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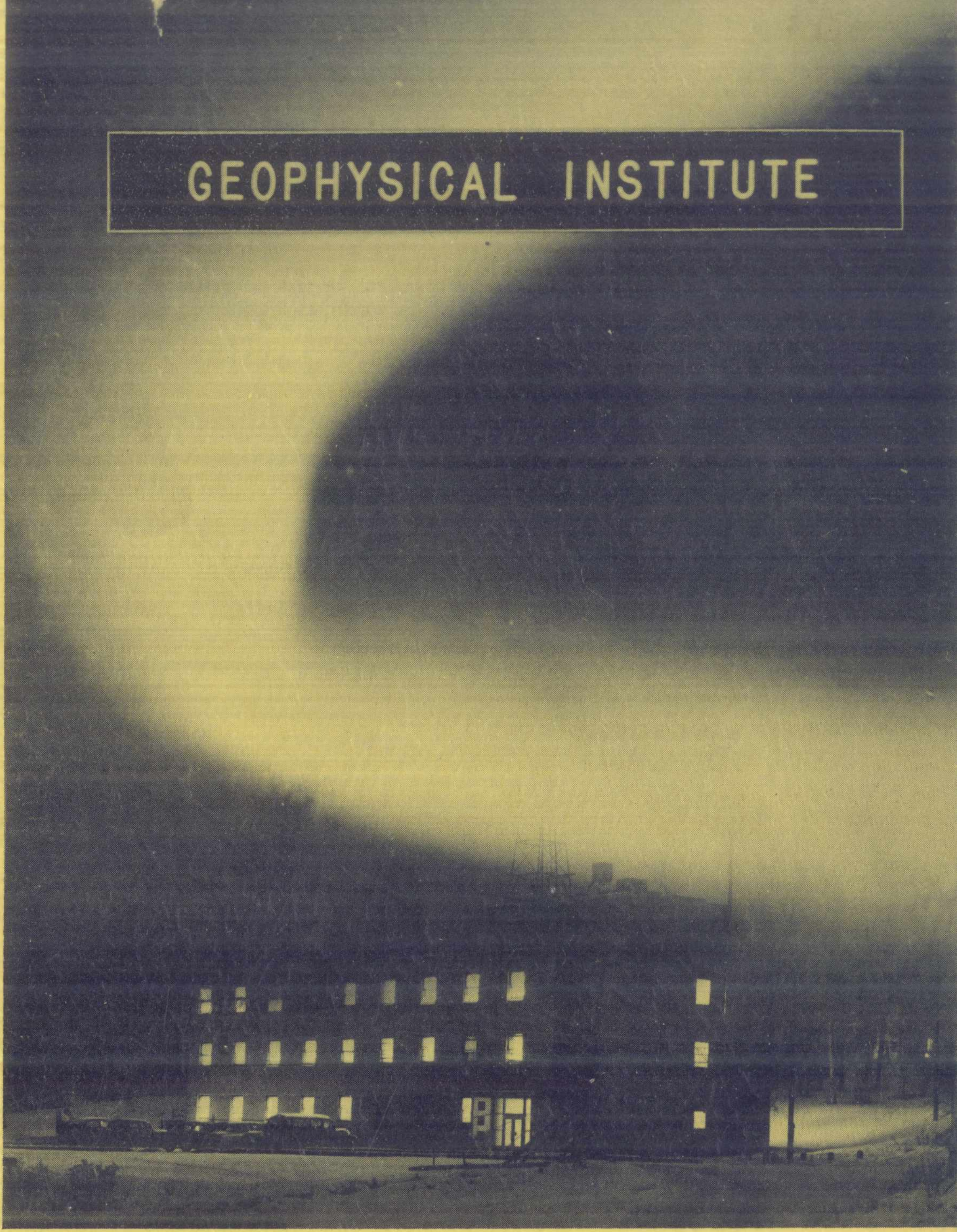

Scientific Report No. 1

EVALUATION OF CHEMICAL METHODS FOR THE DETERMINATION OF ATMOSPHERIC OZONE

By

Nalin R. Mukherjee

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ERRATA

Page	
4	3rd line from bottom read "Gottschalk" instead of Gottschalb.
37	Last line read "the exposed solution" instead of expressed solution.
42 and 44	Tables VIII and IX column 2 read "per 100 cu. meter" instead of per 100 cu. in.
47	10th line from top read "trickled" instead of tricled.
54	The end of 6th line from top omit "H".
58	1st line read "ammonium nitrite" instead of ammonium nitrate.
	11th line from top read "microbes" instead of nicrobes.
66	2nd line from bottom read "(Table XII)" instead of (Table XIII).

ABSTRACT

Since the concentration of the ozone in the atmosphere near the earth's surface is of the order of 10^{-8} gm. per gm. of air, the quantitative determination of this ozone by chemical methods is rather difficult. Therefore, the different methods have been evaluated to determine the best, all conceivable precautions being taken into account.

The chemical methods may be classified into two groups--Titer Methods and Spectro-chemical Methods. Among the former, two; namely, the Thiosulphate and Arsenite Methods, have been proposed and used. For the low concentration of ozone in the atmosphere near the earth's surface, the Thiosulphate Method is found to give unreliable results due to the instability of the thiosulphate solution as well as to various side reactions which could not be controlled. The arsenite solution, however, is much more stable than the thiosulphate solution. Side reactions are very few and can largely be controlled. Reliable results can be obtained by the Arsenite Method when employing proper precautions.

The oxidants and other interfering substances in the atmosphere present serious problems. Some oxidants behave like ozone as far as the reactions with the chemical reagents are concerned. Their occurrence in the atmosphere and their effects on the chemical reagents used for the quantitative determination of the atmospheric ozone are discussed in detail. Suggestions are made for their elimination from the atmosphere without affecting the ozone concentration.

Chapter I

INTRODUCTION

For the quantitative determination of atmospheric ozone two groups of methods, chemical and spectroscopic, have been proposed and used. This report, however, will be confined to the discussion of the former. In every chemical method the ozonized air is mixed with or passed through a reagent or reagents in order to permit oxidation of some constituent by ozone. The amount of ozone is determined either by titration or by measurement of the transmitted intensity of a definite wavelength of light. The small ozone content of the atmosphere near the earth's surface, of the order of 10^{-8} gm ozone per gm air, makes the experimental determination by chemical methods very difficult; therefore, every conceivable precaution must be taken. The chemical methods can be classified into two types: (1) Titer Methods, (2) Spectrochemical Methods.

1. Titer Methods:

In Titer Methods ozonized air is passed through an absorption column with proper packings in which a certain standard solution flows counter-currently to increase the efficiency of absorption (Figure 1). After a definite time the operation is stopped, the absorption column is washed with pure water and the volume of air that has passed through the column is recorded. The total amount of solution and wash water is titrated by a suitable standard solution to determine the quantity of unreacted reagent. A blank solution is made in exactly the same way

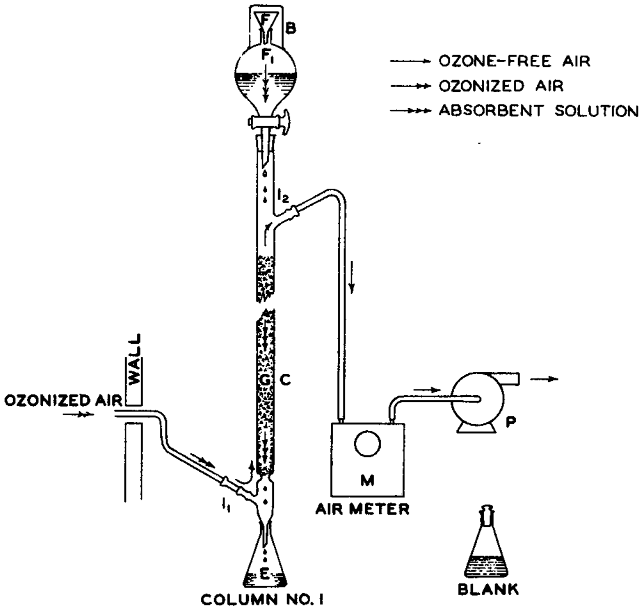

FIGURE 1

ABSORPTION COLUMN FOR THE DETERMINATION OF ATMOSPHERIC OZONE

Legend: All parts are made of pyrex glass except from I_2 to P, where pressure rubber and tygon tubings were used for connections.

W = Wall of the room about 35 feet above the ground.
B, F, F_1 = Beaker, powder funnel, separating funnel (one liter capacity) respectively
C = Absorption column, 5 feet 4 inches long, 1.25 inches internal diameter.
I_1, I_2 = Ground glass joints (air tight).
E = Erlenmeyer flask with ground glass mouth (two liters capacity).
G = About three feet of packings, pyrex glass helices, 3/16 inch i.d., made by Scientific Glass Apparatus Co., Bloomfield, N. J. U.S. Patent 2,037,317.
M = Gas Meter, made by American Meter Co., Albany, N.Y., No. 5,853,958 checked and standardized against a wet gas meter.
P = Suction pump.

and kept in a stoppered bottle near the absorption column during the time of the run. The difference between the titration values of the two solutions in an indirect measure of the amount of ozone. The concentration of ozone is, of course, computed using the air volume.

Sodium arsenite is oxidized quantitatively by ozone to sodium arsenate according to the following equation:

$$AsO_3^{---} + O_3 = AsO_4^{---} + O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Ladenburg[1] finds that the above reaction takes place much more slowly than that between ozone and potassium iodide. Thus, on the basis of equation(1) there is danger of getting ozone values that are too low.

Another very sensitive reaction is the quantitative oxidation by ozone of potassium cyanide to potassium cyanate. Rabbie[2] describes a procedure for the determination of potassium cyanide in strongly alkaline solution in the presence of potassium cyanate. This method can be made so sensitive as to determine 1/20 part of potassium cyanide per million parts of the solution. Unfortunately a strongly alkaline solution will absorb the carbon dioxide of the air, thus making the method unsuitable for the determination of atmospheric ozone.

The oxidizing action of ozone is generally rapid, but especially so in the case of potassium iodide. Fortunately this reaction is also quantitative. Therefore, in the following Titer Methods potassium iodide has been chosen as one of the reagents.

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[1] Ladenburg, Ber. 36, 115, (1903).

[2] Rabbie, Archieves Biochem. 5, 49, (1944).

(a) Potassium Iodide Method: In this method [3,4,5] a neutral buffered solution of potassium iodide is used as the chemical reagent and undergoes the following analytical reactions:

$$O_3 + 2I^- + H_2O = O_2 + I_2 + 2\,OH^- \quad \ldots\ldots\ldots\ldots\ldots (2)$$

$$I^- + I_2 = I_3^- \quad \ldots\ldots\ldots\ldots\ldots (3)$$

The combined equation is, therefore:

$$O_3 + 3I^- + H_2O = O_2 + I_3^- + 2\,OH^- \quad \ldots\ldots\ldots\ldots\ldots (4)$$

The liberated iodine is titrated by standard sodium thiosulphate or sodium arsenite solution and the amount of ozone reacted is calculated according to equation (2).

It was believed that the reaction shown in equation (2) between ozone and potassium iodide takes place via hydrogen peroxide[6]. In other words, it was thought that ozone first reacts with water to form hydrogen peroxide

$$O_3 + H_2O = H_2O_2 + O_2 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

and that this hydrogen peroxide then reacts with potassium iodide, liberating iodine,

$$H_2O_2 + 2I^- = 2OH^- + I_2 \quad \ldots\ldots\ldots\ldots\ldots (6)$$

The combination of equations (5) and (6) yields equation (2). Rothmund and Burgstaller[7], and Jannasch and Gottschalb[8] proved that no hydrogen peroxide is formed in the above manner. Therefore, equation (2) is now considered the reaction between ozone and potassium iodide.

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3. Luther and Inglis, Z. phys. chem. 48, 208, (1903).
4. Ladenburg and Quasig, Ber. 34, 1184, (1901).
5. Treadwell and Anneler, Z. anorg. Chem. 48, 86, (1905).
6. c.f. Arnold and Mentzel, Ber, 35, 2902, (1902).
7. Rothmund and Burgstaller, Monatsh, 34, 665, (1913).
8. Jannasch and Gottschalb, J. prak, Chem. (2), 73, 496, (1906).

Since the liberated iodine (vide equation (2) dissolves very slowly in a dilute potassium iodide solution, the concentration should be made appreciable in order to trap the liberated iodine. In concentration iodide solution, however, there is evidence[9,10] of the formation of ions such as I_5^- and I_7^-. In whatever form iodine exists in potassium iodide solution (I_3^- or I_5^- or I_7^- or a mixture of these) the titration with sodium thiosulphate or sodium arsenite solution will give the same value, because the reaction between potassium iodide and iodine is reversible ($KI + I_2 \rightleftharpoons KI_3$; $KI + 2I_2 \rightleftharpoons KI_5$; $KI + 3I_2 \rightleftharpoons KI_7$).

There are a number of factors whch affect this method seriously. One factor is that the liberated iodine, though remaining in solution in the form of tri-iodide or penta-iodide, etc., ions, is carried off as a vapor in the air current due to the reversible reaction between potassium iodide and iodine. Studies in this laboratory confirm previous workers[11,12] in the above conclusion. Thus, due to these difficulties the use of potassium iodide alone (i.e., without the use of a reagent to absorb the iodine immediately on formation) is not practical. The remaining adverse factors will be discussed in Chapter II.

(b) Thiosulphate Method: The thiosulphate method used employs sodium thiosulphate as an absorbent of the liberated iodine. The method consists of (1) the oxidation by ozone of potassium iodide in the presence of sodium thiosulphate solution buffered by sodium bicarbonate, and (2) the subsequent titration of the remaining unreacted sodium thiosulphate by iodine solution. The difference

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[9] Grace, J. Chem. Soc. 138, 534, (1931).
[10] Briggs et al. J. Phys. Chem. 44, 350, (1940).
[11] Usher and Rao, J. Chem. Soc. 111, 799 (1917).
[12] Regener, Meteor. Z. 55, 459 (1938).

between the titration values of the blank and the solution exposed to ozonized air measures the amount of ozone. The difference between the potassium iodide method and the thiosulphate method is that in the latter a known quantity of sodium thiosulphate is used to prevent the escape of iodine.

The general reactions between ozone and iodide and between iodide and iodine are shown in equations (2) to (4). The iodine liberated by ozone reacts instantaneously with sodium thiosulphate according to the following equation:

$$I_2 + 2S_2O_3^{--} \longrightarrow 2I^- + S_4O_6^{--} \quad \ldots\ldots\ldots\ldots\ (7)$$

thus preventing the loss of iodine (c.f. potassium iodide method). Both sodium thiosulphate and sodium tetrathionate are non-volatile, so that the remaining unreacted sodium thiosulphate is an indirect measure of the quantity of ozone.

(c) <u>Arsenite Method</u>: The arsenite method is the same in principle as the thiosulphate method with sodium arsenite replacing the sodium thiosulphate. The reaction between sodium arsenite and iodine liberated by ozone is

$$I_2 + AsO_3^{---} + H_2O \rightleftharpoons 2I^- + AsO_4^{---} + 2H^+ \quad \ldots\ldots\ (8)$$

This reaction is reversible. In neutral solution it runs quantitatively from left to right and in a strongly acid medium, quantitatively from right to left.

Sodium arsenite is non-volatile and traps the iodine. The difference in titer values obtained in terms of iodine for the blank and the run is the measure of the amount of ozone.

2. Spectro-Chemical Methods:

These methods depend upon the change of color and/or the change in the intensity of color of a reagent solution due to oxidation by ozone. The per cent transmission of a definite wavelength of light is the measure of the quantity of ozone reacted.

(a) Tetrabase Method: The reagent, p-p' tetramethyldiaminodiphenylmethane, or tetrabase, is specific for ozone. It has been found in this laboratory that a good solvent for it is a 50-50 mixture of ethyl alcohol and acetic acid. As far as known, no precise determination of the threshold of reaction has been made; and it does not appear to have been used in the investigation of atmospheric ozone except by Dauvillier[13], who used it to detect qualitatively the presence of very minute quantities of ozone. A set of preliminary experiments in this laboratory shows that there is a possibility of using this method for the quantitative determination of ozone; but the author does not feel ready to make a positive statement until further investigations have been completed.

(b) Fluorescein Method:[14, 15] Fluorescein ($C_{20}H_{12}O_5$) is converted, at first, to its leucoderivative by reduction with zinc and soda. The intensity of the fluorescent color gradually changes due to the oxidation of this leuco-derivative to fluorescein molecule itself.[16] Two molecules of ozone (or 0.29 gms.) destroy

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[13] Dauvillier, J. de Phys. 5, 668, (1934).

[14] Gueron and Prettre, Quar. J. Roy. Meteor. Soc. Supplement to vol. 62, 2, (1936).

[15] Egorov, Berlin. Z. Untersuch. Lebensmitt, 56, 355, (1928).

