proximately 47 kcal. per molecule of acetylene condensed. Calculating the theoretical heat of polymerization from the values of atomic linkages given by Fajans,[12] on the assumption that in the polymerization one C≡C (161.6 kcal.) is broken and one C═C (122.9 kcal.) and one C—C (73.5 kcal.) are formed per molecule of acetylene, one obtains the value 35 kcal. This is not in too good agreement with the experimental value to be sure, but perhaps as satisfactory as one could expect when it is remembered that the atomic linkages are admittedly only average values.

Acknowledgments.—We wish to thank Dr. F. H. Stodola, to whom we are indebted for the analyses of the solid products, and to acknowledge the kindness of Professor A. E. Stoppel who collaborated with us in determining the heats of combustion.

Summary

Cuprene was prepared by polymerization of acetylene by means of radon mixed with the gas. The solid polymer was then exposed to oxygen and the spontaneous reaction with oxygen at room temperature was followed manometrically. Both the solid and gaseous products were analyzed. The solid product after oxidation (which is nearly complete in twelve or fifteen days) contains approximately 25% oxygen. A little carbon monoxide is formed. The complete analysis shows the following reaction equation to be approximately correct

$$(C_2H_2)_{20} + 5^1/_2O_2 \longrightarrow C_{39}H_{40}O_{10} + CO$$

The spontaneous oxidation was also followed gravimetrically by exposing the freshly prepared cuprene to dry air and weighing at intervals. The results agree with the manometric method and analysis both as to extent and rate of oxidation. The heat of combustion of the oxidized cuprene is approximately 30% less than that of the unoxidized cuprene.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 10, 1936

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(12) Fajans, *Ber.*, **53**, 643 (1920); Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., Inc., New York, 1931, p. 323.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Catalytic Method for Determination of Iodine

BY HAROLD P. LUNDGREN[1]

Among the methods used for determination of iodine there are: those determining iodine colorimetrically in a solvent, those titrating iodine using the blue starch–iodine complex as an indicator, those employing a color or precipitation reaction of iodine and those employing the catalytic power of iodine.

It is often necessary to analyze for iodine in concentrations too low to be detected by ordinary colorimetric, volumetric or gravimetric technique. The concentration of iodine may be increased by the Winkler technique until it is within the analytical range. The success of the Winkler method depends on how far the reactions concerned go toward completion. Furthermore, any trace of oxidizing agent left in the solution will cause serious error.

The catalytic methods for determination of iodine are in many cases sensitive to microgram quantities of iodine and are relatively simple and accurate procedures. Bredig and Walton[2] utilized the catalytic activity of iodine in the decomposition of hydrogen peroxide; Bobtelsky and Kaplan[3] utilized the rate of decoloration of permanganate by oxalic acid as catalyzed by iodine. Baines[4] employed the catalytic effect of iodine on the oxidation of thiosulfate by nitrite. Sandell and Kolthoff[5] made use of iodine catalysis in the oxidation of arsenous acid by ceric sulfate in sulfuric acid solution.

It is often necessary to analyze iodine in sulfite solutions since such are commonly used to absorb iodine, especially after combustion technique. In such a solution it would be impossible to apply the previously mentioned catalytic methods since all involve oxidation–reduction reactions and sulfite would interfere.

In a sulfite solution whose hydrogen ion concentration is less than 2 *N*, methylene blue was found to be decolorized more or less rapidly. At an acid concentration of 2 *N*, the reduction of the dye is immeasurably slow; iodide catalyzes the

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(1) The author wishes to acknowledge with thanks the helpful criticism and suggestions of Professor J. F. McClendon, who has interested him in the field of iodine from the biochemical point of view. Abstracted from part of a thesis included among the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Minnesota.

(2) Bredig and Walton, *Z. Elektrochem.*, **9**, 114 (1903).

(3) Bobtelsky and Kaplan, *Z. anorg. Chem.*, **172**, 196 (1928).

(4) Baines, *J. Soc. Chem. Ind. Trans.*, **49**, 481 (1930).

(5) Sandell and Kolthoff, THIS JOURNAL, **56**, 1426 (1934).

reaction, and the rate was found to be proportional to the iodide concentration. Free diffusion of oxygen into the solution must be prevented, although the presence of the small amount of dissolved oxygen at the beginning does no harm, as indicated by the uniformly smooth curves of color depth *versus* time (Fig. 3). Any oxygen present apparently is destroyed before the first reading of color depth can be made. The sealed narrow neck of the reaction vessel (Fig. 1) prevented the introduction of oxygen, and diffusion of the gas above into the liquid was too slow to influence the reaction rate. Bush,[6] through her studies on the reaction of sulfuric acid and potassium iodide, gave an explanation of the reaction mechanism

$$2SO_2 + 4H_2O + 2I_2 = 2H_2SO_4 + 4HI$$
$$4HI + O_2 = 2H_2O + 2I_2$$

Methylene blue may replace oxygen as oxidizing agent in the second equation. It is quite likely that the mechanism is more complicated than indicated, especially in strong acid solution, since sulfurous acid has two oxidation–reduction levels—one in which dithionous acid is formed. Although sulfurous acid does not reduce methylene blue in strongly acid solution, dithionous acid does. Furthermore, the reaction may be complicated by formation of iodine–sulfur complexes which have been shown by Foerster and Gruner[7] to have catalytic properties.

