maximum turbidities before
comparisons were made.

It thus appears that the equal opalescence endpoint for silver bromide titrations is valid at room temperature if the comparisons are made after four to six hours. The high sensitivity of the endpoint is also confirmed; an excess of 0.05 mg. of silver per liter or its bromide equivalent can definitely be detected, although quantitative comparisons of the turbidities of the test suspensions is very difficult. It is imperative that the nephelometer tubes used be clear and free from surface scratches.
THE ATOMIC WEIGHT OF SODIUM
INTRODUCTION

The first modern determination of the atomic weight of sodium was made by Richards and Wells (11) in 1905. Their classic experiments on the atomic weights of chlorine and sodium are well known, and the present-day value for sodium is based on their data. They made ten determinations of the ratio NaCl:Ag, yielding values for the atomic weight of sodium of 22.997 and 22.998 respectively when recalculated on the basis of the 1939 values for the antecedent weights.

Determinations designed especially to obtain the atomic weight of sodium have also been performed by Goldbaum (12), Johnson (13), and Greene and Josie (14). The results of these determinations are tabulated below:

1. Goldbaum.

NaCl:Cl . . . . . . . . . . . 22.996
NaBr:Br . . . . . . . . . . . 22.997

In these experiments an aqueous solution of sodium bromide or chloride was electrolyzed, using a weighed anode and a mercury cathode which amalgamated the liberated sodium. The halide precipitated on the anode and the increase in weight represented the halide content of the salt, excepting the small amount remaining in solution which was determined nephelometrically. Eighteen experiments on the two solts were in excellent agreement. One criticism of this work is that the samples used were very small, often
between one and two grams. The electrolytic method offers no great advantage over the usual precipitation of silver halide, and introduces possible complications at the electrodes.

2. Johnson.

\[
\text{NaCl:Ag} \quad \ldots \ldots \ldots \quad 22.994
\]

3. Greene and Josie.

\[
\text{NaCl:Ag} \quad \ldots \ldots \ldots \quad 22.994
\]

In addition to these direct determinations, there are available a number of determinations of mass ratios involving the atomic weight of other elements. Assuming suitable values for the necessary antecedent atomic weights, the atomic weight of sodium can be calculated from these ratios. Not all are suitable for such calculations, however. The best of these determinations are those involving sodium carbonate, which have been recalculated by Scott and Hurley on the basis of the value 12.010 for carbon. A summary of these follows:

1. Richards and Hoover (15).

\[
\text{Na}_2\text{CO}_3:2\ \text{AgBr} \quad \ldots \ldots \ldots \quad 22.993
\]

\[
\text{Na}_2\text{CO}_3:2\ \text{Ag} \quad \ldots \ldots \ldots \quad 22.994
\]

2. Baxter and Hale (16).

\[
\text{Na}_2\text{CO}_3: \text{I}_2\text{O}_5 \quad \ldots \ldots \ldots \quad 22.994
\]

A survey of these determinations made since the analyses of Richards and Wells indicates rather strongly that the value 22.997 for sodium is too high. The only exception to this observation is found in the electrolytic determinations of
Goldbeum. In one respect, at least, the situation with regard to the atomic weight of sodium is unique. The atomic weights of practically all other elements which are available as simple halides have been determined by the titration of both the chloride and the bromide with silver. For sodium, however, no accurate measurement of the ratio NaBr:Ag has been made. Richards and Wells made two supplementary measurements of this ratio in connection with the purification of NaBr.2H2O which they had prepared to be used in establishment of its transition point as a fixed point in thermometry (17), but these are the only such analyses which have been reported.