[16] Benoist, Paris C.R. Acad. Sci. 168, 612, (1919).

one molecule of fluorescein (or 1 gm). Maché[17] and Heller[18] point out the necessity of operating this method at constant p^H without any mention of the p^H values. The fluorescein method is of interest because its leuco-derivative is reported to be specific for ozone and also insensitive to oxygen, to oxygenized water and to blue oxides. However, due to the difficulty of preparing the leuco-derivative and to the destruction of fluorescein itself by ozone, this method does not appear to be promising. Preliminary experiments performed in this laboratory show that the quantitative determination of atmospheric ozone by this method is questionable.

(c) Dihydroacridine Method: Dihydroacridine is oxidized by ozone, molecule by molecule, into fluorescent acridine and the change of intensity of color is a measure of the amount of ozone. Since dihydroacridine is sensitive to blue oxides and other oxidizing agents, this method does not appear to be even as good as the fluorescein method.

(d) Other Methods: A number of other reagents which are insensitive to oxygen, oxygenized water and other oxidizing agents but specific in changing color due to oxidation by ozone can be used. Leuco-rosaniline may be mentioned as one. Further studies on this are needed.

The methods of Type 1 have been studied extensively and discussed in detail. Though some preliminary investigations of Type 2 methods have been performed in this laboratory and some results are encouraging, further studies are necessary.

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17. Maché, ibid, 200, 1760, (1935).
18. Heller, ibid, 200, 1936, (1935).

3. General Considerations:

In the determination of any substance by Titer Methods errors in the final result may arise from a number of causes. This is especially so when these methods are applied for the measurement of such a small concentration of a gas as atmospheric ozone. Therefore, it is very important to follow closely the procedures of quantitative analysis to eliminate mechanical and other obvious errors. The general principles normally followed, which are of importance to the Titer Methods, are summarized below:

(1) Solutions should be made from chemically pure reagents and solvents. They should be stored in a suitable place: cool, if decomposed by heat; dark, if affected by white light, etc. The solutions should be stable during the period of storage.

(2) The reagent should be specific for the substance to be determined, so that impurities from whatever source, are not acted upon.

(3) The reagents and the products formed during reactions should be non-volatile and stable so that loss due to vaporization and decomposition may be negligible.

(4) The rate of reaction between the reagents and the substance to be determined should be as fast as possible so that side reactions will not affect the result. If a current of gas containing the substance to be determined is to be passed through a solution, instantaneous reaction is essential to eliminate loss of the substance with the effluent gas.

(5) If side reactions are possible, precautions (use of inhibitors, control of p^H, etc.) should be taken to minimize their effects.

(6) In any titer method the determination of the exact end point is important and, therefore, the accuracy of the end point determination should be known.

(7) The burette, pipette and other instruments used should be calibrated.

For the thiosulphate and arsenite methods, Items 2, 3, and 4 have already been discussed. Item No. 7 is described in any standard book on quantitative analysis. The rest will be discussed in detail.

Chapter II

CRITICAL REVIEW OF THIOSULPHATE AND ARSENITE METHODS

1. Importance of p^H:

In both the thiosulphate and arsenite methods, the solution must be kept neutral in every phase of the chemical reactions. If the solutions should become alkaline in the course of the reactions, the results will be untrustworthy on account of the following reactions:

$$I_3^- + OH^- = 2I^- + HIO \quad \ldots\ldots\ldots\ldots\ldots (9)$$

HIO tends to decompose in alkaline solution into iodate and iodide,

$$3HIO + 3OH^- = 2I^- + IO_3^- + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots (10)$$

Combination of equations (9) and (10) produces equation (11), which represents the hydrolysis or reaction with hydroxide, of iodine or tri-iodide.

$$3I_3^- + 6OH^- = 8I^- + IO_3^- + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots (11)$$

Upon calculating the equilibrium constant[19,20] of equation (11) it can be shown that for an accuracy of 0.001% the hydrogen ion concentration should be between 2×10^{-5} ($p^H = 4.7$ approximately) and 5×10^{-12} ($p^H = 11.3$ approximately). In a solution as acid as $p^H = 4.7$, the reducing action (c.f. equations (7) and (8)) of thiosulphate and arsenite is quite slow, making possible the escape of the volatile iodine with the air current. Moreover, thiosulphate is decompose with the precipitation of sulphur even in a dilute acid solution.

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[19] Swift, "Introductory Quantitative Analysis" Prentice-Hall, New York (1950) pp. 181, 175.

[20] McAlpine, J. Chem. Ed. 26, 362, (1949).

$S_2O_3^{--} + 2H^+ \longrightarrow H_2SO_3 + S$ . . . . (12)

Simultaneously the side reaction[21] indicated below is possible.

$5S_2O_3^{--} + 6H^+ \longrightarrow 2S_5O_6^{--} + 3H_2O$ . . . . (13)

If the concentration of iodine varies locally, perhaps due to too rapid addition, there is danger of hydrolysis (see equation (11)) because the optimal p^H value is 11.3. Therefore, for the quantitative determination of iodine, which is a measure of the quantity of ozone (c.f. equation (2)), the p^H of the solution must be maintained at about 7 throughout the reaction.

2. Buffer for Constant p^H:

The buffer must maintain a constant p^H, approximately 7, so as to prevent the side reactions already discussed and must itself not be oxidized by iodine or reduced by iodide and sodium thiosulphate or sodium arsenite. Sodium bicarbonate is a good buffer reagent for both the thiosulphate and arsenite methods. This has been confirmed in this laboratory and also by Regener[12] who states that the addition of sodium bicarbonate to a solution of sodium thiosulphate and potassium iodide or to a solution of sodium arsenite and potassium iodide does not modify in any way the liberation of iodine by ozone.

Sodium bicarbonate added to an acid solution will produce carbonic acid, and since the solubility of carbon dioxide in water is constant at a given temperature and pressure, the concentration of carbonic acid in a solution saturated with carbon dioxide is fixed by the temperature and pressure. In this buffer system

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[21] Zaiser and LaMer, J. Colloid. Sci. 3, 571, (1948).

$$\left[H^+\right] = \frac{\left[H_2CO_3\right]}{\left[HCO_3^-\right]} \cdot K \quad \ldots\ldots\ldots\ldots (14)$$

where K is the equilibrium constant for the reaction $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ · K at 20°C and one atmosphere pressure is equal to 3.5×10^{-7}.

Carbonic acid is relatively slightly soluble in water and its saturated solution at 20°C and 760 mm. pressure has a molar concentration of about 3.4×10^{-2}. Therefore, in a solution saturated with carbon dioxide, the hydrogen ion concentration is

$$\left[H^+\right] = \frac{3.4 \times 10^{-2}}{\left[HCO_3^-\right]} \times 3.5 \times 10^{-7} = \frac{1}{\left[HCO_3^-\right]} \times 1.19 \times 10^{-8} \quad \ldots\ldots\ldots\ldots (15)$$

If the sodium bicarbonate concentration is 0.119 N, then

$$\left[H^+\right] = \frac{1.19 \times 10^{-8}}{0.119} = 10^{-7} \text{ (i.e. } p^H = 7) \quad \ldots\ldots\ldots\ldots (16)$$

By adding a definite excess of bicarbonate, the solution can be buffered at a desired p^H. In this laboratory, however, 0.119 N in sodium bicarbonate (vide Chapter IV (2)) is maintained in a 0.03 N thiosulphate or arsenite solution. The calculated hydrogen ion concentration (vide equation (16)) is 1×10^{-7} gm. ions per liter ($p^H = 7$). If all the thiosulphate or arsenite of 100 ml of the 0.03 N solution is titrated by iodine the hydrogen ion concentration at the maximum may be shifted to 1.023×10^{-7} ($p^H = 6.99$).

Due to the reversible nature of equation (8) a change of p^H from 7 to 6.99 would cause an error in ozone value of the order of 10^{-8} molar, which is negligible. In fact the error caused by this effect will be even smaller, due to the fact that both the original and exposed solutions are titrated under the same experimental conditions. In addition it should be mentioned that the carbon dioxide of the air, which comes in contact with the solution continuously will buffer the latter against the decrease in hydrogen concentration.

3. Stability of Thiosulphate Solution:*

The determination of ozone according to the mechanism illustrated by equations (2), (3), (4) and (7) is based on the assumption that no side reactions occur. But this is not the case. One source of error lies in the decomposition of sodium thiosulphate by mechanisms other than its reaction with iodine. This decomposition is known to take place under a wide variety of conditions.

(a) Effect of Carbon Dioxide and Acids: Since sodium thiosulphate in aqueous solution is decomposed by an acid, carbon dioxide will react with it slowly according to reactions shown in equations (12) and (13). To increase the stabilit Topf[22] recommends the preparation of the solution in pure water (conductivity water) that has been boiled. Treadwell[23] suggests that the sodium thiosulphate solution be prepared in ordinary distilled water and standardized only after eight to fourteen days' standing so that all the carbonic acid originally present in the solution will have undergone reaction and thus rendered the solution

---

* The name "Thiosulphate Solution" will be used hereafter for a solution, which contains sodium thiosulphate, potassium iodide and sodium bicarbonate as buffer. For a solution; which contains a metallic thiosulphate only, the full name of the salt such as sodium thiosulphate solution will be used.

[22] Topf, Z. Analyt. Chem. 26, 137, (1887).

[23] Treadwell, "Analytical Chemistry," John Wiley & Sons, New York, 5th edn., Vol. II, (1919) pp. 645, 652.

unsusceptible to any noteworthy change for a month or more. But this does not provide a solution for the present case as in the determination of atmospheric ozone it is necessary to expose the solution to air containing carbon dioxide. Sodium thiosulphate solution prepared in this laboratory with the precautions suggested by Treadwell (loc. cit.), except that no inhibitors were added, was decomposed slightly (about 4%) as found by iodine titration after a period of two months standing in a closed bottle in the cupboard (c.f. Rice et al.[29]). A similar report of slow decomposition in spite of precautions is given by Kolthoff and Sandell.[24]

Dinegar[25] et al discuss the acid catalyzed decomposition of sodium thiosulphate solution according to the following reactions.

$$S_2O_3^{--} + H^+ \rightleftharpoons HS_2O_3^- \quad \ldots\ldots\ldots\ldots (17)$$

$$HS_2O_3^- + S_2O_3^{--} \longrightarrow HS_2O_3 \cdot S_2O_3^{---} \quad \ldots\ldots\ldots\ldots (18)$$

$$HS_2O_3 \cdot S_2O_3 \longrightarrow 2S + HSO_3^- + SO_3^{--} \quad \ldots\ldots\ldots\ldots (19)$$

The obvious way to minimize these reactions is to increase the p^H of the solution so as to cause equation (17) to take place very slowly. If the p^H is raised to 8, the reaction still occurs, the equation being modified to:

$$S_2O_3^{--} + H_2O \rightleftharpoons HS_2O_3^- + OH^- \quad \ldots\ldots\ldots\ldots (20)$$

The effect of raising p^H is more than this; the basic equation (7) between thiosulphate and iodine is modified due to the side reaction

$$S_2O_3^{--} + 4I_2 + 10\,OH^- = 2SO_4^{--} + 8I^- + 5H_2O \quad \ldots\ldots (21)$$

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[24] Kolthoff and Sandell, "Text Book of Quantitative Inorganic Analysis," Macmillian Co., New York, (1936) pp. 560, 589.

[25] Dinegar, Smellie and LaMer, J. Am. Chem. Soc. <u>73</u>, 2050, (1951).

The influence of equation (21) does not become pronounced until the p^H is above 6. The above equation indicates that less thiosulphate will be required for the same amount of iodine and therefore, the result will indicate too small an amount of ozone. On the otherhand, the reverse will be the case when the remaining unreached thiosulphate is titrated by iodine in potassium iodide solution. Since these errors tend to cancel each other, the adverse effect on the final result theoretically should be small. But, during titration the rate of addition of iodine solution is not constant and the amount of iodine used during titration is always much greater than that liberated by ozone and therefore, two opposing effects may not cancel each other and consequently a large error may result.

(b) <u>Oxidation by Oxygen</u>: Thiosulphate is known to be oxidized by oxygen

$$S_2O_3^{--} \longrightarrow SO_3^{--} + S \quad \text{(very slow)} \quad \ldots\ldots\ldots\ldots (22)$$

$$SO_3^{--} + 1/2\ O_2 \longrightarrow SO_4^{--} \quad \text{(relatively fast and measurable)} \quad \ldots\ldots\ldots (23)$$

The assumption of an intermediate sulphite formation is strongly favored by the traces of metallic ion present in the solution; this will be discussed later. The combined equation (24) is

$$S_2O_3^{--} + 1/2\ O_2 \longrightarrow SO_4^{--} + S \quad \ldots\ldots\ldots\ldots (24)$$

Schulek[26] claims that he detected sulphide during the decomposition of thiosulphate. He suggests the following reaction

$$S_2O_3^{--} + H_2O \longrightarrow SO_4^{--} + H_2S \quad \ldots\ldots\ldots\ldots (25)$$

$$H_2S + 1/2\ O_2 \longrightarrow H_2O + S \quad \ldots\ldots\ldots\ldots (26)$$

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[26] Schulek, Z. analyt. Chem. <u>68</u>, 387, (1926).

According to his view the diminution of the titer of very dilute solution may be expressed as

$$2S_2O_3^{--} + H_2O = 1/2\ O_2 \longrightarrow S_4O_6^{--} + 2OH^- \ldots\ldots\ldots (27)$$

(c) Effect of Metallic Ions: Traces of metallic ions in the water catalyze the air oxidation of thiosulphate. The potential of the reaction

$$2H_2O = O_2 + 4H^+ + 4e^- \ldots\ldots\ldots\ldots\ldots (28)$$

would indicate that it should oxidize thiosulphate quite completely, but the solution saturated with oxygen is actually affected very little.[27] A trace of copper, however, strongly catalyzes the decomposition of thiosulphate. Abel[28] explains the catalytic action of copper in the following way;-

$$2Cu^{++} + 2S_2O_3^{--} \longrightarrow 2Cu^+ + S_4O_6^{--} \text{ (instantaneous)} \ldots\ldots (29)$$

$$2Cu^+ + 1/2\ O_2 \longrightarrow 2Cu^{++} + O^{--} \text{ (measurably slow)} \ldots\ldots (30)$$

$$O^{--} + 2H^+ \longrightarrow H_2O \text{ (instantaneous)} \ldots\ldots\ldots\ldots\ldots (31)$$

$$2S_2O_3^{--} + 2H^+ + 1/2\ O_2 \longrightarrow S_4O_6^{--} + H_2O \ldots\ldots\ldots (32)$$

Thus, the oxidation of thiosulphate continues in a cycle as long as oxygen is present, and since oxygen is a constituent of air it will always be present in the solution. The inhibition of the decomposition, however, can be achieved with alkaline substance by the direct precipitation of copper. Ordinary distilled water often contains traces of copper derived from the storage system and the still, if made of copper. Abel (loc. cit.) recommends that the solution be prepared by

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27. Kilpatrick and Kilpatrick, J. Am. Chem. Soc. 45, 2132, (1923).
28. Abel, Ber. 56. 1076, (1923; Z. anorg. Chem. 74, 395. (1912).

redistilled water, which has been obtained from a glass still and freed from copper as far as possible. Kilpatrick et al (loc. cit.) and Rice et al[29] find that a sodium thiosulphate solution prepared in ordinary distilled water was 20 per cent decomposed after fifty-one days; in twice-distilled water, about 4 per cent; and in gas-free water, 1.5 per cent. It can be mentioned here that the use of sodium carbonate wll improve the stability of a thiosulphate solution by removing copper ions. The entire mechanism of the decomposition of a thiosulphate solution is complicated and, therefore, in spite of the above-mentioned precautions it is necessary to restandardize such a solution after it has stood for a week or even less.

(d) Effect of Dilution by Water: Even if the thiosulphate solution is properly buffered and free from metallic ions, especially copper ions, and the water used for dilution has been redistilled, an increase in dilution will increase the instability of the solution because the added water will contain oxygen and carbon dioxide in solution. The instability can be reduced by diluting with gas-free conductivity water and storing in a filled stoppered bottle kept in the dark. This, again, does not solve the problem in the present case, because the thiosulphate solution had to be exposed to the air current during the determination of ozone.