Purification of compounds of sodium offers some difficulty because of the similarity of their physical and chemical properties to those of the most likely impurities. Investigators of the NaCl:Ag ratio have resorted to precipitation of sodium chloride from hydrochloric acid, followed by many fractional crystallizations with rejection of large head and tail fractions. Fusion removes traces of water and occluded gases. Sodium bromide possesses excellent properties for efficient purification. It may be synthesized from re-agents which may be highly purified, and recrystallized in a lattice form different from that of all probable impurities (18, 19, 20).
Throughout this work the utmost care was observed regarding cleanliness, and all materials used were highly purified. The purification of water, nitric acid, and other common reagents of atomic-weight analyses has been described in detail in many atomic-weight papers. The silver used was purified by Hurley for the evaluation of the ratio benzoyl chloride:silver (8). It had been stored in stoppered weighing bottles which were kept in a desiccator over fused sodium hydroxide. To remove the remote possibility that any surface oxidation had occurred, the silver was heated to 400° C. in a system evacuated to 10⁻³ mm. of mercury by means of a Langmuir pump in series with a Cenco Hyvac pump.

**Preparation and Purification of Sodium Bromide.**

It was desired to prepare sodium bromide by the reaction of bromine with some sodium compound which would not introduce by-products difficult to remove. An attempt was made to accomplish this result by the action of bromine on sodium oxalate, analogous to Richards and Mueller's preparation of potassium bromide (21). Preliminary experiments proved this reaction to be unsuitable, however, because oxalic acid was "salted out" when the concentration of sodium bromide became appreciable. This decreased the velocity of the reaction below a practical rate, since the action of bromine on oxalic acid in the solid state is very slow. It was found that this disadvantage was eliminated if sodium formate was used in place of the oxalate. Reaction with bromine has been used as a basis for the determination of formic acid (22). The
reactions which occur in this synthesis of sodium bromide may be represented by the following equations:

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + \text{HCO}_3^- & \rightarrow \text{NaHCO}_3 + \text{Na}_2\text{O}^- \\
\text{Na}_2\text{O}^- + \text{Br}_2 & \rightarrow \text{HBr} + \text{NaBr} + \text{CO}_2 \\
\text{HBr} + \text{NaHCO}_3 & \rightarrow \text{NaBr} + \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

\[
\text{Na}_2\text{CO}_3 + \text{HCO}_3^- + \text{Br}_2 \rightarrow 2\text{NaBr} + 2\text{CO}_2 + \text{H}_2\text{O}
\]

The carbon dioxide can be removed by gentle boiling, leaving only a solution of pure sodium bromide in water. The method calls for highly purified sodium carbonate, formic acid, and bromine.

The sodium carbonate was purified by repeated crystallization from pure water. Its solubility is greatest at temperatures just exceeding the melting point of the decahydrate, i.e. about 35°C, and decreases rapidly with temperature. The solid phase in stable equilibrium with a saturated solution below 31°C is the decahydrate (23), but under certain conditions a metastable heptahydrate is obtained which is very difficult to filter. When this occurred the solution was reheated to dissolve the undesired hydrate, and again crystallized by cooling. On some occasions the solution was seeded with a few crystals of decahydrate from another fraction of the crystallization. The starting material consisted of 800 grams of C. P. anhydrous sodium carbonate. The progress of the purification is represented in fig. 4. Porcelain vessels were used in some instances in the crystallizations represented above the dotted line, but all of those below the line were performed entirely in platinum. The solutions of sodium car-
bonate were filtered through a Munroe crucible before each crys-
stellization. Several nephelometric tests were made on various
fractions during the process, but none showed the presence
of a detectable amount of halide.

![Diagram](image)

Fig. 4

Fractions A and B contained 1040 grams of sodium carbonate
as the decahydrate. This is slightly less than half of the
original carbonate.

The formic acid was obtained from 600 ml. of the C. P.
acid which gave a negative test for halide. This material
was distilled three times in an all glass apparatus and con-
densed in quartz. The first quarter and the last 25 ml.
were rejected in each distillation. By this procedure 200
ml. of the pure acid was obtained.

Preliminary purification of bromine was accomplished by
distillation of two pounds of Mallinckrodt's analytical grade
bromine from a 50% solution of C. P. sodium bromide (24). The distillation was carried out in two steps, using one pound of bromine in 600 ml. of sodium bromide for each distillation. The pyrex distilling flask was fitted with a ground glass stopper, and the side arm extended directly into a quartz condenser. The adapter and receiving bottle were of pyrex glass, so that at no time during the distillation did the bromine come in contact with a chemically active surface. From both distillations 785 grams of bromine were obtained. The bromine at this point may have contained traces of iodine which were carried over with the bromine. Any chlorine would have been converted into chloride by displacement, and therefore would remain with the residue in the still.

The purified bromine, formic acid, and sodium carbonate were used in the synthesis of sodium bromide by the method already outlined. Three portions of about 0.4 mol each were taken from fraction A of the sodium carbonate and dissolved in one liter of water. Formic acid, diluted with an equal volume of water, was added to the carbonate solution in an amount slightly in excess of that required for half neutralization. This amount was determined by the analysis of a small portion of the carbonate solution. This excess is necessary to insure the complete conversion of the sodium carbonate into sodium bromide. Bromine was then added slowly to the mixture from a dropping funnel, the stopcock of which contained no lubricant. The reaction is exothermic, and the flask was cooled in a water bath to prevent distillation of the bromine as
it was added to the hot solution. Slightly more than the stoichiometrical amount of bromine was used, evidenced by a permanent light brown color. Concentration of the solution by gentle boiling removed the excess bromine, and left a clear solution of sodium bromide. When the volume was reduced to 300 ml, the solution was transferred to a 500 ml platinum evaporating dish, and further evaporation on an electrical hot plate at 45°C yielded crystals of NaBr·2H₂O. Control of the evaporating temperature is necessary because the solid phase which separates from the solution above 52°C contains some anhydrous salt which forms a hard bulky mass very difficult to handle (25). After appreciable crystallization had occurred the solution was cooled to 5°C. in an ice bath, and the crystals transferred to Buchner funnels which fitted into centrifuge cups. The crystals were centrifuged for several minutes at about 1500 r. p. m., after which they were washed with distilled water and centrifuged again. The separated mother liquor and the wash water were caught in small flasks and returned to the decanted solution in the platinum dish. Because of the great solubility of sodium bromide in water, the crystallization process is not very efficient. Further evaporation yielded more NaBr·2H₂O and the operations were repeated until only a small fraction of the sodium bromide remained in solution. The crystals of the dihydrate thus obtained were combined and twice recrystallized by evaporating the solutions at 50°C. and reclaiming the sodium bromide in the mother liquor as in the previous step.
An odor of bromine was noticed when the crystals were dissolved for the first crystallization, indicating that some occlusion had occurred. No odor was detectable when the crystals were dissolved for the second time. About 85% (293 grams) of the theoretical yield of NaBr·2H₂O was obtained. Five or six evaporations were necessary to obtain this efficiency. Experiments previously described on the silver bromide endpoint were conducted on a precipitate prepared from 11.2 grams of this material.

The sodium bromide was next dissolved in 800 ml. of water in a two liter distilling flask, and was used to generate the bromine for the final synthesis of sodium bromide. A 0.5 M solution of twice recrystallized potassium permanganate was added slowly from a dropping funnel which fitted into the flask. After liberation of a small amount of bromine, the funnel was removed and the solution boiled for ten minutes to eliminate any iodine which might be present. The funnel was then replaced, and the addition of permanganate continued. The bromine liberated from the solution was condensed and collected as described for the first distillation. When 70 grams had been collected the distillation was stopped and the receiving bottle changed. This first cut will be referred to as bromine I. The process was then continued until potassium permanganate equivalent to 80% of the theoretical quantity of bromine had been added. These calculations were based on the reduction of MnO₄⁻ to MnO₂. The bromine obtained in the second part of the process (50 grams) will be called bromine
The second synthesis of sodium bromide from the bromine so obtained was performed exactly as described in the first preparation, except that fraction B of the sodium carbonate was used. The formic acid was again tested to insure the absence of halides. The conversion was carried out in two steps, using bromine I in the first step and bromine II in the second. The resulting products were kept separate, and were called NaBr I and NaBr II respectively. These preparations were recrystallized in the manner described for the first sodium bromide. The crystallization diagrams are given in figures 5 and 6. "Preparation I" and "Preparation II" are central fractions of these crystallizations.