(e) Decomposition by Micro-organisms: Investigations[27, 30, 31] have shown that the major cause of deterioration of thiosulphate solution is the growth of micro-

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29. Rice, Kilpatrick, Lemkin, J. Chem. Soc. 45, 1361, (1923).
30. Mayr. Z. analyt. Chem. 68, 274, (1926); 73, 321, (1928).
31. Stoffe, Chem. Abs. 17, 2900, (1923).

organisms (thiobacteria). Apparently there exist in air sulphur-consuming bacteria. These bacteria also withdraw sulphur from thiosulphate, thus converting it to sulphite which in turn is easily oxidized to sulphate by oxygen. The speed of decomposition at first increases with rising temperature. At a temperature of about 80°C the bacterial action will presumably stop due to the death of bacteria. Therefore, a solution brought to the boiling point and then cooled in a stoppered bottle may be stable so far as bacterial action is concerned. But the bacterial decomposition will start again when the cold solution is exposed to the atmospheric air for the determination of ozone. The optimal p^H of bacterial decomposition lies between 8 and 9. According to Mayr[30] carbonates and especially ammonium carbonate favor the growth of bacteria because of the carbon they contain, and should, therefore, be excluded from a thiosulphate solution which is to be stored. He did not find any suitable substance that hindered the decomposition of thiosulphate by micro-organisms. He also states that there are three active kinds of thiobacteria which cause the three following sets of reactions

$$2Na_2S_2O_3 + H_2O + O = Na_2S_4O_6 + 2NaOH \quad \ldots\ldots\ldots \quad (33)$$

$$Na_2S_2O_3 = Na_2SO_3 + S \text{ and } Na_2SO_3 + O = Na_2SO_4 \quad \ldots\ldots \quad (34)$$

$$2Na_2S_2O_3 + H_2O + O = Na_2S_4O_6 + NaOH \text{ and } S + 3O + H_2O = H_2SO_4 \quad \ldots\ldots\ldots\ldots \quad (35)$$

The intermediate product, sodium sulphite of equation (34), may react with iodine (vide equation (74)) during titration unless it has been oxidized to sodium sulphate. If oxygen and the carbonates are absent in the sterile thiosulphate solution, bacterial action has very little effect.[30] In the determination of atmospheric ozone, however, thiosulphate solution has to be exposed to the air which contains thiobacteria, oxygen, and carbon dioxide.

(f) Effect of Light: Light favors the decomposition [27, 33] of the thiosulphate solution. Photons probably provide the activation energy for action of microorganisms and other chemical reactions.

The mechanism of the decomposition of thiosulphate seems to be very complicated. It is not surprising that in systematic studies one almost always comes upon new irregularities,[32-36] apparently because diverse processes are superimposed, each of which is affected by different factors. Even the reaction between sodium thiosulphate and iodine is not as simple as shown in equation (7). Abel,[28] Batey,[34] and Ashley[35] etc., find that oxidation may proceed further than sodium tetrathionate to form sodium sulphate. If the solution is alkaline or acidic, the side reactions between iodine and thiosulphate are numerous. (vide Chapter II, (1) and (3a)).

From the foregoing, it can be seen that the thiosulphate method is not reliable when determining very low concentrations of ozone.

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32. Waterman, Chem. Weekbl. 15, 1098, (1918).
33. Kolthoff, Z. analyt. Chem. 60, 341, (1921).
34. Feigel, Ber. 56, 2086, (1923); Batey, Analyst, 36, 132, (1911).
35. Hahn and Windish, Ber. 55, 3163, (1923); Ashley, Am. J. Sci. (4) 19, 237, (1905).
36. Skrabal, Z. analyt. Chem. 64, 107, (1924).

4. Stability of the Arsenite Solution:

The "Arsenite Solution," of the following discussions, consists of sodium arsenite and potassium iodide with sodium bicarbonate as buffer. If the solution contains only sodium arsenite it will be designated as "sodium arsenite solution." The reaction between liberated iodine from potassium iodide and sodium arsenite has been shown in equation (8). The equilibrium constant[37, 38] for this reaction has been found to be 5.5×10^{-2} at 20°C.

(a) Effect of Carbon Dioxide and Acids: The reaction (equation (8)) can be made to go quantitatively in either direction according to the principle of Le Chatelier. If the hydrogen ion produced during the course of the reaction is removed instantaneously, the reaction proceeds quantitatively from left to right. But in the presence of any acid the reaction will take place in the opposite direction. It follows, therefore, that for the quantitative determination of liberated iodine, the solution should never be acidic. On the other hand the presence of free alkali is also not permissible due to the reaction between iodine and the hydroxyl ion to form iodide, hypoiodite and iodate as shown in equations (9) to (11). Therefore, the solution should be buffered for $p^H = 7$. No reference is known to the author regarding the fact that carbon dioxide reacts with a neutral solution of sodium arsenite.

(b) Oxidation by Oxygen and Metallic Ions: Under certain conditions the strength of the arsenite solution may decrease because of oxidation by oxygen. According

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[37] Washburn and Strachan, J. Am. Chem. Soc. 35, 681, (1913).

[33] Roebuck, J. Phys, Chem. 6, 365 (1902); 9, 727, (1905).

to Reinders and Vles[39] oxidation of arsenite to arsenate by oxygen takes place only in the presence of metallic ions as catalysts. Of the catalysts, the copper ion[40] is the detrimental one, others can be neglected if the solution is neutral or feebly alkaline. Francis[41] studied the rate of oxidation of sodium arsenite. The reactions between copper and arsenite are as follows: cupric ion forms a cupri-arsenite complex, which is reduced to a cupro-complex, whereupon the arsenite is oxidized to arsenate. The cuperous compound is again quickly oxidized by the oxygen of the air. Since the reactions are cyclic, decomposition will increase rather rapidly. Even in the presence of copper the velocity of reaction is conditioned by the hydrogen ion concentration. In neutral or acid solution the reactions are immeasurably small, but in alkaline solutions they are measurable, even though an alkali has a tendency to precipitate copper as hydroxide. The maximum effect[42,43] of these reactions is found at about 0.05 N solution in potassium hydroxide (p^H = 12.7 approximately). Beyond this point the velocity of the reaction again decreases. In an alkaline solution a substance like finely powdered charcoal acts as a catalyst to bring forth the decomposition of arsenite. Therefore, an arsenite solution made from pure chemical substances using conductivity water and buffered to neutrality gives the greatest stability.

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[39] Reinders and Vles, Rec. trav. chim. 44, 29, (1925).
[40] Jenkins and Berger, U. S. Patent No. 159,662, (1926).
[41] Francis, J. Am. Chem. Soc. 48, 655, (1926).
[42] Kolthoff, Z. analyt. Chem. 60, 393, (1921).
[43] Rheinthaler, Chem. Ztg. 36, 713, (1912).

(c) Effect of Dilution by Water: If the arsenite is neutral and free from copper ions the dilution will not have any or will have only very little effect compared to thiosulphate solution; increase in the total amount of dissolved carbon dioxide and oxygen in the dilutent water will have no effect on the neutral arsenite solution in the absence of copper ions.

(d) Decomposition by Micro-organisms: Green[44] isolated from arsenical cattle-dipping fluids a bacterium able to grow in culture media containing 1% As_2O_3 as arsenite and to bring about its oxidation to arsenate. Turner[45] reports a similar kind of bacterium and states that oxidation of arsenite is completely inhibited outside the range of p^H 3-11, and by chemicals, such as, cyanide, azide, carbon monoxide, etc. But these substances cannot safely be applied in the present method on account of the strong oxidizing action of ozone. Apparently arseno-bacteria are not present in the air as are thio-bacteria so that the stability of arsenite solution is not affected as is thiosulphate solution.

(e) Effect of Light: No literature reference has been found in regard to the action of light on a neutral arsenite solution free from metallic ions, particularly copper ions. In the presence of copper ions, however, the oxidation[40] of arsenite by atmospheric oxygen takes place even in the dark. Presence of light may hasten the oxidation.

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[44] Green, Rep. Dir. Vet. Res., South Africa 5-6, 593, (1918).

[45] Turner, Nature, 164, 76, (1949).

From the foregoing discussions it is apparent that a neutral (buffered) arsenite solution free from metallic ions is much more stable than a thiosulphate solution. In the determination of atmospheric ozone, therefore, results obtained by the arsenite method should be much more reliable than those by thiosulphate. This was verified in this laboratory. A report on this point will be submitted later. However, the presence of oxidants in the atmosphere, especially oxides of nitrogen and sulphur, will affect both the thiosulphate and arsenite methods in that many of these oxidants will undergo reactions similar to those of ozone. Detailed accounts of their possible sources when present in the atmosphere, and their effects on the arsenite method are given in the Appendix.

Chapter III

DETERMINATION OF END POINT DURING TITRATION

Several methods are available for the determination of the end point in the iodometric reactions. Iodine, or the triodide ion, has detectable color in daylight in a concentration from 4 to 10 x 10^{-6} N, provided the solution does not contain any other colored substance.[19] Iodine in small concentration, such as, 2 x 10^{-3} N can be detected by using 10 ml. of chloroform or carbon tetrachloride or benzene.[19, 24] Since the solubility of iodine in water is very small compared to that in these organic solvents, the sensitivity of the detection by organic solvent is fairly high. The sensitivity, however, drops considerably in the presence of an aqueous iodide solution due to the equilibrium distribution of iodine between the iodide solution and the organic solvent. This method is not recommended because of the complication of using an organic solvent with aqueous solutions and also because of the availability of more sensitive and simple methods.

Another unique method for the detection of iodine is the reaction between iodine or the tri-iodide ion and β-amylose, the latter being a constituent of soluble starch.[46] According to Rundle et al[46] the amylose molecules are long helical chains. The helix of proper size permits iodine molecules to enter with their long axis coincident with the axis of the helix. The β-amylose-iodine complex gives an intense blue color, which is easily detectable in daylight. Treadwell[23] illustrates in detail that the intensity of color and sensitivity of detection

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[46] Rundle, Foster and Baldwin, J. Am. Chem. Soc. <u>66</u>, 2116, (1944).

are very high in the presence of an appreciable concentration of an alkali iodide, preferably potassium iodide. In the absence of an alkali iodide an iodine concentration of from 4 to 8 x 10^{-5} N is required to give detectable color.[19] The sensitiveness of this reaction decreases with rise of temperature; at 25° C it is ten times as sensitive[24] as at 50° C. During titration, the temperature of the solution should be kept at about 20° C. At room temperature a solution containing iodine from 8 to 16 x 10^{-6} N and potassium iodide at least 4 x 10^{-5} N gives an easily visible blue color with starch solution. Some workers[42] claim the detection of the blue color of β -amylose-iodine at an iodine concentration as low as 4 x 10^{-7} N.

In this laboratory, the concentration of iodine in potassium iodide solution is maintained at approximately 0.02 N. As stated before, the detectable iodine concentration is from 8 to 16 x 10^{-6} N. Assuming that for 10 x 10^{-6} N (or 1 x 10^{-5} N) iodine concentration the detection of color of β -amylose-iodine complex is fairly easy in daylight, one drop (approximately 0.03 ml.) of 0.02 N iodine solution is equivalent to 2,000 drops of 1 x 10^{-5} N iodine solution. The normality of an arsenite or thiosulphate solution is maintained in this laboratory at about 0.03. One drop of 0.03 N arsenite or thiosulphate solution is equivalent to 3000 drops of 1 x 10^{-5} N iodine solution. Therefore, according to equation (2) the amount of ozone required to liberate a detectable amount of iodine (i.e., 1 x 10^{-5} N iodine) in one liter of iodide solution is 24 x 10^{-5} gm. Assuming that the concentration of ozone in the atmosphere near the earth's surface is 10^{-8} gm ozone per gm. of air or 1.294 x 10^{-11} gm ozone per ml. of air at N.T.P., 18.55 x 10^{3} liters of air will have to be passed through a liter solution of iodide to produce a detectable color due to the β -amylose-iodine complex. For the thiosulphate or arsenite method, however, the amount of thiosulphate or arsenite is titrated by iodine in the presence of a starch solution. Therefore, one drop of excess iodine (0.02 N), being equivalent to 2,000 drops of detectable iodine (1×10^{-5} N), will be sufficient to bring forth the blue color detectable in daylight.

Another sensitive method for the determination of the end point is conductometric titration. An apparatus similar to the description of Scott[47] was set up in the laboratory and a few measurements were made with the necessary precautions. The blue color of the β -amylose-iodine complex did not appear in a solution containing 25 ml. of about 0.03 N arsenite solution and 200 ml. of distilled water, until one drop (0.03 ml.) drop of iodine solution had been added in excess of the end point indicated by conductometric titration. In the determination of ozone both the blank solution and the solution exposed to ozonized air are titrated under the same experimental conditions and the difference of these two titer values is the indirect measure of the amount of ozone. Assuming that the observer is sensitive to the blue color of β -amylose-iodine, the difference in titer values of the blank solution and solution exposed to ozonized air should be the same by either method. This has been experimentally confirmed in this laboratory. If it is desired to eliminate the personal factor of color sensitiveness and to employ automatic recording, the conductometric titration is more convenient. In this laboratory the β -amylose-iodine titration is used almost exclusively.

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47. Scott and Furman, "Standard Methods of Chemical Analysis", Van Nostrand Co., New York, 5th edn., vol. II, p. 2308, (1939).

Chapter IV

EXPERIMENTAL PROCEDURE AND RESULTS

Comparative studies of the stability of the thiosulphate and arsenite solutions have been made to evaluate these two methods. A brief summary of the procedure for making the solutions is given below.

1. Preparation of Thiosulphate Solution:

In a liter of boiled, distilled water 40 gms of sodium bicarbonate and 24 gms of potassium iodide were dissolved. Thirty gms of hydrated sodium thiosulphate were added slowly to the above buffer solution. After complete dissolution, the solution was diluted to four liters. The resulting solution was allowed to stand for about two weeks, approximately one-third of this time in room light and the rest of the time in the dark. At the end of this stabilizing period the solution was standardized by titration with recently standardized (within an hour) solution of iodine in potassium iodide, using starch as an indicator.

2. Preparation of Arsenite Solution:

A measured amount (about 6 gms) of arsenious oxide (As_2O_3) was added carefully to 60 ml 1N sodium hydroxide solution and was dissolved completely by slow heating and stirring. The resultant solution was neutralized with 1N hydrochloric acid from a burette. Twenty-four gms of potassium iodide and 40 gms of sodium bicarbonate were dissolved in 2 liters of boiled distilled water. The neutralized sodium arsenite solution was added to this bicarbonate and iodide solution and the resultant solution diluted to four liters. It was allowed to stand for about two weeks, approximately one-third of this time in the room light and the rest of the time in the dark. At the end of this stabilizing period, the solution was standardized by titration with standard potassium iodate using starch as an indicator, and additional sodium bicarbonate as buffer during titration.

3. Effect of p^H:

As mentioned in the theoretical discussion, the p^H has a considerable effect on the stability of the solution and the reliability of the titer values. For the following experiments the thiosulphate and arsenite solutions were prepared according to the usual procedure except that the buffer, sodium bicarbonate, was not added. After a stabilizing period of two weeks 500 ml of the solution were placed in each of three flasks; one of them was made acidic by adding a few drops of dilute hydrochloric acid, the second alkaline by adding a few drops of dilute sodium hydroxide and the third was buffered by sodium bicarbonate. The p^H of each solution was determined by a Hellige p^H comparator, which reads to an accuracy of 0.2. A set of six Erlenmeyer flasks was chosen for each series of experiments. In each set of flasks two received 25 ml acidic solution from a pipette, two more received 25 ml alkaline solution, and the last two 25 ml of buffered solution. Each sample was diluted by adding 750 ml distilled water. One set of three flasks was exposed to the atmosphere and room light, while the other was kept stoppered in the dark. After a period of 48 hours the solutions

TABLE 1 Effect of p^H

In each case 25 ml of the solution was diluted with about 750 ml distilled water. Normality of iodine in potassium iodide solution = 0.018137. Since some sulphur was precipitated in acidic thiosulphate solution (p^H = 4.6) no titration was performed on these samples. One ml of 0.018137 N iodine solution is equivalent to 4.353 x 10^{-4} gm ozone.

ml IODINE SOLUTION NEEDED FOR 25 ml OF THE ORIGINAL SOLUTION											
EXPT. NO.	THIOSULPHATE SOLUTION						ARSENITE SOLUTION					
	p^H = 4.6		p^H = 7.2		p^H = 11.0		p^H = 4.8		p^H = 7.2		p^H = 11.4	
	CLOSED AND DARK	OPEN AND LIGHT	CLOSED AND DARK	OPEN AND LIGHT	CLOSED AND DARK	OPEN AND LIGHT	CLOSED AND DARK	OPEN AND LIGHT	CLOSED AND DARK	OPEN AND LIGHT	CLOSED AND DARK	OPEN AND LIGHT
I	Sulphur Precipitation and hence no titration		38.06	37.41	47.70	48.53	28.13	29.13	37.13	37.08	39.92	41.22
II			38.04	37.82	46.92	49.10	27.65	29.08	37.12	37.10	39.82	41.18
III			38.10	37.50	46.85	47.35	28.31	29.06	37.13	37.10	39.46	41.92

were titrated with standard iodine solution using starch as an indicator. Each experiment was repeated; the results are shown in Table I. This shows that both solutions are affected considerably by acidity and alkalinity.

Except for the experiment on the effect of p^H, all experiments were conducted with the thiosulphate and arsenite solutions, buffered and prepared according to the procedure already described. All titrations were done by standard iodine in potassium iodide solution using starch as an indicator.

4. Effect of Dilution by Water

In each case 25 ml of the buffered solution was taken in an Erlenmeyer flask and diluted by adding different amounts of distilled (D) or conductivity (C) water. Immediately after dilution each solution was titrated; the results are shown in Table II.

In the case of the thiosulphate solution it was thus found that the titer values progressively decreased with dilution due to increased decomposition whereas the arsenite solution was apparently not affected by dilution.