Fig. 5

Head Fraction

Prep I

46 g.m.

Tail Fraction

Fig. 6

Head Fraction

Prep II

23 g.m.

All rejected head and tail fractions of these two crystallizations were combined and recrystallized. The diagram for this step is given in figure 7.

Fig. 7
A central fraction, "Preparation III," was divided into two portions by fractional crystallization. The first crystals to appear (15 grams) were called "Preparation IIIa," and the crystals from the remaining solution were called "Preparation IIIb" (20 grams).

These four samples were stored in platinum or silica dishes, and placed in a desiccator over fused sodium hydroxide for several months to remove the water of crystallization. The desiccator was evacuated to about 30 mm. of mercury. The salt effloresced, leaving the sodium bromide as a white finely divided powder. These samples were used for the determination of the ratio $\text{NaBr:Ag}$. 
**Weighing.**

The weighings were made by the method of double weighing on a No. 10 Troemner balance, using brass weights which had been calibrated by Richard's method (26). The air density was measured by Baxter's bulb method (27) after each weighing, and all weights were reduced to the vacuum basis. In calculating vacuum corrections the following densities were used: platinum = 21.5, silver = 10.5, weights = 8.36, sodium bromide = 3.205, aluminum = 2.7. The method of calculating the vacuum correction for the fused sodium bromide sample will be discussed later.

**Fusion and Weighing of Sodium Bromide.**

Approximately five grams of the dehydrated salt was taken for each analysis. The sample was fused in a platinum boat in an atmosphere of pure dry nitrogen, and bottled by means of the "Harvard bottling apparatus" (28, 29). In carrying out the fusion it is necessary to remove all traces of oxygen and water to prevent a partial decomposition resulting in loss of bromine or hydrobromic acid (30, 31).

The nitrogen in which the sodium bromide was fused was obtained from a commercial cylinder. It had been prepared by fractional distillation of liquid air. In order to remove any oxygen impurity, the nitrogen was passed through a 12 mm. pyrex tube containing 50 cm. of tightly rolled copper net spirals. This tube was heated to about 400°C. by a ribbon burner. Reaction with oxygen caused the appearance of the dark oxide on the surface of the copper, which was occasionally
regenerated by heating in a stream of pure electrolytic hydrogen. After the removal of oxygen the nitrogen was passed through a drying train consisting of six Bamberling towers filled with glass beads. The first two contained 50% potassium hydroxide and the last four contained concentrated sulfuric acid. Following this, the gas passed through a glass tube 80 cm. long filled with small pieces of sodium hydroxide which had been fused with a few crystals of potassium permanganate to remove any organic matter. Finally, the nitrogen was passed through a U tube containing phosphorus pentoxide suspended on glass beads. This powerful desiccant remained as a white powder throughout the experiment, an evidence of the high efficiency of the drying train. The connection between the nitrogen tank and the glass tube containing the copper was made by means of a rubber tube which had been carefully cleaned. The remainder of the apparatus was constructed entirely of glass. A ground glass joint connected the drying train to the bottling apparatus. The arrangement of the equipment is shown in figure 8.

A sample of sodium bromide weighing about five grams was placed in a platinum boat and put in the quartz heating tube of the bottling apparatus. The system was swept out with nitrogen for one hour. The sample was then heated at a temperature of about 200°C for four hours by means of a tube furnace which fitted around the quartz heating tube. After this period of drying the temperature was raised to about 400°C, and there maintained for an additional two hours. Following this treatment the temperature was quickly raised to about
770°C. and held there until the salt had melted completely. The heating was then discontinued. During the entire drying and heating process a steady stream of nitrogen was passed through the apparatus. In most fusions a faint white smoke was observed emerging from the end of the heating tube. Tests on this vapor showed that it was neither acidic nor basic. It probably consisted of finely divided sodium bromide which had vaporized during fusion. The fused bromide was in every case perfectly clear and colorless, and there was no evidence of attack of the platinum boat (30). After twelve such fusions the boat had the same weight as at the start.

When the salt had reached room temperature the flow of nitrogen was stopped, and air was drawn through the drying system by means of an aspirator connected to the fusion tube through a trap bottle and a calcium chloride tube. A three-way stop cock between the copper spirals and the Emmerling towers permitted the introduction of air which had been filtered through a tower of clean cotton and glass wool. After air had been drawn through the apparatus for at least one hour, the boat was gently pushed into the weighing bottle and the stopper tightly inserted by means of a clean glass rod.

In each fusion a small amount of the sodium bromide vaporized from the boat and condensed on the wall of the tube. This deposit was washed out with pure water and tested with a few drops of methyl red. On several occasions this solution gave a slightly basic reaction indicating some decomposition, but in no case was it basic to phenolphthalein. A loss of
bromine would cause a high value for the atomic weight of sodium, but analyses of these samples did not show this result. It is reasonable to assume that any decomposition of the sodium bromide occurred in the vapor state, and that the products were carried beyond the boat by the flow of nitrogen.

The weighing of the stoppered bottle containing the sample was accomplished by suspending it vertically from the hook on the balance arm by means of an aluminum harness. Rest points were taken after allowing the bottle to hang thus for fifteen minutes with the door of the balance case open. The boat was then transferred to a three liter Erlenmeyer glass-stoppered flask containing 800 ml. of water. The weighing tube was always washed several times, and the wash water was added to the flask. At least twelve hours were allowed for solution of the sodium bromide, after which the boat was removed by means of a hook on a glass rod and placed in a clean beaker. It was washed eight times with small portions of water which were returned to the solution. The boat was then placed in the heating tube of the bottling apparatus, and the same operations were repeated which were employed in the fusion of the sample except that no nitrogen was passed through the apparatus. The bottle containing the empty boat was weighed by a procedure identical with that used in weighing the sample. The difference between the two weights, corrected to a vacuum basis, represents the vacuum weight of the sodium bromide. The reduction of the weights to a vacuum basis, however, involves many quantities and introduced unexpected difficulties.
Six preliminary analyses were discarded because insufficient data were available for the accurate calculation of these corrections.

In weighing the sample in the weighing bottle, three components are in effect involved—the weight of the bottle and its stopper, the weight of the air contained in the bottle, and the weight of the boat, either empty or with the sodium bromide. The latter seems to offer no difficulty. The boat was weighed alone several times during the experiment, and remained constant throughout. The sodium bromide after fusion consisted of relatively few large crystals whose volume could be accurately calculated. The volume of air contained in the bottle was calculated for each case from recorded values of temperature and pressure at the time of bottling, and the interior volume of the bottle, assuming the ideal gas laws to hold. There is no way to check the reproducibility of this step independently of the third consideration, the weight of the bottle and its stopper. The vacuum correction for the bottle can be accurately obtained by determining its exterior volume, but the condition of its surface may, however, introduce a source of error. Static surface charges of electricity were dissipated by a piece of uranium ore which was kept in the balance case. No attempt was made to correct for the condensation of water vapor on the surface of the bottle. This will depend to some extent on the relative humidity, but no quantitative relation has been found. The vacuum weight of the bottle and the empty boat, calculated from the data of five consecutive analyses, is given below.
### Vacuum Weight

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>Relative Humidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.10607</td>
<td>42%</td>
</tr>
<tr>
<td>35.10621</td>
<td>56%</td>
</tr>
<tr>
<td>35.10709</td>
<td>62%</td>
</tr>
<tr>
<td>35.10607</td>
<td>31%</td>
</tr>
<tr>
<td>35.10594</td>
<td>35%</td>
</tr>
</tbody>
</table>

The effect of these variations on the mass ratio under investigation will be considered later.