5. Effect of Exposure in the Room

Twenty-five ml of the buffered solution were taken in a set of Erlenmeyer flasks and diluted with different amounts of distilled water. These diluted solutions in stoppered flasks were kept in the laboratory room for forty-eight hours and then titrated, whereas the stock of original concentrated solution was kept in a stoppered bottle in the dark. The titers of these diluted solutions were compared to those of solutions diluted with respective amounts of distilled water

TABLE II Effect of Dilution by Water

Normality of iodine in potassium iodide solution = 0.018137. One ml of this iodine solution is equivalent to 4.353×10^{-4} gm of ozone.

Legend: D = Distilled Water
C = Conductivity Water

Expt. No.	ml IODINE SOLUTION NEEDED FOR:															
	25 ml of Thiosulphate Solution Diluted With About								25 ml of Arsenite Solution Diluted With About							
	1000 ml of		750 ml of		500 ml of		250 ml of		1000 ml of		750 ml of		500 ml of		250 ml of	
	D	C	D	C	D	C	D	C	D	C	D	C	D	C	D	C
I	38.30	38.35	38.38	38.40	38.51	38.53	38.50	38.55	37.14	37.15	37.15	37.15	37.15	37.15	37.15	37.14
II	38.32	38.35	38.38	38.45	38.48	38.57	38.57	38.57	37.14	37.14	37.15	37.15	37.15	37.15	37.15	37.13
III	38.30	38.35	38.35	38.42	38.47	38.57	38.51	38.54	37.15	37.14	37.15	37.15	37.15	37.13	37.13	37.15
IV	38.35	38.30	38.51	38.50	38.49	38.53	38.56	38.55	37.10	37.14	37.14	37.15	37.15	37.15	37.15	37.15

immediately before titration. Table III shows, in terms of iodine solutions, the difference between the titration values of the original and exposed solutions at different dilutions.

TABLE III Effect of Exposure in the Room

Normality of iodine solution = 0.018137. One ml of iodine solution is equivalent to 4.353 x 10^{-4} gm ozone.

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR:								
Expt. No.	25 ml of Thiosulphate Solution Diluted with Distilled Water				25 ml of Arsenite Solution Diluted with Distilled Water			
	1000 ml	750 ml	500 ml	250 ml	1000 ml	750 ml	500 ml	250 ml
I	1.62	1.13	0.96	0.48	0.16	0.03	0.03	0.01
II	1.79	1.13	0.70	0.51	0.20	0.16	0.04	0.03
III	1.61	1.21	0.75	0.58	0.00	0.05	0.04	0.06
IV	1.53	1.10	0.32	0.36	0.07	0.03	0.00	0.02

Table III shows that there is a considerable difference in titer values for thiosulphate solutions when the original, concentrated solution is kept in a stoppered bottle in the dark and the diluted solutions in stoppered bottles are exposed to room atmosphere and light. Therefore, the following experiments were designed. All the procedures were maintained as above except that the original concentrated solution in the stoppered bottle was also exposed to the same conditions as the diluted solutions. The results are shown in Table IV.

TABLE IV Effect of Exposure in the Room

Normality of iodine solution = 0.018137. One ml of iodine solution is equivalent to 4.353×10^{-4} gm ozone.

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR:								
Expt. No.	25 ml of Thiosulphate Solution Diluted with Distilled Water				25 ml of Arsenite Solution Diluted with Distilled Water			
	1000 ml	750 ml	500 ml	250 ml	1000 ml	750 ml	500 ml	250 ml
I	0.54	0.51	0.41	0.39	0.03	0.01	0.00	0.01
II	0.59	0.39	0.41	0.31	0.02	0.02	0.02	0.00
III	0.46	0.33	0.26	0.17	0.01	0.00	0.01	0.01

Tables III and IV show that the thiosulphate solution loses considerable stability in the presence of room lights as well as in darkness. The arsenite solution is also found to be affected in some cases, but to a much smaller degree.

6. Stability of the Solutions in Absence of Light

The general procedures were the same as for the effect of room exposure (vide Part 5 of this Chapter) except that all of the diluted and original, concentrated solutions were kept inside a closed cupboard, which was almost free from exposure to light. The results are shown in Table V.

TABLE V Stability of Solutions in Absence of Light

Normality of iodine solution = 0.01817. One ml of iodine solution is equivalent to 4.353×10^{-4} gm ozone.

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR:								
Expt. No.	25 ml of Thiosulphate Solution Diluted with Distilled Water				25 ml of Arsenite Solution Diluted with Distilled Water			
	1000 ml	750 ml	500 ml	250 ml	1000 ml	750 ml	500 ml	250 ml
I	0.34	0.31	0.30	0.28	0.00	0.01	0.02	0.00
II	0.25	0.32	0.51	0.31	0.04	0.03	0.00	0.01
III	0.42	0.18	0.32	0.27	0.01	0.01	0.00	0.00

The stability of the arsenite solution in absence of light is very good, whereas the thiosulphate solution decomposes slowly even in darkness.

7. Effect of Ultraviolet Light

In each case 25 ml of the original concentrated solution was diluted with distilled water in a wide mouth (1.75 inch i.d.) non-stoppered Erlenmeyer flask, which was exposed to a G-E Reflector lamp. (Type RS, 275 Watts, 110-115 volts, 50-60 cycle) for one hour and then titrated. The results are shown in Table VI as the difference between the titer values of the original and exposed solutions, both being diluted just before exposure and titration. The negative values in the table signify that the titer value of the exposed solution is greater than that of the corresponding diluted original solution.

TABLE VI Effect of Ultraviolet Light

Normality of iodine solution = 0.01989. One ml of iodine solution is equivalent to 4.7736 x 10^{-4} gm ozone.

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR:						
Expt. No.	25 ml of Thiosulphate Solution Diluted with Distilled Water			25 ml of Arsenite Solution Diluted with Distilled Water		
	1000 ml	750 ml	500 ml	1000 ml	750 ml	500 ml
I	-0.32	-0.35	-0.54	-0.05	+0.07	-0.05
II	+0.50	-0.30	-0.72	-0.02	-0.02	-0.00
III	+0.40	+0.54	-0.58	-0.03	-0.04	-0.00
IV	-0.35	-0.36	- - -	-0.00	-0.05	- - -

The exposure to ultraviolet light affects both the solutions, but the arsenite solution to a much smaller degree. In the case of the thiosulphate solution the negative values are too large to be regarded as experimental errors of titration.

Probably some reactions take place among the reagents under the influence of ultraviolet light that produce one or more components which in turn consume some additional iodine during titration. For the thiosulphate solution the following reactions are suggested as possible:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \quad \ldots\ldots\ldots\ldots (36)$$

Since the sodium bicarbonate of the thiosulphate solution is dilute (0.119 N) and only part of the bicarbonate is decomposed according to equation (36), the solution will be quite dilute with respect to sodium carbonate and as such, will partly hydrolyze.

$Na_2CO_3 + H_2O = 2NaOH + CO_2$ . . . . (37)

Sodium hydroxide and atmospheric oxygen are responsible for the following reactions:[48, 49]

$6NaOH + 3Na_2S_2O_3 = 2Na_2S + 4Na_2SO_3 + 3H_2O$ . . . . . . (38)

$2Na_2S + H_2O + 2O_2$ (dissolved oxygen) $= Na_2S_2O_3 + 2NaOH$. (39)

The combination of equations (38) and (39) is:

$4NaOH + 2Na_2S_2O_3 + 2O_2 = 4Na_2SO_3 + 2H_2O$ . . . . . . (40)

For every two molecules of sodium thiosulphate four molecules of sodium sulphite are formed. Two molecules of sodium thiosulphate consume one molecule of iodine (vide, equation (7)), whereas four molecules of sodium sulphite consume four molecules of iodine (vide equations (40) and(74)). Sodium sulphite is also formed due to the action of bacteria on sodium thiosulphate (vide equation (34)). Since the p^H of the solution is 7 or above, the reaction shown in equation (21) may also take place. All of these consume more iodine than indicated by equation (7). Therefore, the titer value of blank thiosulphate solution will be less than that of exposed solution and the difference will be negative. However, sodium thiosulphate itself may be decomposed, but the resultant effect of the above reactions and thiosulphate decomposition is such that more iodine is consumed by expressed solution than by the blank solution.

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48. Lung, Ber. 12, 404, (1879); 16, 2914, (1883); Chem. Ind. 6, 298, (1883).
49. Lung and Smith, J. Soc. Chim. Ind. 2, 460, 525, (1883); 3, 287, (1884).

Another explanation is possible. If enough sodium bicarbonate is decomposed by ultraviolet light, the solution will lose its buffer action and will be slightly alkaline. Either due to local concentration of iodine during titration or due to the fact that a part of the iodine will undergo hydrolysis in alkaline solution according to equation (11), more iodine will be required for the titration of exposed solution making the difference of titer values negative.

Though the negative values in the case of arsenite solutions are small enough to be considered as experimental errors, the consistency of the negative results in a few cases demands an explanation. Possibly the second explanation given for thiosulphate solution (i.e. hydrolysis of iodine due to alkalinity) can also be applied to the arsenite solution.

8. Effect of Sunlight:

The procedures in this experiment are just like the preceding except that the solution, in stoppered bottles, was exposed to Arctic sunlight for about sixteen hours during April 1952 at College, Alaska. Results are recorded in Table VII.

TABLE VII Effect of Sunlight

Normality of iodine solution = 0.01989. One ml of iodine solution is equivalent to 4.7736 x 10^{-4} gm ozone.

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR:								
Expt. No.	25 ml of Thiosulphate Solution Diluted with Distilled Water				25 ml of Arsenite Solution Diluted with Distilled Water			
	750 ml	500 ml	250 ml	100 ml	750 ml	500 ml	250 ml	100 ml
I	0.95	- - -	1.04	1.27	0.09	0.12	0.13	0.17
II	1.42	1.00	1.56	1.05	0.06	0.05	0.11	0.08

Comparing the data of Tables III, IV and VII it is found that for exposures of the same number of hours the decomposition of both thiosulphate and arsenite solutions due to room light is a little less than that due to sunlight.

Since stoppered pyrex glass flasks of thickness about 3mm were used during exposure, it is assumed that ultraviolet rays are completely cut off by the glass. Decomposition in these cases is therefore assumed to be due to ordinary light free from ultraviolet rays.

9. Effect of Carbon Dioxide and Oxygen:

It has already been mentioned that the thiosulphate solution is decomposed by carbon dioxide and oxygen under ordinary conditions, and still more by the presence of metallic ions, especially those of copper. The arsenite solution, however is not affected by carbon dioxide. Oxygen oxidizes the arsenite solution to a measureable extent only in the presence of copper ions. The distilled water used for these experiments was free from metallic ions. The apparatus used is shown in Fig. 2, and consists of two interconnected absorption columns of the type shown in Fig. 1.

Twenty-five ml of the thiosulphate and arsenite solutions were pipetted into each of three two-liter Erlenmeyer flasks and each was diluted by 1000 ml of distilled water. One of the stoppered flasks containing the diluted solution was used as a blank and kept lying near the absorption columns during the entire experiment. One flask was poured carefully into the funnel F_1 of the absorption column 1. The flask was washed several times and the wash water added through

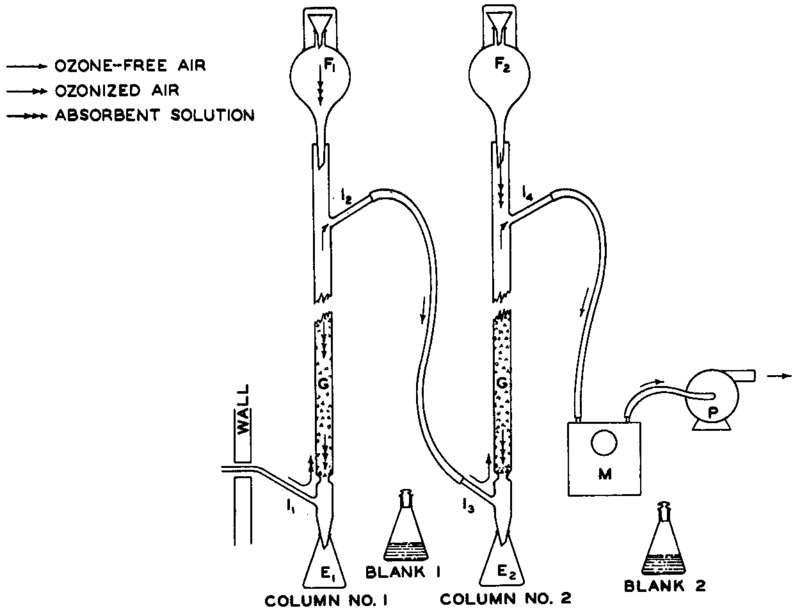

FIGURE 2

ABSORPTION COLUMNS IN SERIES TO STUDY THE EFFECT OF OZONE-FREE AIR ON ABSORBENT (SOLUTION)

Legend: Every part of the apparatus is made of pyrex glass except sections I_2 to I_3 and I_4 to P where the connections were made of pressure rubber tubing.

All other symbols have the same significance as in Figure 1.

the funnel F_1. The third flask was emptied into absorption column 2. The solution from each of the funnels was then allowed to fall drop by drop on the absorption packings* of the respective column. Air was drawn through the columns connected in series (Fig. 2) by a suction pump via a gas meter.** For each experiment the absorption columns were operated for about twenty-four hours. At the end of the operation each absorption column was washed into the Erlenmeyer flask at the bottom of the column. The solution and the wash water in each flask were titrated by iodine in potassium iodide. The blank solution was diluted to the same volume as the corresponding exposed solution and titrated. The difference between the titer values of the blank and run solutions was expressed in terms of ozone concentration and recorded in column 1 of Tables VIII and IX. The value of the actual ozone concentration for this period was determined by the arsenite method in a separate absorption column. The absorption column 2 of Fig. 2 was run with the arsenite solution for a part of the time and the thiosulphate solution for the rest of the time but absorption column 1 was always run with the arsenite solution. The actual ozone concentration (obtained from absorption column 1 of Fig. 2) was compared with and found to be within 10% of the value of actual ozone concentration obtained by the arsenite method in the separate absorption column mentioned above. An average of these two values for each day is shown in column 2 of Tables VIII and IX. The percentage error for each day is shown in column 3 of Table VIII for thiosulphate method and in column 3 of Table IX for the arsenite method.

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* Pyrex Brand Glass Helices, 3/16 inch internal diameter, made by Scientific Glass Apparatus Company, Bloomfield, N.J., U.S. Patent 2,037,317.
** Gas Meter made by American Meter Company, Albany, N.Y., Meter No. 5,853,958. - checked and standardized against a wet Gas Meter.