**Precipitation of Silver Bromide.**

The precipitation of the bromide with silver nitrate was performed in the conventional manner. From the weight of the sodium bromide the equivalent weight of silver was calculated using 22.994 as the atomic weight of sodium. An amount within a few mg. of the calculated quantity was weighed out and dissolved in 25 ml. of 1:1 nitric acid in a flask fitted with a Richards tower. The oxides of nitrogen were driven off by heating the solution on an electric hot plate, and the silver nitrate solution was then diluted to 700 ml. Before addition of the silver, the sodium bromide solution was acidified with 1:1 nitric acid. The acid, together with the excess in the silver, was calculated to be 0.14 M in a final volume of two liters. The precipitation was carried out by adding the silver slowly to the sodium bromide solution with constant agitation. After the precipitation was completed the solution was adjusted to the theoretical endpoint by the addition of silver nitrate or sodium bromide from standard solutions containing 0.1 mg. of silver per liter or its bromide equi-
valent. These standard solutions were prepared from purified silver and sodium bromide.

The solutions were shaken vigorously several times over a period of three to four days and were allowed to stand for at least two days before nephelometric tests were begun. The final volumes were between 1700 and 2600 ml. The endpoint was determined nephelometrically by tests such as those described in the first part of this thesis. Suitable additions from the standard solutions of silver nitrate or silver bromide were made, if necessary, until the test suspensions showed equal opalescence according to the procedure previously described. When three consecutive tests gave this result the solutions were taken to be at the stoichiometrical point.
RESULTS OF THE ANALYSES

The results of the analyses are given in Table V. All weights given have been corrected to the vacuum basis. The additions listed in the fifth column include only those made as a result of the nephelometric measurements.

The precision of the determinations of the mass ratio is not as high as could be desired, and might have been improved by the use of somewhat larger samples. The source of the variations is probably to be found in the difficulty in obtaining the weight of the sodium bromide samples. This question has already been discussed. The discordant value obtained in analysis 4 is unquestionably due to this source, for in this analysis the weight obtained for the bottle and the empty boat differed one milligram from the mean value obtained in the other analyses. The error in question would seem to be an indeterminate one, and would have either a positive or negative value depending on the condition of the weighing bottle at two different times, i. e. when weighed with the sodium bromide sample and when weighed with the empty boat. This being the case, some cancelation of errors might be expected in the calculation of the mean of an extended series of analyses. To what extent such a cancelation occurred in the series reported cannot, of course, be determined.

The atomic weight of sodium derived from these measurements is 22.989. This value is much lower than any previously obtained using mass ratios obtained by methods of chemical analysis. This raises the question of the purity of the silver and the sodium bromide used in this work. The source of any
<table>
<thead>
<tr>
<th>No. of Analysis</th>
<th>Sample of NaBr</th>
<th>Weight of NaBr</th>
<th>Initial Weight of Ag</th>
<th>Weight of Ag Added</th>
<th>Corrected Weight of Ag</th>
<th>Ratio NaBr:Ag</th>
<th>Atomic Weight of Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Prep. IIIb</td>
<td>4.82222</td>
<td>4.84545</td>
<td>-.00002</td>
<td>4.84541</td>
<td>0.95394</td>
<td>22.995</td>
</tr>
<tr>
<td>2</td>
<td>Prep. IIIa</td>
<td>4.32965</td>
<td>4.53875</td>
<td>-.00021</td>
<td>4.53854</td>
<td>0.95397</td>
<td>22.999</td>
</tr>
<tr>
<td>3</td>
<td>Prep. I</td>
<td>5.21415</td>
<td>5.46597</td>
<td>-.00031</td>
<td>5.46628</td>
<td>0.95388</td>
<td>22.988</td>
</tr>
<tr>
<td>4</td>
<td>Prep. II</td>
<td>4.26643</td>
<td>4.47306</td>
<td>-.00058</td>
<td>4.47364</td>
<td>0.95368</td>
<td>22.967</td>
</tr>
<tr>
<td>5</td>
<td>Prep. IIIa &amp; Prep. IIIb</td>
<td>4.80689 &amp; 5.03904</td>
<td>5.03941</td>
<td>-.00037</td>
<td>5.03941</td>
<td>0.95386</td>
<td>22.986</td>
</tr>
<tr>
<td>6</td>
<td>Prep. I</td>
<td>5.22954</td>
<td>5.48209</td>
<td>-.00073</td>
<td>5.48282</td>
<td>0.95381</td>
<td>22.980</td>
</tr>
<tr>
<td>7</td>
<td>Prep. II</td>
<td>5.32057</td>
<td>5.00531</td>
<td>-.00015</td>
<td>5.00547</td>
<td>0.95386</td>
<td>22.987</td>
</tr>
<tr>
<td>8</td>
<td>Prep. I</td>
<td>6.20982</td>
<td>6.51003</td>
<td>.00000</td>
<td>6.51003</td>
<td>0.95389</td>
<td>22.989</td>
</tr>
</tbody>
</table>