TABLE VIII EFFECT OF CARBON DIOXIDE AND OXYGEN ON THIOSULPHATE SOLUTION

Effect of ozone free air during 24 hrs. on thiosulphate solution. Difference in titer values expressed in terms of ozone concentration as mgm O_3 per 100 cu. meter of air at N.T.P.	For the same 24 hrs.; Actual ozone concentration determined by arsenite method as mgm O_3 per 100 cu. In. of air at N.T.P.	% error $= \frac{\Delta}{M} \times 100$
Δ	M	
0.08	4.87	1.6
0.17	4.58	3.7
0.14	4.97	+2.8
-0.80	5.45	-14.7
0.36	3.85	+9.4
-0.67	6.12	-11.0
-0.01	5.82	-0.2
-1.80	3.58	-50.3
0.94	4.32	+21.8
1.10	4.32	25.5
1.44	4.78	30.1
2.85	5.00	57.0
2.79	4.60	60.7
2.08	5.13	40.6

TABLE VIII (Continued)

Difference in titer values	Actual Ozone conc.	% Error	Difference in titer values	Actual Ozone conc.	% Error
Δ	M		Δ	M	
1.90	5.65	33.6	1.12	2.50	44.8
4.02	4.13	97.3	1.40	3.39	41.3
1.69	4.48	37.7	0.35	3.24	10.8
2.23	4.89	45.6	-0.72	2.76	-26.1
2.28	4.88	46.7	-0.19	2.44	-7.8
1.29	3.09	41.8	-0.67	4.97	-13.5
2.67	4.27	62.5	-1.57	2.80	-56.1
1.53	3.82	40.0	-0.91	1.47	-61.9
1.50	4.04	37.1	-2.38	2.92	-81.5
0.82	4.82	17.0	-2.45	1.92	-127.6
0.48	4.14	11.6	-0.12	2.32	-5.2
0.86	3.28	26.2	-0.90	1.16	-77.6
2.53	3.74	67.7	-1.05	2.34	-44.9
2.92	3.01	97.0	-1.42	2.16	-65.7
2.51	2.39	105.0	-1.53	2.93	-52.2
1.55	2.17	71.4	-2.61	3.09	-84.5
1.04	2.29	45.4	-3.94	1.80	-218.9
0.49	2.85	17.2	-2.44	2.60	-93.9
0.88	3.17	27.8	-2.42	2.50	-96.8
-0.09	----	----	-5.64	3.45	-163.5
0.78	3.30	23.6	-3.88	2.99	-129.8
0.57	3.78	15.1	-1.97	2.93	-67.2
			-2.61	1.88	-138.3

TABLE IX EFFECT OF CARBON DIOXIDE AND OXYGEN ON ARSENITE SOLUTION

Effect of ozone free air during 24 hrs, on arsenite solution. Difference in titer values expressed in terms of ozone concentration as mgm O_3 per 100 cu. meters of air at N.T.P.	For the same 24 hrs.; Acutal ozone concentration determined by arsenite method as mgm O_3 per 100 cu. In. of air at N.T.P.	% error $= \frac{\Delta}{M} \times 100$
Δ	M	
0.15	5.73	2.6
0.05	7.02	0.7
0.13	5.50	2.4
0.11	5.44	2.0
0.00	6.34	0.0
0.00	4.64	0.0
0.05	5.58	0.9
0.00	5.44	0.0
0.00	4.02	0.0
0.02	5.55	0.4
0.12	5.54	2.2
0.00	5.40	0.0
0.11	5.12	2.2
0.07	4.37	1.6
0.00	4.62	0.0
0.00	4.97	0.0
0.00	4.51	0.0
-0.05	5.99	-0.8

TABLE IX (Continued)

Difference in titer values Δ	Actual ozone conc. M	% error
0.07	6.28	1.1
0.03	5.85	0.5
0.00	5.81	0.0
0.04	4.16	1.0
0.02	5.85	0.3

Tables VIII and IX show that ozone-free air affects the thiosulphate solution considerably whereas the arsenite solution is affected very little. Each of the values expressed as M in Column 2 of the tables is the concentration of atmosphere ozone obtained on the particular day by the arsenite method. Assuming those to be the actual concentration of ozone on those days the percentage of error in the Thiosulphate Method ranges from +105% to -219% (vide Column 3 of Table VIII) and in the case of the Arsenite Method ranges from +2.6% to -0.83% (vide column 3 of Table IX). The reason for negative values is not quite clear except experimental errors and the explanations given in connection with equations (36) to (40) in part 7 of this chapter and the explanation given below. Though the percentage of errors of the Arsenite Method may be regarded as experimental, those for the Thiosulphate Method are too large to be so considered. If the ozone-free air contains sulphur dioxide, sodium sulphite and bisulphite will be formed as a result of reactions between sulphur dioxide and sodium bicarbonate (c.f. equations (72) and (73)). Sodium bisulphite and sulphite react with iodine (c.f. equations (74) and (75)) during titration. If both sulphur dioxide and hydrogen sulphide are present in the ozone-free air the reaction between them in presence of water may produce thiosulphuric acid.[50,51] The thiosulphuric acid and its salts will consume iodine during titration. Since the atmospheric air is passed through the absorption Column No. 1 (Fig. 2) to free it from ozone, the sulphur dioxide and hydrogen sulphide present in the air, will react with sodium bicarbonate or with each other in the same manner as described above. Therefore, the exit air from the Column No. 1 should be free from these gases. However, the rates of these reactions are slow and there is a possibility of some of these gases being present in the exit air of Column No. 1. When this exit air is introduced to Column No. 2, further reactions may take place. It should be mentioned that the exit air of the Column No. 1 has been carried through a ten-foot length of one inch (internal diameter) soft rubber tubing on its way to Column No. 2. This vulcanized rubber tubing may contribute, though unlikely, minute quantities of sulphur compounds[52] such as hydrogen sulphite and sulphur dioxide, which may in turn produce traces of thiosulphuric acid and its salts. There is another possible source of sulphur dioxide: In the presence of excess air sodium tetrathionate, which is formed as a result of the reaction between sodium thiosulphate and iodine (or some other agents), will decompose to give a sulphur dioxide as a primary product.[53]

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50. Förster and Mommensen, Ber., 57, (B), 258, (1924).
51. Förster and Hornig , Z. anorg. Chem. 125, 86, (1922).
52. c.f. Besset and Durrant, J. Chem. Soc. 151, 1401, (1927).
53. Cornog and Henderson, J. Am. Chem. Soc. 46, 1978, (1924).

On the other hand, sodium thiosulphate may be destroyed by various mechanisms as discussed in Chapter II. Whether the percentage of error is negative or positive depends on the result of these two opposing effects.

10. Effect of Dripping Over Glass Helices

For this set of experiments the rate of dripping of the thiosulphate and arsenite solutions and other experimental conditions were the same as in the preceding with the exception that no air was passed through the Column. The inlet and the outlet (I_1 and I_2 of Fig. 1.) for the air were kept closed by glass stoppers. The solution, dripping from the separating funnel, F_1, on the glass helices (for specifications see Fig. 1) spread into a large surface and tricled down the column to the Erlenmeyer flask E at the bottom. The purpose of these experiments was to find whether the spreading of the solution over a large surface of the helices had any effect. The results are shown in Table X for the thiosulphate solution and in Table XI for the arsenite solution.

TABLE X EFFECT OF SPREADING THE THIOSULPHATE SOLUTION ON LARGE SURFACES

Normality of iodine solution = 0.019896 (for Expt. Nos. 1 - 37 inclusive).

Normality of Iodine solution = 0.019568 (for the rest of the experiments).

1 ml of iodine solution is equivalent to 4.775×10^{-4} gms O_3 (for Expt. Nos. 1 - 37 inclusive) and 4.696×10^{-4} gms O_3 (for the rest of the experiments).

TABLE X (Continued)

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR					
Expt. No.	25 ml of thiosulphate solution diluted with about 1000 ml of distilled water	Expt. No.	25 ml of thiosulphate solution diluted with about 1000 ml of distilled water	Expt. No.	25 ml of thiosulphate solution diluted with about 1000 ml of distilled water
1	-0.11	19	0.70	37	1.22
2	+0.04	20	0.41	38	0.79
3	+0.01	21	1.08	39	+0.92
4	+0.03	22	0.78	40	-0.03
5	-0.27	23	0.85	41	+1.07
6	+0.02	24	0.61	42	0.83
7	-0.34	25	0.67	43	0.95
8	-0.41	26	0.71	44	0.75
9	-0.03	27	0.35	45	1.50
10	-0.33	28	0.42	46	0.33
11	+0.32	29	0.43	47	0.22
12	-0.42	30	0.29	48	0.36
13	-0.28	31	0.71	49	0.46
14	-0.19	32	0.70	50	0.57
15	+0.40	33	0.73	51	+0.06
16	+0.27	34	1.18	52	-0.16
17	00.75	35	1.34	53	+0.53
18	0.31	36	0.67	54	+0.26

TABLE XI EFFECT OF SPREADING THE ARSENITE SOLUTION ON LARGE SURFACES

Normality of iodine solution = 0.019966

1 ml of iodine solution is equivalent to 4.792×10^{-4} gms O_3

DIFFERENCE IN TITER VALUES IN ml OF IODINE SOLUTION FOR					
Expt. No.	25 ml of arsenite solution diluted with about 1000 ml of distilled water	Expt. No.	25 ml of arsenite solution diluted with about 1000 ml of distilled water	Expt. No.	25 ml of arsenite solution diluted with about 1000 ml of distilled water
1	+0.01	4	+0.02	7	+0.02
2	-0.02	5	0.00	8	0.00
3	+0.01	6	0.00	9	-0.01

In this case also the thiosulphate solution is much more affected than the arsenite solution. The values in the case of arsenite solution (Table XI) may be considered due to experimental error, whereas those for the thiosulphate solution are too large to be so considered. Due to spreading of the solution into a large surface on the glass helices the action of light, (vide Tables III and IV of this chapter), and decomposition of different kinds (vide chapters II and IV) may cause results such as shown in Table X.

11. Discussion of Results

In all the experiments except those on p^H it is found that the thiosulphate solution is affected to a greater extent than the arsenite solution. So far as the

p^H is concerned, both the solutions are affected considerably, when they are strongly alkaline or acidic, due to the side reactions already discussed (vide Chapter II). If an arsenite solution is buffered so as to be in the range of p^H 7 to 8 (preferably at 7 in all phases of the reactions and experimental procedure) and made from pure chemicals using conductivity water free from any metallic ions, specially copper, its stability is much better than that of a thiosulphate solution made with the same care. Therefore, in this laboratory the Arsenite Method for the determination of atmospheric ozone has been adopted for future work. The question may be asked as to whether the Arsenite Method determines the actual concentration of atmospheric ozone. All that can be said is that the Arsenite Method is decidedly better than the Thiosulphate Method and that it should be checked and standardized against an artificially ozonized air of known composition produced in the laboratory under controlled conditions. However, statistical analysis of the data from the two absorption columns operated simultaneously and using both the Thiosulphate and Arsenite Methods, reveals that the Arsenite Method is the more consistant of the two. This analysis will be given in a later report.

In the determination of ozone concentration by the Arsenite Method the volume of atmospheric air passed through the absorption column (Fig. 1) should be considerable (say, more than 10^4 liters). The more air, the greater the amount of ozone and, therefore, the greater the difference in the titer values between the blank and run solutions (c.f. Chapter I, (1C)) and the smaller is the percentage of error due to experimental procedure. If the flow rate of the atmospheric air through the absorption column is high the height of the absorption packings and the rate of dripping of the arsenite solution should be increased correspondingly to ensure the complete absorption of the ozone.

As stated before, (vide the end of Chapter II) the oxidants may be present in the atmosphere depending upon local conditions. Some of these undergo reactions with the arsenite solution in the same way as ozone and, therefore, for the absolute value of ozone concentration the oxidants and their concentrations in the atmosphere near the earth's surface should be determined and the necessary correction made. In some localities, however, the concentrations of the oxidants in the atmosphere may be too small to affect the ozone value determined by the Arsenite Method. The occurrence and the effect of oxidants are discussed in detail in the Appendix.

APPENDIX

EFFECT OF DIFFERENT CONSTITUENTS OF POLLUTED AIR

The different constituents of polluted air may react with themselves in many different ways in the atmosphere. In this report the discussions will be mainly confined to their effect on the Arsenite Method after entering the absorption column. It has been shown that the Arsenite Method is better than the Thiosulphate Method for the determination of atmospheric ozone, and therefore, the Thiosulphate Method will not be referred to in this discussion. It should, however, be pointed out that the oxidants and other constituents of the atmosphere affect the Thiosulphate Method to a greater degree than they do the Arsenite Method. Ozone itself undergoes various reactions with the different constituents of a polluted air in the atmospheric space, but the discussion will be restricted to reactions which are possible in the absorption column.

The effect of the constituents of air free from ozone and oxidants on the Arsenite Method have already been treated (vide Chapter II, Part (4) and Chapter IV, Part (9)). Since atmospheric air has been passed through the absorption column No. 1, (Fig. 2) prior to its introduction to the absorption column No. 2, the constituents of the air leaving absorption column No. 1 are, presumably, oxygen, nitrogen, carbon dioxide and inert gases. Atmospheric air, however, may contain various other substances[54-56] depending upon the degree of pollution

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[54] Third Interm Report Smog Problems in Los Angeles (1950), p.8.

[55] Adel, Scientific Report No. HA-1, Contract AF 19(122)-198, U.S. Air Force, Cambridge Research Center, October, 1951.

[56] Hewson, Compendium Meteor, Am. Meteor. Soc..(1951), p. 1139.

Of these, oxidants are of importance here, because the chemical methods for the determination of atmospheric ozone may be seriously affected by them. The oxidants likely to be present in the atmosphere have been described as ozone, hydrogen peroxide, nitrogen oxides, organic peroxides, and others.[54] Since our purpose is to determine the concentration of atmospheric ozone, the oxidants other than ozone, their sources, concentrations, and their effects on the Arsenite Method require discussion.

1. <u>Hydrogen Peroxide (H_2O_2):</u>

Hydrogen perioxide (commonly expressed as HO · OH) is formed as a result of various reactions including the direct combination[57] of oxygen molecules and atomic hydrogen under certain circumstances. Gerb and Harteck[58] report that at a very low temperature a different form of hydrogen peroxide, possibly  $\begin{matrix} H \\ H \end{matrix} > O \longrightarrow O$ is produced by the interaction of atomic hydrogen and oxygen. Hydrogen peroxide is also formed at high temperatures[59] (about 2000°C). Since atomic hydrogen is assumed to be present in the upper atmosphere of the earth (c.f. Bates and Nicolet[60]), especially near and in the polar zones, there may be a possibility of the formation of hydrogen peroxide.

Ultraviolet radiation from the sun is known to assist in forming hydrogen peroxide. Charitschkoff[60] reports that hydrogen peroxide can be detected in water, having a little oxygen in solution, after exposure to bright sunlight at 9°

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[57] Thorn and Roberts, "Inorganic Chemistry", Interscience Publishers, New York, 5th Edition, (1949) pp. 415, 678, 167.

[58] Gerb and Harteck, Ber., <u>65</u>, (B) 1551, (1932).

[59] c.f., Mellor, "Inorganic and Theoretical Chemistry", Longmans Green & Co., London, Vol. I, (1927), pp. 922-928, 907.

[60] Charitschkoff, J. Russ. Phys. Chem. Soc. <u>42</u>, 900, (1910); Bates and Nicolet, J. Geophys. Res. <u>55</u>, 301, (1950).

to 20°C for 12 days, at 19° to 31°C for 8 days, and at 21° to 41° for 7 days. According to Tian (vide ref. 59) ultraviolet light of short wave length (λ 2500-3000) decomposes hydrogen peroxide solution ($H_2O_2 = H_2O + O$) at a measurable rate. On the other hand, water is decomposed by the rays in the extreme ultraviolet (less than λ 1900) according to the reversible reaction $2H_2O \rightleftharpoons H_2O_2 + H_2$. The combination of these two equations is H $H_2O = H_2 + O$, which is the usual equation for the decomposition of water. If, however, water contains dissolved oxygen, the liberated hydrogen may unite with oxygen in a primary way to form hydrogen peroxide. On the other hand, some of the dissolved oxygen may, under the influence of the ultraviolet rays of the sun, form ozone which will react with hydrogen peroxide according to the equation:

$$O_3 + H_2O_2 = H_2O + 2O_2 \quad . . . . (41)$$

It should be pointed out that the above reaction is found to be slow.[6] Manganese salts, however, accelerate this reaction.[61] No reaction between ozone and water has been found to take place under the influence of ultraviolet rays.

In the presence of sunlight and water vapor the chlorophyll of plants reacts on the carbon dioxide of the air forming formaldehyde and percarbonic acid.[62,63]

$$3H_2O + 3CO_2 = 3H_2CO_3 = 2H_2CO_4 + HCHO . . . . (42)$$

The percarbonic acid decomposes into carbon dioxide and hydrogen peroxide.

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61. Inglis, J. Chem. Soc. 83, 1010, (1903).
62. Bach, Compt. Rend. 116, 1145, (1893); 118, 286, 1218, (1894); Ber. 27, 340, (1894).
63. Bach and Chodat, Ber. 35, 2466, (1902).

Fischer and Ringe[64] report that hydrogen peroxide is formed if a mixture of steam and air is passed quickly through a stream of electric sparks and then rapidly cooled. On this basis it may not be futile to postulate that hydrogen peroxide is formed by atmospheric electric discharge during thunderstorms, because all the conditions stated by Fischer and Ringe are fulfilled.

In an industrial city there are a number of other sources[59] of hydrogen peroxide, such as different oxidation processes, chemical reactions etc. in the industrial plants. But hydrogen peroxide is decomposed by light, metallic surfaces, finely divided carbon particles etc. It also combines with many organic and inorganic salts in the same way as water of crystallization.[65-68] Many of these chemicals, such as ammonium salts, nitrates, chlorides, etc., are present in the lower atmosphere along with dust and carbon particles. Ozone destroys hydrogen peroxide as shown in equation (41). All these processes of destruction indicate that the concentration of hydrogen peroxide in the lower atmosphere should be nil or immeasurably low. This is confirmed by an experiment performed in connection with the smog problem.[54] If, by any chance, hydrogen peroxide is found to be present in the atmosphere it will react with the potassium iodide of the Arsenite Method in the same manner as ozone. But hydrogen peroxide reacts slowly with a 2% solution of potassium iodide,[69] the reaction being slower the greater the dilution of the potassium iodide solution.

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[64] Fischer and Ringe, Ber. <u>41</u>, 945, (1908).

[65] Wieder, Ber. <u>31</u>, 516, (1898).

[66] Willstäter, ibid, <u>36</u>, 1828, (1903).

[67] Tanatar, ibid, <u>42</u>, 1544, (1909).

[68] Curtis, J. Am. Chem. Soc. <u>42</u>, 720, (1920).

[69] Regener, Investigation in the Physics of Atmospheric Ozone, Report No. 12, Contract W28-099-ac-379, Air Material Command and Uni. New Mexico, Nov. 30, 1950, Section 5.

In this laboratory the concentration of potassium iodide in the arsenite solution used for the determination of atmospheric ozone is about 0.006% (vide Chapter IV, Part (2)). However, the reaction between ozone and potassium iodide is very fast and efficient.[69] Therefore, in a very dilute solution (0.006% in KI) ozone will react with potassium iodide in preference to hydrogen peroxide. Assuming that hydrogen peroxide is present in appreciable concentration in the atmosphere, precautions are suggested elsewhere (Appendix, Part (6)).

2. Nitrogen Oxides:

There are a number of nitrogen oxides,[57] of which five (nitrous oxide, N_2O; nitric oxide, NO; nitrogen trioxide, N_2O_3; nitrogen peroxide N_2O_4 or NO_2; nitrogen pentoxide N_2O_5) are commonly known. Among these, nitrous oxide occupies a special position, because the rest of them are easily interconvertible. Nitrous oxide, however, can be obtained by the reduction of the higher oxides, but it cannot be directly oxidized to them.

(a) Nitrous Oxide (N_2O): The existence of nitrous oxide in the earth's atmosphere has been reported by a number of workers.[55, 70-72]

Nitrous oxide is not easily formed by the direct union of nitrogen and oxygen. From thermodynamic considerations, Matignon[73] states that nitrogen and oxygen combine to form nitrous oxide at 3000° C and 3000 atm. Ultraviolet rays do not produce nitrous oxide.[74] Warburg and Leithäuser[75] found that nitrous oxide and

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[70] Shaw, Sutherland and Wormel, Phys. Rev., 74, 978, (1948).
[71] Kriegel, Geophysics, 9, 447, (1944).
[72] Taylor, Brown, Young and Headington, Anal. Chem. 20, 396, (1948).
[73] Matignon, Compt. Rend. 154, 203, (1912).
[74] Berthelot and Guadechon, ibid, 150, 1517, (1910).
[75] Warburg and Leithäuser, Sitzber. Akad., Berlin, p. 148, (1908).

nitrogen pentoxide are formed when a mixture of nitrogen and oxygen is passed through a silent electric discharge or ozonizing tube. When the mixture is sparked between platinum electrodes,nitrous oxide and nitrogen peroxide are produced. But nitric oxide and nitrogen peroxide are formed when the mixture is exposed to a high voltage alternating arc. Hence, it can be said that there is a possibility of the formation of nitrous oxide during thunderstorms.

Nitrogen is an essential element for the maintenance of soil fertility. For utilization by plants nitrogen is needed in inorganic form as salts of ammonia, nitrous acid, and nitric acid. Organic nitrogen in the soil is largely in the form of proteins and their derivatives. The amino-acids within the proteins provide the opportunity for certain kinds of microbes to react and release ammonia in the following way:[55]

$$\underset{\text{(Glutamic Acid)}}{HOOC\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot COOH} + H_2 = \underset{\text{(Butyric Acid)}}{HOOC\cdot CH_2\cdot CH_2CH_3} + CO_2 + NH_3 \quad . \; . \; (43$$

This ammonia may form salts due to the presence of different kinds of anions in the soil or it may form nitrous acid due to bacterial action

$$2NH_3 \; + \; 3O_2 \; = \; 2HNO_2 \; + \; 2H_2O \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (44)$$

The oxidation of nitrous acid to nitric acid may take place due to another set of bacteria

$$2HNO_2 \; + \; O_2 \; = \; 2HNO_3 \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (45)$$

The interaction between hitherto unreacted ammonia and liberated nitrous acid and nitric acid forms respectively nitrite and nitrate of ammonia. Since nitrous acid or nitrite is easily oxidized to nitric acid or nitrate, ammonium nitrate will probably be present in larger quantity than ammonium nitrate. Moreover, inorganic, commercial ammonium salt fertilizers are almost always added to the soil either as ammonium nitrate or ammonium sulphate, but not as ammonium nitrite. As a convenient method of laboratory preparation nitrous oxide is obtained by heating (170° - 260° C) ammonium nitrate. Therefore, it is probable that slow decomposition of ammonium nitrate in the soil produces nitrous oxide.[71] Kriegel[71] also points out that, "In connection with the studies of decomposition of vegetation under aerobic conditions, it has been shown by this laboratory that a gas having properties similar to nitrous oxide forms a large portion of the condensed fraction." On the other hand soil biologists believe that one of the end products of the series of actions of nicrobes on proteins in the soil may be nitrous oxide.[55] The formation of nitric acid from proteins has been mentioned. The reduction on nitric acid to nitrous oxide, according to soil biology, takes place in the following fashion:

$$HNO_3 + H_2 = H_2O + HNO_2 \tag{46}$$

$$HNO_2 + H_2 = H_2O + HNO \tag{47}$$

$$2HNO = H_2N_2O_2 \tag{48}$$

$$H_2N_2O_2 - H_2O = N_2O \tag{49}$$

or

$$HNO + H_2 = H_2NOH \tag{50}$$

$$2H_2NOH = H_6N_2O_2 \tag{51}$$

$$H_6N_2O_2 - H_2 = H_4N_2O_2 \tag{52}$$

$$H_4N_2O_2 - H_2 = H_2N_2O_2 \tag{53}$$

$$H_2N_2O_2 - H_2O = N_2O \tag{54}$$

Taylor, et al[72] found that a typical soil gas consists of ethane, propane, water and nitrous oxide. Of these, the nitrous oxide is found to be the predominant gas. Therefore, the soil may be the principal source of nitrous oxide in the atmosphere. Similar mechanisms of decomposition of organic substances to nitrous oxide may take place, even on a larger scale, in the seas.[55]

As pointed out before, nitrous oxide is ordinarily resistant to conversion into other oxides of nitrogen and also to oxidizing and reducing agents. However, it decomposes into its elements or forms other oxides when passed through red-hot porcelain or platinum tubes, etc.[76] The conditions for the above decomposition are not available in the earth's atmosphere. Since hydrogen sulphide and ammonia may be present in the lower atmosphere depending upon the local pollution, (see appendix, Part (5)) the following reactions[76] are possible during a thunderstorm. Under the influence of the electric spark, hydrogen sulphide and nitrous oxide react to give sulphur dioxide, water and nitrogen; carbon monoxide and nitrous oxide give nitrogen and carbon dioxide.

There is no literature reference known to the author for any reaction between ozone and nitrous oxide. As stated before nitrous oxide is ordinarily resistant to oxidizing agents, but in some cases, red heat or electric spark makes the oxidation of nitrous oxide possible. Therefore, it may be postulated that ozone may oxidize nitrous oxide due to electric discharges during thunderstorms.

Dumreicher[76] observes that nitrous oxide reacts with hydrogen iodide to form a white cloud, which gradually reddens and in which iodine crystals appear.

$$N_2O + 10HI = 2NH_4I + H_2O + 4I_2 \qquad \ldots\ldots\ldots\ldots (55)$$

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76. c.f. Mellor, "Inorganic and Theoretical Chemistry", Longmans, Green & Co., London, <u>VIII</u>, 394-400, 206-212, 530-531, (1927).

The reaction is possible due to the extreme instability of hydroiodic acid giving rise to nascent hydrogen and iodine. But nitrous oxide, being ordinarily resistant to oxidizing and reducing agents, should not react in neutral solution with either potassium iodide or sodium arsenite. Therefore, the presence of nitrous oxide in the lower atmosphere should not affect the Arsenite Method of ozone determination.

(b) Nitric Oxide (NO): In general, nitric oxide is regarded as the first product of oxidation of nitrogen, although other oxides may form under certain conditions. There is a large number of processes for formation of nitric oxide, but only those which are directly or indirectly connected to the formation of nitric oxide in the earth's atmosphere,[77-81] will be discussed here. Nitric oxide is produced in air along with ozone by silent electric discharge, the high potential A. C. arc, and the electric spark. It is also produced when air is passed over white-hot surfaces, and by burning hydrocarbons, carbon monoxide, or hydrogen in the air. Nitric oxide also forms when nitrogen peroxide is treated with water and when nitric acid reacts with metals such as, copper, bismuth, lead, silver and mercury. It is known that nitric oxide is formed as an intermediate product during the oxidation of ammonia to nitric acid,[76] but the concentration of ammonia in the atmosphere is too low for the above oxidation. Nitric oxide may also be formed as a result of bacterial action. Tacke and Lebedeff[76] found that the

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77. Manchot, Ber., 41, 471, (1908).
78. Fischer and Marx, ibid., 39, 2557, 3631, (1906); 40, 443, 1111, (1907).
79. Muthmann and Hofer, ibid., 36, 438, (1903).
80. Nerst, Z. anorg. Chem. 49, 213, (1906).
81. Haber and Coates Z. phys. Chem 69, 337, (1909).

result of the action of bacterium hartebii on nitrates, which are present in the soil and in dust, is the formation of nitric oxide.

In conclusion, it can be said that nitric oxide may be formed in large amounts by electric discharges during thunderstorms and in electric generating stations. In an industrial area it may also be produced by various chemical reactions.

Nitric oxide combines with oxygen easily at ordinary temperatures forming nitrogen peroxide. The latter combines with cold water or water vapor to form nitrous acid and nitric acid,

$$2NO + O_2 = 2NO_2 \qquad \ldots\ldots\ldots\ldots \quad (56)$$

$$2NO_2 + H_2O = HNO_2 + HNO_3 \qquad \ldots\ldots\ldots\ldots \quad (57)$$

Warm aqueous solutions of nitrous acid, however, decompose in the following way:

$$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O \qquad \ldots\ldots\ldots\ldots \quad (58)$$

This nitric oxide of equation (58) is again oxidized by oxygen and more nitric acid is produced as a result of the above reactions.

Pinkus and Schulthess[82] observe that the reaction between concentrated ozone and nitric oxide takes place with the evolution of light and has the characteristics of an explosion when the concentration of ozone is low. In the earth's atmosphere, nitric oxide and ozone are present only in such very low concentration, that the reaction between them should not produce any light or explosion; it should, however, be a mere oxidation similar to that by oxygen. A mixture of

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82. Pinkus and Schulthess, J. chim. Phys, 18, 366, (1920); Helvetica chim. Acta. 4, 288, (1921).

nitric oxide, sulphur dioxide and oxygen in the presence of water always forms nitrous oxide[83] and sulphur trioxide; the latter combines with a further quantity of nitric oxide forming nitrosylsuphur trioxide, which is also formed by the action of nitrogen peroxide on sulphur dioxide. The nitrosylsulphur trioxide reacts with water forming sulphuric acid and nitric oxide, and the latter goes through the cycle again.

$$SO_2 + 2NO = SO_3 + N_2O \quad \ldots\ldots\ldots\ldots (59)$$

$$SO_3 + NO = SO_3 \cdot NO \quad \ldots\ldots\ldots\ldots (60)$$

$$SO_2 + NO_2 = SO_3 \cdot NO \quad \ldots\ldots\ldots\ldots (61)$$

$$SO_3 \cdot NO + H_2O = H_2SO_4 + NO \quad \ldots\ldots\ldots\ldots (62)$$

Nitric oxide and carbon monoxide do not react with each other at the ordinary temperature and pressure. Briner and Wroczynsky[84] found that even at a pressure of 50 atmospheres there is no reaction between them; however, there is evidence of a chemical change at about 500 atmospheres pressure.

Nitric Oxide is susceptible to oxidizing and reducing agents under certain circumstances. Nitric oxide reacts slowly with dilute hydrogen sulphide. It has no reaction on potassium iodide,[76] a constituent in the Arsenite (and also Thiosulphate) Method for the determination of ozone. The vital reaction in the present case is the oxidation of sodium arsenite to socium arsenate,[85,86] by nitric oxide.

$$AsO_3^{---} + 2NO = AsO_4^{---} + N_2O \quad \ldots\ldots\ldots\ldots (63)$$

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83. Lunge, Ber., 14, 2196, (1881).
84. Briner and Wroczynsky, Z. anorg. Chem. 63, 49, (1909).
85. Gutmann, Ber., 55, (B), 3007, (1922).
86. Klemenc, ibid., 58 (B), 492, (1925).

This reaction is favored by an alkaline solution. In neutral solution the reaction is very slow, whereas the liberation of iodine from potassium iodide by ozone is very fast and the subsequent reaction between iodine and sodium arsenite is also very fast. However slow the reaction of equation (63) may be, it is a threat to the Arsenite (or Thiosulphate) Method.

(c) Nitrogen Trioxide (N_2O_3): Ordinarily nitrogen trioxide is not stable. Dixon and Peterkin[87] believe that when nitric oxide and nitrogen peroxide molecules collide with each other, a weak union takes place and forms nitrogen trioxide. Wourtzel[88] reports that in a stoichiometric mixture of nitric oxide and nitrogen peroxide, 2.5% of nitrogen trioxide is formed. In the liquid state nitrogen trioxide (m. pt. -14.4° C) is stable, but complete dissociation into nitric oxide and nitrogen peroxide takes place in the gaseous state[89] at room temperature. Therefore, nitrogen trioxide is not likely to be present in the earth's atmosphere.

(d) Nitrogen Peroxide (NO_2): In general, nitrogen peroxide in the gaseous state is represented by the formula NO_2 but in the liquid state by the formula N_2O_4 (nitrogen tetroxide). Since the subject under discussion here is the occurrence of this substance in the earth's atmosphere, it will be referred to as nitrogen peroxide (NO_2).

It has been mentioned before that nitrogen peroxide is easily formed from nitric oxide by its union with oxygen at ordinary temperatures. In the laboratory,

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[87] Dixon and Peterkin, J. Chem. Soc. 75, 613, (1899).
[88] Wourtzel, Compt. Rend., 170, 109, (1920).
[89] Lunge and Porchneff, Z. anorg. Chem. 7, 209, (1894).

when a bottle containing colorless nitric oxide is opened, a brown colored gas appears immediately at the mouth of the bottle, showing the instantaneous formation of nitrogen peroxide. Raschig[90] states that by the action of air on nitric oxide nitrogen isotetroxide is formed instead of nitrogen tetroxide. Müller,[91] however, does not confirm this statement. In this report it is considered that nitrogen peroxide is the only product of the union of nitric oxide and oxygen. Nitrogen pentoxide decomposes to nitrogen peroxide when exposed to light.[92] In an industrial area nitrogen peroxide may frequently be formed by various chemical reactions.[93, 76]

Nitric oxide is oxidized to nitrogen peroxide, but the latter again decomposes photochemically to the former.[94] The reactions of nitrogen peroxide with water, sulphur dioxide and sulphur trioxide have been discussed (c.f. equations (57) and (59-62)). Nitrogen peroxide reacts with gaseous hydrogen sulphide with the formation of sulphur, nitric oxide, and water

$$NO_2 + H_2S = NO + H_2O + S \qquad \ldots\ldots\ldots\ldots (64)$$

Besson and Rosset[95] report that a moderate reaction takes place between ammonia and nitrogen peroxide at -20° C producing nitrogen, nitric oxide, water, ammonia, and ammonium nitrate, but the reaction becomes energetic at a higher temperature. Nitrogen peroxide reacts slowly with ammonium chloride[94] in the cold. In a sealed tube and at 100° C, the reaction is complete with the formation

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[90] Raschig, Chem. Ztg. 31, 359, (1907); Z. anorg. Chem. 84, 115, (1913); "Schwefel-und Stickstoffstudien," Leipzig, 20, (1924).

[91] Müller, Z. anorg. Chem. 76, 324, (1912); 86, 230, (1914).

[92] Berthelot, Compt. Rend. 217, 83, (1898).

[93] Bogorodsky, J. Russ. Phys. Chem. Soc. 37, 703, (1905).

[94] Norrish, Nature, 119, 123, (1927); J. Chem. Soc. 151, 761, (1927).

[95] Besson and Rosset, Compt. Rend. 142, 633, (1906).

of chlorine, nitrogen, nitrous oxide, nitrogen trioxide, nitrosyl chloride, water and nitric acid. The action of nitrogen peroxide on ammonium nitrate or sulphate results in the production of nitrogen and nitric acid or nitrogen and a mixture of nitric and sulphuric acids.

It is known that nitrogen peroxide does not combine with oxygen either at high or low temperature. But it is oxidized to nitrogen pentoxide by ozone.[96,97] Wulf, et al[98] state that at 25° the oxidation of nitrogen peroxide by ozone is instantaneous. Pinkus and Schulthess[82] draw a similar conclusion in regard to the reaction of ozone and nitrogen peroxide and that of ozone and nitric oxide. Carbon monoxide which may be present in the atmosphere is oxidized to carbon dioxide at ordinary temperature by nitrogen peroxide. It oxidizes potassium iodide to iodine and sodium arsenite to sodium arsenate.

$$NO_2 + 2I^- + H_2O = I_2 + NO + 2\,(OH)^- \quad \ldots\ldots\ldots\ldots (65)$$

$$NO_2 + AsO_3^{---} = NO + AsO_4^{---} \quad \ldots\ldots\ldots\ldots (66)$$

But the last mentioned reaction (equation (66)) is so slow that in a mixture of potassium iodide and sodium arsenite, nitrogen peroxide reacts with the former only as long as this is present in sufficient amount. On the other hand the oxidation of these by ozone (vide equations (1) and (2)) is much more rapid than by nitrogen peroxide,[69] and therefore, the presence of the latter in the atmosphere may not be as detrimental as often considered. However, it is certainly one of the objectionable components of polluted air so far as the determination of atmospheric ozone by the Arsenite Method is concerned. Means for eliminating nitrogen peroxide are suggested elsewhere (vide Appendix. Part (6)).