Mean excluding #4  
Probable error

Ag = 107.880  
Br = 79.916
error of this sort is not likely to be found in the purity of the silver since it was purified by standard methods long used in work of this sort. The purification of the sodium bromide may, however, be called into question. Inert impurities, and bromides of metals with an equivalent weight above that of sodium, would cause a high value for the mass ratio. Among the metals this leaves as possibilities only lithium, magnesium, and calcium, all of which are extremely unlikely to have been present. Of the possible halide impurities, iodide would increase the ratio and chloride would decrease it. Thus, if the low results are due to impurities in the materials, chloride is probably the impurity in question. As was pointed out in the description of the purification of sodium bromide, considerable pains were taken to eliminate this impurity by the double distillation of the bromine. The crystallization process could also have been effective in this respect since the sodium bromide was separated as the dihydrate, a form without analogy in the chloride series at the temperatures used.

The value 22.989 for the atomic weight of sodium is in much better agreement with the values obtained from physical data than those from the chemical analyses. Since there is only one stable isotope of sodium, chemical and physical determinations are directly comparable. The only reliable physical values available have all been obtained by the study of nuclear reactions. Accurate mass-spectrographic determinations are lacking. Three physical values have been reported. Pollard and Brasefield (32) derived the value 22.9972 from a study of the reaction

\[
\text{Ne}^{20} + \text{He}^{4} \rightarrow \text{Na}^{23} + \text{H}^{1}
\]
This corresponds to 22.9915 on the chemical scale using 1.000025 as the conversion factor. Very recently Murrell and Smith (33) bombarded sodium with deuterons, and from the reaction

\[ \text{Ne}^{23} + \text{H}^2 \rightarrow \text{Ne}^{21} + \text{He}^4 \]

they calculated the mass of Ne\(^{23}\) to be 22.9961. This converts to a chemical value of 22.9907. They also recalculated the older data of Lawrence (34) using a later value for the stopping power of aluminum foil, and obtained the almost identical value of 22.9906 (chemical scale). Lawrence's original value was even lower. These measurements are direct and capable of very high precision.

The evidence in favor of a value for the atomic weight of sodium considerably lower than the present international value seems irrefutable, and the work here reported lends support to this view. From a quantitative standpoint, however, the value 22.989 resulting from this work must be regarded as preliminary until better agreement between the various types of determinations, both chemical and physical, can be obtained.
SUMMARY
An extended series of experiments was performed to establish the sensitivity of the nephelometric endpoint in silver chloride titrations. It was shown that the presence of a precipitate of silver chloride does not affect the endpoint, and that an excess of 0.1 mg. of silver per liter or its chloride equivalent can definitely be detected. This confirms the results of Baxter and Alter rather than the low sensitivities reported by Briscoe and Johnson.

Experiments on solutions of silver bromide showed that the equal opalescence endpoint is valid for this titration if comparisons are made four to six hours after preparation of the test suspensions. The endpoint is estimated to be determined to within 0.05 mg. of silver per liter or its bromide equivalent.

A determination of the ratio of sodium bromide to silver was made. The results of seven analyses give a mean value for this ratio of 0.95388±0.000014, from which the atomic weight of sodium is calculated to be 22.989±0.0016. This result is presented only as a preliminary value, as the precision of the measurements is not as high as could be desired. This value is much lower than any yet reported from chemical measurements, but is in rather good agreement with recent physical data. These results, together with those of Johnson and Greene and Josie from determination of the ratio of sodium chloride to silver, indicate that the present international value of the atomic weight of sodium is several units too high.
REFERENCES

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