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96. Helbig, Atti. Accad. Lincei. (5) 11, (ii), 311, (1902).
97. Foster and Kock, Z. angew. Chem. 21, 2161, 2209, (1908).

(e) Nitrogen Pentoxide (N_2O_5): Nitrogen pentoxide (m. pt. 29°- 30° C) is solid at room temperatures. As mentioned before, it is formed in the earth's atmosphere mainly by the action of ozone on nitrogen peroxide.[96,98] Anderegg, et al[99] report that when ozonized air is passed through an absorbent solution, the formation of fog is due chiefly to hygroscopic nitrogen pentoxide.

Nitrogen pentoxide combines with water to form nitric acid. It is a strong oxidizing agent and reacts similarly to nitrogen peroxide. Therefore, nitrogen pentoxide in the atmosphere is also an undesirable substance so far as the determination of atmospheric ozone is concerned.

(f) Oxides of Nitrogen as a Group: In the countryside the principal sources of nitrogen oxides are thunderstorms and the decomposition of organic matters in the soil. In city and industrial areas the sources are thunderstorms, gases from industrial plants and decomposition of sewage. It has been shown in the preceding discussions that nitrous oxide, nitrogen peroxide, nitric acid and various nitrates may be present in the earth's atmosphere. Gluckauf, et al[100], however, assume nitrogen peroxide to be the only nitrogen oxide present in the lower atmosphere.

Their determinations show that nitrates and/or nitrites obtained from the atmosphere are greater during thunderstorms than during ordinary rains. A compilation of data made by Clark[101] shows that nitrogen compounds are brought to the earth's surface by ordinary rain in different parts of the world (Table XIII). The data are expressed as pounds per acre per annum.

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98. Wulf, Daniels, and Karrer, J. Am. Chem. Soc. 44, 2398, (1922).
99. Anderegg, et al, J. Am. Chem. Soc. 39, 2581, (1917); 43, 967, (1921); Proc. Indiana Acad. 175, 181, (1922).
100. Gluckauf, Heal, Martin, and Paneth, J. Chem Soc. P. 1, (1944).
101. Clark, "The Data of Geochemistry," Washington D. C. 52, (1920).

TABLE XII Nitrogen Brought to the Earth's Surface by Rain

Locality	AMMONIACAL	NITRIC	TOTAL
Rothamsted, England	2.71	1.13	3.84
Paris	–	-	8.93
Caracas, Venezuela	-	0.516	-
Gembloux, Belgium	-	-	9.20
Barbados	1.009	2.443	3.452
British Guiana	1.006	1.886	3.541
Kansas, U.S.A.	2.63	1.06	3.69
Utah, U.S.A.	5.06	0.356	5.42
Mississippi, U.S.A.	-	-	3.636
New Zealand	-	-	2.08
Iceland	0.802	0.263	1.065
Hebrides	0.311	0.289	0.600

In tropical regions free nitric acid is reported to be present at some seasons. Hayhurst and Pring[102] state that the amount of nitric acid in the atmosphere varies from time to time. It is less than 1 part per 4 x 10^9 parts of air and is higher at higher altitudes. The ratio of the oxides of nitrogen in the upper to the lower atmosphere is 2.23:1 at an elevation of 8500 ft., and 1.76:1 at 2600 ft.

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[102] Hayhurst and Pring, J. Chem. Soc. 97, 868, (1910).

3. Organic Peroxide

Some organic substances (e.g., unsaturated hydrocarbons, ethers etc.) on long standing in the atmosphere are oxidized by oxygen to corresponding peroxides. As an example, ether is oxidized to peroxidic substances.[103] Organic peroxides are also formed by the combination of aldehydes and hydrogen peroxide, both of which may be present in the atmosphere at certain localities (vide sections on hydrogen peroxide and aldehydes). Wieland (c.f. ref. 103) proves that dihydroxyethyl peroxide is formed by the reaction of hydrogen peroxide on acetaldehyde

$$2CH_3CHO \quad + \quad H_2O_2 \quad = \quad CH_3 \cdot CHOH \cdot O \cdot O \cdot CHOH \cdot CH_3 \quad ....(67)$$

Since organic peroxides, in general, decompose by themselves and also serve as oxidizing agents for other organic substances, and for many reducing compounds such as, carbon monoxide, hydrogen sulphide, sulphur dioxide, etc., present in polluted atmosphere, their concentration in the atmosphere is practically nil. This is confirmed by experimental determinations in the industrial city of Los Angeles.[54] If organic peroxides are present in any locality in measurable concentration, the Arsenite Method of determination of atmospheric ozone will be affected by the oxidation of potassium iodide and also presumably by that of sodium arsenite.

4. Oxides of Sulphur

Though there are a number of sulphur oxides, sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are the only ones likely to be present in the atmosphere.

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103. Karrer, "Organic Chemistry," Elsevier Publish Co., New York, (1950), 118, 166-170.

Schenk[104] however, reports that sulphur monoxide (SO) is produced to a percentage not exceeding 40% along with sulphur dioxide by the combustion of sulphur in the air. It is also formed by the thermal dissociation of thionyl chloride or bromide. The chemical reactions of sulphur monoxide are similar to those of sulphur dioxide and therefore, in this report, both are referred to as sulphur dioxide.

(a) Sulphur Dioxide: Sulphur dioxide occurs in gaseous exhalations of volcanoes and fumaroles. It is also formed in the atmosphere when volcanic molten lava comes in contact with air. It is found in springs of water near active volcanoes. Witz[105] finds sulphur dioxide a normal constituent of the atmosphere of cities and industrial areas. This existence can be explained in the following ways. Hydrogen sulphide is found in the air of sewers and cesspools (vide also section on hydrogen sulphide). Hydrogen sulphide burns in excess air on contact with a flame forming sulphur dioxide and water (Dalton, Pedler).[106] Hydrogen sulphide reacts with carbon dioxide when in contact with a red-hot surface with the formation of water, carbon monoxide, sulphur and possibly carbonyl sulphide.[107,108] Sulphur then forms sulphur dioxide on contact with the red-hot surface.

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[104] Schenk, Z. anorg. Chem. 211, 150, (1933); 220, 268, (1934); 229, 305, (1936).
[105] Witz, Compt. Rend., 100, 1358, (1885).
[106] c.f. Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green & Co., (1947), Vol. X, p. 128.
[107] Meyer and Schuster, Ber. 44, 1931, (1911).
[108] Gautier, Compt. Rend., 143, 7, (1906).

Hydrogen sulphide is oxidized to sulphuric acid by bacteria.[109] Sulphuric acid reacts with hydrogen sulphide forming water and sulphur dioxide. Sulphur dioxide also reacts with hydrogen sulphide, precipitating sulphur.

Coal contains sulphur. A good variety of coal contains a low percentage (0.01 to 0.15%), and a poor variety contains a high percentage. Therefore, sulphur dioxide whether in small or large percentage is invariably a constituent of the flue gases from coal furnaces. Commercial petroleum also contains sulphur in low percentage and flue gases from commercial oil burners contain a small amount of sulphur dioxide.

Sulphur dioxide is also produced during roasting of pyrites and other sulphides. The waste gases from sulphuric acid and many other chemical plants contain sulphur dioxide.

All these are responsible for the sulphur dioxide in the atmosphere, especially in city and industrial areas.

Sulphur dioxide forms sulphurous acid with water. The sulphurous acid decomposes in sunlight and forms sulphuric acid, sulphur and water.[110]

$$3H_2SO_3 = 2H_2SO_4 + S + H_2O \quad \ldots\ldots\ldots\ldots\ (68)$$

Sulphur dioxide appears to react with coloring matter in the presence of water (vapor or liquid) forming sulphuric acid and hydrogen.

$$SO_2 + 2H_2O = H_2SO_4 + 2H \quad \ldots\ldots\ldots\ldots\ (69)$$

Nascent hydrogen bleaches by reducing the coloring agent. Ammonia reacts with it in the presence of water forming ammonium sulphite. Neumann and Wilczewsky[111] represent the reaction between sulphur dioxide and chlorine

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109. Jacobsen, Beitr. Hölland Gesamt. Microbiol. 3, (1914).
110. Förster, Lange, Drossback and Seidel, Z. anorg. Chem. 128, 245, (1923).
111. Neumann and Wilczewsky, Z. angew. Chem. 36, 377, (1923).

(the latter may also be a constituent in city of industrial areas) in the presence of water as:

$$SO_2 + H_2O + Cl_2 = SO_3 + 2HCl \quad \ldots\ldots\ldots\ldots (70)$$

SO_3 may combine with a further quantity of water to form sulphuric acid. The general reactivity of SO_2 increases in the presence of ultraviolet radiation.

Nitric and/or nitrogen peroxide react with sulphur dioxide in the presence of water producing sulphuric acid (vide equations (59-62)). When dilute, nitric oxide, sulphur dioxide and oxygen react on one another in the presence of water, producing traces of nitrous oxide.[112,113]

Schulze[114] finds that a mixture of sulphur dioxide and oxygen reacts with heated potassium iodide solution forming potassium sulphate and iodine.

$$2KI + SO_2 + O_2 = K_2SO_4 + I_2 \quad \ldots\ldots\ldots\ldots (71)$$

In the cold, the above reaction is immeasurably slow. Since SO_2 is acidic in nature a neutral buffered solution of potassium iodide will not be affected. There is no evidence that SO_2 reacts with a neutral solution of sodium arsenite. Therefore, the presence of a low concentration of sulphur dioxide in the atmosphere is not likely to interfere with the Arsenite Method provided the solution is buffered to be neutral or slightly alkaline. On the other hand, sodium bicarbonate, the buffering agent in the Arsenite Method will react with sulphur dioxide in the following way:

$$2NaHCO_3 + SO_2 = Na_2SO_3 + 2CO_2 + H_2O \quad \ldots\ldots\ldots\ldots (72)$$

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112. Lunge, "Recherches sur les reactions entre le peroxyde d'azote et l'anhydride sulfureux," (1928).
113. Bailey, Ann. Report on Alkali, 62, 12, (1926).
114. Schulze, J. prakt. Chem. (2) 24, 168, (1881).

By a side reaction a small amount of sodium hydrogen sulphite may also be produced.

$$NaHCO_3 + SO_2 = NaHSO_3 + SO_2 \quad \ldots\ldots\ldots\ldots (73)$$

An aqueous solution of sodium sulphite of very low concentration (< 0.002 N - Na_2SO_3) is oxidized readily to sulphate by atmospheric oxygen at room temperature.[115,116] Mittra and Dhar[117] report that the oxidation of sodium sulphite by atmospheric air as a primary reaction is accelerated in the presence of sodium nitrite, potassium oxalate, ferrous ammonium sulphate, sodium arsenite, manganous cobaltous or nickelous hydroxide or sodium thiosulphate. In the Arsenite Method the presence of sodium arsenite as a constituent in the arsenite solution is an advantage because the oxidation of sodium sulphite and bisulphite (c.f. equations (72) and (73)) by atmospheric oxygen will be accelerated considerably in the presence of sodium arsenite, and additional iodine will not be consumed during the titration by sodium sulphite and bisulphite (vide equations (74 and 75)). Sodium hydrogen sulphite is oxidized to sulphate and hydrogen sulphate by atmospheric oxygen.[118]

Raschig[119] finds that nitric oxide reacts with a solution of sodium sulphite forming nitrosulphuric acid. The latter will be neutralized in the Arsenite Method by sodium bicarbonate before it reacts with potassium iodide, because acid-alkali reactions are almost instantaneous. Nitrogen peroxide also oxidizes

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115. Limière and Seyewetz, Bull. Soc. Chim. (3) 33, 444, (1905); Rev. Gén. Chim. 7, 111, (1894).
116. Bigelow, Z. phys. Chem. 26, 493, (1898).
117. Mittra and Dhar, Z. anorg. Chem. 122, 146, (1922).
118. Isnard, J. Pharm. Chim. (8) 6, 211, (1927).
119. Raschig, Z. angew. Chem. 17, 1398, (1904); 18, 1302, (1905).

sulphite to sulphate. The mechanism of this reaction may be that nitrogen peroxide, due to greater affinity, reacts with water forming nitrous and nitric acids or nitric oxide and nitric acid (vide equations (57) and (58)) and nitric acid in turn oxidizes sulphite to sulphate.

If sodium sulphite and bisulphite formed as a result of the reaction between sulphur dioxide and sodium bicarbonate (c.f., equations (72) and (73)), are oxidized completely by atmospheric oxygen, oxides of nitrogen etc., no harm is done so far as the determination of atmospheric ozone by the Arsenite Method is concerned. Otherwise, sodium sulphite and a part of the sodium hydrogen sulphite will react with iodine liberated from the potassium iodide by ozone.

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI \quad \ldots\ldots\ldots\ldots (74)$$

$$NaHSO_3 + I_2 + H_2O = NaHSO_4 + 2HI \quad \ldots\ldots\ldots\ldots (75)$$

According to the Le Chatelier principle this reaction will be reversed if the original solution is acidic. Ozone also reacts with sodium sulphite forming sodium sulphate and dithionate.[120]

$$3Na_2SO_3 + 2O_3 + H_2O = Na_2SO_4 + Na_2S_2O_6 + 2NaOH + 2O_2 \quad \ldots\ldots\ldots\ldots (76)$$

If the original solution is alkaline, it is obvious that ozone will not react with sulphite. In neutral buffered solution the above reaction will take place. The rates of reaction between ozone and potassium iodide and subsequently between iodine and sodium arsenite are more rapid than those represented in equations (74-76). Therefore, even if the reactions represented by equations (72) and (73)

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[120] Riesenfeld and Egidius, Proc. Akad, Amsterdam, 85, 217, (1914).

take place and sodium sulphite and bisulphite are not oxidized completely by atmospheric oxygen, the quantitative determination of the atmospheric ozone will probably not be affected seriously.

(b) Sulphur Trioxide: It has already been mentioned that sulphur dioxide is more reactive in the presence of ultra-violet radiation. One example of this increased reactivity is the formation of sulphur trioxide[121-123] with a better yield when the mixture of sulphur dioxide and oxygen is exposed to ultraviolet.

Since the earth's atmosphere is exposed to the ultraviolet rays from the sun, sulphur trioxide is formed provided sulphur dioxide is present. Sulphur trioxide exists in volcanic gases. It is also formed to an extent of about 2% during the combustion of sulphur in air.[124,125] The sulphur in coal or coal gas, on combusion, gives sulphur trioxide along with sulphur dioxide. It is also obtained in the flue gases of roasting furnaces for pyrites, and of sulphuric acid plants. Sulphur trioxide is a product of decomposition of sulphur dioxide by heat, light, or electric spark. Therefore, in an atmosphere which contains sulphur dioxide, formation of sulphur trioxide is a possibility during thunderstorms.

Sulphur trioxide combines with water to form sulphuric acid. It unites with sulphur to form blue sulphur hemitrioxide and some sulphur dioxide. Its reaction with oxides of nitrogen have been discussed elsewhere (c.f. equations (60) and (62)). It reacts with potassium iodide liberating iodine, and sodium bicarbonate

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[121] Berthelot, Compt. Rend. 86, 20, (1878).
[122] Cohen and Becker, Z. phys. Chem. 70, 88, (1910).
[123] Kühne, British Patent No. 17,520, (1908).
[124] Kastle and McHargue, Am. Chem. J. 38, 465, (1907).
[125] Norrish and Rideal, J. Chem. Soc. 123, 3202, (1923).

forming sodium sulphate and carbon dioxide. Since sulphur trioxide is strongly acidic it will react mainly with sodium bicarbonate when brought in contact with the buffered arsenite solution. The sodium sulphate and carbon dioxide formed as a result of the reaction are not harmful so far as the determination of atmospheric ozone is concerned.

(c) Oxides of Sulphur as a Group: From the foregoing discussions it is apparent that if oxides of sulphur are found to be present in the earth's atmosphere, sulphur dioxide will be much more plentiful than sulphur trioxide. Moreover, sulphur trioxide is not supposed to exist as such for a long period because water vapor converts it to sulphuric acid. It is suggested that sulphuric acid and the sulphates found in the rain water are, in part, derived from the water volatilized from the seas, lakes and rivers. In general, the atmosphere of the city and industrial areas contains more sulphur compounds than that of the country side. 1.8 c.c. of sulphur dioxide was obtained per cubic meter of the air of Lille,[126] and 0.003281 gms of sulphur dioxide per 100 liters of the air of Berlin, Germany.[127] A number of other workers[128-130] made observations in regard to the presence of sulphur dioxide in the atmosphere of different parts of the world.

Sulphur trioxide or sulphuric acid in low concentration cannot produce any adverse effect on a neutral arsenite solution properly buffered, but sulphur dioxide may undergo a number of detrimental reactions. Removal of the oxides of sulphur will be discussed later.

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126. Ladureau, Ann. chim. phys. (5) 29, 427, (1883).
127. Haehhel, Z. angew. Chem. 35, 618, (1922).
128. Artis, Chem. News, 113, 3, (1916).
129. Peck, ibid., 116, 283, (1917).
130. Miller, J. Agric. Sci., 1, 292, (1905).

5. Other Chemicals

Besides the above chemicals there may be numerous other chemicals in the atmosphere such as ammonia, ammonium sulphate and nitrate, hydrogen sulphide, formic acid, formaldehyde, acrolein, higher aldehydes and methyl ketones, tary organics, volatile organics, carbon particles, sand particles, sodium chloride and other sodium salts, calcium sulphate and other calcium salts, compounds of aluminum, silicon, titanium, lead, copper and iron, fluorides, chlorides, bromides, iodides, etc. The occurrence and the concentration of these in the earth's atmosphere depend on the locality and the degree of pollution. As for example, halides, and salts of calcium, sodium, etc., will be found to occur in greater quantity near oceans, seas, rivers, or lakes; whereas, dust, carbon particles, aldehydes, acrolein, and other organics will be found in higher percentage in the atmosphere near the city or industrial areas. Due to the circulation and diffusion of air some of these substances are likely to be found in the lower atmosphere everywhere.

Some chemicals occur in immeasurably small quantities and some, such as halides, sulphates, oxidized salts of metals, carbon and sand particles, and organics do not (presumably) interfere with the buffered arsenite solution. These can be eliminated from the picture. However, ozone may react with some of them, such as the bromides, iodides, and organics while in the atmosphere or in the absorption column provided they remain in the column while the air flows through it.

In addition to the oxidants such as the oxides of nitrogen and sulphur and their corresponding acids and salts, the other substances which may be present in an appreciable quantity in the atmosphere are ammonia, hydrogen sulphide and aldehydes. Their formation and effects will be discussed now.

(a) Ammonia: Ammonia in the air occurs mostly in the form of its salts, because the oxidants and their acids, the organics and the other acidic substances all readily combine with ammonia. Occasionally ammonia may occur as NH_3 and NH_4OH in the atmosphere of certain localities where ammonia is manufactured or ammonia is used as a reagent in the manufacture of some other substances.

The ammonia in the earth's atmosphere is largely a product of organic decomposition (c.f. equation (43)). It is brought back to the earth by rain the form of nitrate or nitrite, and occasionally sulphate and chloride. Besides this, ammonia may be present in the effluent gases of certain chemical plants. Many workers[128-132] have determined the amount of ammonia in rain water and falling snow.

If ammonia is present in the atmosphere as sulphate, nitrate or chloride, etc., it does not interfere with either ozone in low concentration or with the arsenite solution. In the form of sulphite or nitrite, however, it has a tendency to act as a reducing agent on contact with ozone. But sulphite and nitrite are also oxidized slowly by atmospheric oxygen in the presence of moisture. If free ammonia is present the Arsenite Method is not affected. Dry ammonia does not

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131. Fries and Knight. Proc. Iowa Acad. 30, 375, (1923).
132. Shutt and Hedley, Trans. Roy. Soc. Canada, (3) 19, 1, (1925).

react with ozone,[133] and in the presence of moisture a reaction takes place only when the concentration of each is high. If the gases are very dilute the reaction is so slow as to be negligible.[59] Free ammonia on contact with the buffered arsenite solution will react with sodium bicarbonate forming ammonium carbonate and sodium carbonate.

$$2NaHCO_3 + 2NH_3 = (NH_4)_2CO_3 + Na_2CO_3 \ldots\ldots\ldots\ldots (77)$$

Both of the products, ammonium carbonate and sodium carbonate, will be converted into the corresponding bicarbonate by the carbon dioxide of air.

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 \ldots\ldots\ldots\ldots (78)$$

$$(NH_4)_2CO_3 + CO_2 + H_2O = 2NH_4 \cdot HCO_3 \ldots\ldots\ldots\ldots (79)$$

Therefore, the effect of ammonia is harmless.

(b) Hydrogen Sulphide: Bacterial decomposition of sulphur compounds is a source of hydrogen sulphide. It is found in the air of sewers and cesspools, in the emanations from moist earth or moist slag containing pyrites or other metal sulphides, in the air where albuminous substances putrify, in the air and water of the springs[134] near active volcanoes, in volcanic gases, and in the air of stagnant or sluggish lakes or pools, (c.f. Lake Washington Ship Canal,[135] San Francisco Bay,[136] Black Sea,[137] etc.).

Direct union[138] of the elements of sulphur and hydrogen begins at 120° C and is appreciable at 200° C. Hydrogen sulphide is a constituent of the flue gases

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133. Ilosva, Ber. 27, 3500, (1894).
134. Goldschmidt, J. Frank. Inst. 177, 455, (1904).
135. Smith and Thomson, J. Ind. Eng. Chem. 19, 822, (1927).
136. Miller, Ramage, and Lazier, Uni. California Zool. Publ. 31, 201, (1928).
137. Archangelsky, Neftyanoe Khozyiastvo, 10, 483, (1926).
138. Januario, Gazz. Chim. Ital., 10, 46, (1880).

from furnaces burning coal or oil and from chemical plants handling sulphur and sulphur compounds.

Dry hydrogen sulphide is found to be decomposed by active radiation[74, 139-142] of wave length in the range 2300 Å to 1800Å, into hydrogen and sulphur. In the presence of moisture, oxygen, and sunlight, the hydrogen sulphide decomposes slowly, forming water and sulphur. Its oxidation by oxides of nitrogen and sulphur has been discussed. Ozone oxidizes it to sulphur and water. Iodine reacts slowly with hydrogen sulphide forming sulphur and hydroiodic acid. In an acidic solution it does not react with iodine. In neutral arsenite solution, iodine liberated by ozone will react with sodium arsenite, at a much faster rate than with hydrogen sulphide. Except for local pollution of the atmosphere with hydrogen sulphide by the effluent gases from chemical plants or coal furnaces, the concentration of hydrogen sulphide in the atmosphere will be low, and will be destroyed by the oxidants present in the atmosphere. Its effect on the Arsenite Method could be considered negligible.

(c) Aldehydes: Low molecular weight aldehydes are generally found only in traces in the atmosphere. Formaldehyde (HCHO) is formed during the incomplete combustion of organic substances such as coal, charcoal, wood, sugar, etc.[103] It has been mentioned that chlorophyll reacts with carbon dioxide in the presence of sunlight and water vapor forming formaldehyde and percarbonic acid.[62, 63]

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139. Henri, "Structure des Molecules," Paris, 100, (1925).
140. Gerke, J. Am. Chem. Soc. 49, 2671, (1927).
141. Tamm, Z. phys. Chem. 105, 356, (1923).
142. Smits and Aten, Z. Elektrochem., 16, 264, (1910).

Acetaldehyde[103] (CH_3CHO) is formed in small quantities in the manufacture of alcohol by fermentation and is, therefore, to be expected near ethyl alcohol brewery plants.

Higher aldehydes may be formed in very small quantities by bacterial and/or thermal decomposition[103] of certain vegetable oils and carbonaceous materials.

Acrolein ($CH_2:CH\cdot CHO$), an unsaturated aldehyde, is formed in small quantities during the distillation of fats and the dehydration of glycerol. Aldehydes may be present in cities and industrial areas. In general, aldehydes are easily oxidized to their corresponding acids. Ozone and even atmospheric oxygen react with aldehydes to form acids.

$$-CHO \quad + \quad O \quad = \quad -COOH \qquad \ldots\ldots\ldots\ldots \text{(80)}$$

Aliphatic aldehydes are also oxidized by salts of heavy metals, such as those of silver and gold.[103] Aldehydes react with ammonia forming aldehyde ammonias. Oxides of nitrogen, especially nitrogen peroxide and nitric acid, behave as oxidizing agents towards aldehydes, as does also sulphur trioxide.

From the foregoing it can be said that there may be traces of aldehydes in the lower atmosphere, the quantity varying with the locality. If the concentration is not high these will be oxidized to their corresponding acids which may enter the absorption column in place of the aldehydes themselves. The buffer agent neutralizes these acids. Due to the action of the oxides of sulphur on the buffer (sodium bicarbonate) sodium bisulphite may be present in the absorption column (c.f. equation (73)). If so, the aldehydes will form additional compounds, which will, for the most part, precipitate out, thus removing any deleterious effects that the aldehydes might have caused. If sodium bisulphite is not present and the aldehydes of the atmosphere are not oxidized to their acids, they will enter the absorption column along with the air and will be oxidized by the ozone and/or the oxygen in the column. In a locality where sources of aldehydes are not apparent, their concentration in the atmosphere will be low and they will be oxidized to their acids in the column almost instantaneously. Their effects can safely be neglected provided a buffered arsenite solution is used.

6. Suggestions for the Elimination of the Effects of Oxidants in the Determination of Ozone by a Titer Method

As has been stated, the kinds and quantities of oxidants present in the atmosphere near the earth's surface depend on local conditions. Prior to choosing a method for the elimination of atmospheric ozone, the number of oxidants and their concentrations should be determined in that particular locality. It may be said, in general, that oxides of nitrogen and sulphur will be present in the atmosphere in most parts of the earth's surface. Reagents are known which absorb the atmospheric oxidants, but some of these reagents also react with ozone. Therefore, reagents should be chosen so that they absorb completely oxidants other than ozone and do not affect ozone at all.

If a mixture of ozone and hydrogen peroxide be passed through a concentrated solution of chromic acid, hydrogen peroxide alone is decomposed, ozone remaining unaffected.[143] McLeod[144] reports that a mixture of sodium bicarbonate,

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[143] Engler and Wild, Ber., 29, 1940, (1896).
[144] McLeod, Chem. News. 40, 307, (1879).

potassium dichromate and sulphuric acid arrests hydrogen peroxide without affecting ozone in a mixture of the latter two. Kaiser and McMaster[145] find that nitric oxide is also arrested by the mixture used by McLeod. They also find that for a mixture of ozone, hydrogen peroxide, chlorine, and nitrous oxide passed through a solution of potassium permanganate, only ozone escapes unchanged. A potassium permanganate solution also absorbs nitrogen peroxide. Sulphur dioxide is absorbed completely by a concentrated alkaline solution of potassium permanganate.[146,147] Since the oxidation potential of potassium permanganate is very high (+1.203 in a 0.2 molar solution with reference to normal hydrogen electrode[57]) compared to other common oxidizing agents, it will oxidize most of the oxidizable substances. Hydrogen sulphide and the aldehydes are also oxidized by the potassium permanganate solution. If sulphur trioxide or sulphuric acid, and nitric acid are present in the atmosphere, the alkalinity of the permanganate solution will trap them completely. Therefore, all the common oxidants except ozone, as well as any other detrimental substances likely to be present in the lower atmosphere, will be absorbed completely by a concentrated, alkaline, permanganate solution.

Ozone, however, is soluble in water. The partition coefficient[148] of ozone under equilibrium condition between an ozonized gas at one atmospheric pressure and water is 0.482 at 13° C, 0.456 at 15° C, 0.381 at 19° C, 0.270 at 27° C, 0.195 at 33° C, 0.112 at 40° C, and 0.000 at 60° C. As seen from the above

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[145] Kaiser and McMaster, Am. Chem. J. 39, 96, (1908).
[146] Kolthoff, Pharm. Weekbl. 61, 841, (1924).
[147] Hendrixson, J. Am. Chem. Soc. 45, 1319, 2156, (1925); Proc. Iowa Acad. 32, 322, (1925).
[148] Mailfert, Compt. Rend. 119, 951, (1894).

figures, the solubility of ozone decreases with temperature and according to Frohlich[149] it increases with pressure. The solubility of ozone in water is augmented by the presence of acids[7,148,150,151] and in an acidified water it decreases with increasing acid concentration.[152] In concentrated alkali solution ozone is decomposed.[153] In feebly alkaline solution such as 0.005 N and 0.00002 N solution of sodium carbonate, the solubility of ozone is small compared to that in neutral or acid aqueous solution and the decomposition of ozone is also small compared to that in a concentrated aqueous alkaline solution. A neutral salt solution in water, such as sodium or magnesium chloride, dissolves ozone in a greater quantity than neutral water. The aqueous solution of ozone in the presence of these salts has a greater stability. For stability of an aqueous solution of ozone Langheld[154] recommends a quinine salt and Fraser[155] paraldehyde. Therefore, a concentrated permanganate solution containing paraldehyde, quinine salt and a little sodium chloride, made slightly alkaline by adding sodium carbonate, should be a good scrubbing solution for oxidants other than ozone and for other detrimental substances in the air. The p^H in alkaline range may play an important role. The solution may be most effective for the absorption of all interfering substances except ozone at a definite p^H. If so, it should, of course, be buffered for that optimal p^H. If this solution is used at

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149. Frohlich, Prometheus, 2, 625, (1891).
150. Moufang, Worschr. Bauerei, 29, 434, (1911).
151. Burger, ibid., 30, 285, (1913).
152. Luther and Inglis, Z. phys. Chem. 43, 203, (1903).
153. Graf, Z. angew. Chem. 3, 494, (1890); German Patent D.R.P., No. 52,452 (1890).
154. Langheld, Chem. Ztg. 22, 212, (1898).
155. Fraser, Z. angew. Chem. 23, 84, (1910).

any temperature below 60° C (c.f. Mailfert[148]), it should be saturated with ozone either by artificial means (i.e. producing ozone in the laboratory by an ozonizer and passing the ozonized gas through the permanganate solution until saturated) or by passing atmospheric air through it for a sufficient time. According to Ladenberg[1] a liter of water at 0° C dissolves 20 mgms of ozone, at 2° C 10 mgms, and 28° C 1.5 mgms. On the assumption that the concentration of atmospheric ozone is as low as 10^{-8} gm per gm of air (i.e. 1.294 x 10^{-11} gms ozone per ml. of air at N.T.P.), the volume of atmospheric air at N.T.P. required to saturate one liter of water at 28° C is 1.159 x 10^5 liters.

The presence of paraldehyde, quinine salt, sodium chloride, and sodium carbonate in potassium permanganate solution may modify the solubility of ozone, which, therefore, should be determined experimentally. If atmospheric air is passed through a scrubber or any suitable absorption apparatus, using slightly alkaline solution (made so by sodium carbonate) containing an appreciable amount of potassium permanganate and small amounts of paraldehyde, quinine salt, and sodium or magnesium chloride, the out-going air should contain oxygen, nitrogen, carbon dioxide, inert gases and ozone; the concentration of ozone should be the same as the original. The out-going air from the scrubber should be passed through the absorption column as shown in Figure 1 for the quantitative determination of ozone by the Arsenite Method.

The carbon dioxide of the air may react slowly with sodium carbonate in the permanganate solution to form sodium bicarbonate and, therefore, sodium carbonate should be added from time to time to the permanganate solution to maintain the optimal p^H.

The permanganate solution will be concentrated after some time due to evaporation and loss of water by entrainment with the air current. Some dissolved ozone in the permanganate solution may be released to be absorbed by the arsenite solution. This loss of water from the permanganate solution can be calculated from the knowledge of the percentage humidity of the atmospheric air and entrainment loss. Therefore, an adequate amount of pure water should be added to the permanganate solution and the rate of addition should be adjusted to maintain a constant volume of the permanganate solution. A number of suggestions can be made for the prevention of the entrainment loss. In the present case a simple one is to maintain the air flow through the scrubber at a reasonably low rate much below the flooding point and to pass the out-going air from the scrubber through a long hard glass tube prior to its introduction to the ozone absorption column. The scrubber and the absorption column of the Arsenite Method are connected in series by this long hard (pyrex or neutral) glass tube similar to Figure 2.

As a result of the reaction with oxidants and others, potassium permanganate itself will be destroyed, and therefore, more should be added from time to time to maintain the necessary high concentration in the scrubbing solution. If potassium permanganate is added to the scrubber in the form of solution, the latter will have to be saturated with ozone. Therefore, potassium permanganate should preferably added in the form of solid. Since the rate of dissolution of a substance is proportional to the surface area, potassium permanganate should be added in powdered form. The rate of dissolution of potassium permanganate in water is very high, therefore, when powdered it will dissolve more quickly than in large crystals. Sodium carbonate for the maintenance of the definite p^H, as mentioned before, should also be added in the form of anhydrous solid. However, a happy combination can be suggested. The water required for the maintenance of the constant volume of the scrubbing solution can be used for the dissolution of the proper amount of these reagents (e.g., potassium permanganate and sodium carbonate etc.) for the scrubbing solution and this solution can be added drop by drop at an experimentally determined rate to maintain a constant volume of the scrubbing solution and the concentration of the reagents. Experimental studies are necessary to determine the best conditions for this method of scrubbing.

A mixture of dry potassium permanganate and chromic acid may also be used for removing the oxidants of the atmospheric air except ozone.

A number of other suggestions might be made, but the author feels that the experimental studies should precede the voluminous writing of such suggestions.