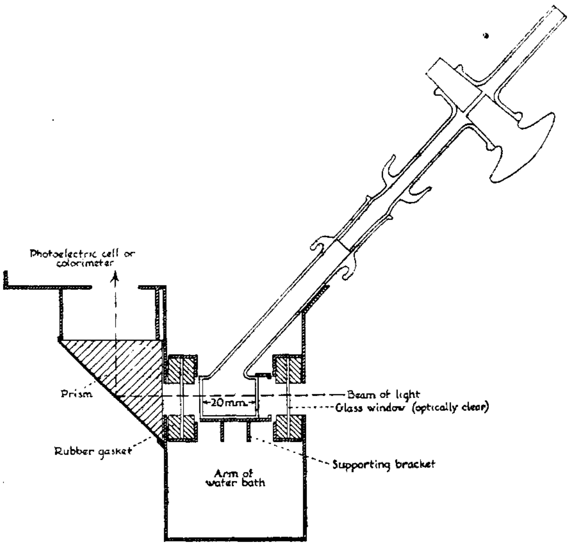

Fig. 1.

Although the mechanism is not understood, as low as 0.3 microgram of iodide may be detected, and chloride or bromide does not interfere. The closed system described below is employed to prevent free circulation of air above the liquid during the determination. Evacuation of the apparatus gave rise to erratic results when less than 5 micrograms of iodide was used. An increase in temperature increases the rate of fading of the indicator. When small quantities (0.3–5γ) of iodide are involved, the acid concentration is so great that it causes a slow decomposition of methylene blue, yielding colored products interfering with the measurement of fading time. By using the correct color filter together with the apparatus shown in Fig. 1, the color fading due to the main reaction may be successfully followed.

Apparatus.—The solution is placed in a cylindrical reaction container[8] made of optically clear glass which holds about 4 cc. of fluid. The container rests in the arm of a waterbath between two windows of optically clear glass as shown in Fig. 1. A beam of light from a constant source after passing through the fading solution is reflected upward by a prism. Its intensity can be measured either by means of a colorimeter or by a photoelectric cell.[9] The plunger of the stationary side of the colorimeter is set directly in line with the beam of light from the fading solution and the color intensity of this is compared with that of a standard solution of methylene blue in the movable cup. The amperage obtained from the photoelectric cell is directly proportional to the intensity of light falling upon it. For convenience, since it is not necessary to know the absolute value of the intensity, the reading of the microammeter may be taken as the intensity.

The light from a 400-watt lamp was monochromatized by passing through color filter H. R. Signal Red No. 243 (Corning). This filter has only 5% transmission at 608 mμ and 40% at 622 mμ; it permits the passage of the excess of red which has not been absorbed by the methylene blue and holds back the yellow color present in the fading solution.

Analytical

A. Reagents and Technique. Potassium Iodide.—Mallinckrodt Anal. Reag. (recryst.). A standard solution was prepared so that 0.1 cc. = 1 microgram of iodine (as KI).

Methylene Blue.—National Aniline Co. 88% (recryst. twice). The solution used in the reaction contained 1 g./100 cc. of water. The solution used as a standard for colorimetric comparison contained 1 mg./100 cc. of water.

Sodium Sulfite.—Merck C. P. (recryst.). A saturated aqueous solution was used.

Hydrochloric Acid.—Grasselli concentrated.

The reagents are placed in the reaction container as follows. To 0.4 cc. of a standard solution of iodide and 0.5 cc. of satd. aq. sodium sulfite are added 3.5 cc. of concentrated hydrochloric acid and 0.1 cc. of methylene blue solution (1 g./100 cc.). Calibrated Bausch and Lomb micro-

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[6] Bush, *J. Phys. Chem.*, **33**, 613 (1929).

[7] Foerster and Gruner, *Z. anorg. Chem.*, **203**, 245 (1932).

[8] Made by Bausch and Lomb Optical Company.

[9] The Duboscq type colorimeter and Weston photronic cell were used.

pipets were used for transferring the liquids. The stopcock is then closed and the reaction container is placed in a water-bath at 80°.

Measurement

A. With Colorimeter.—As the solution fades the color intensity of the standard solution of methylene blue (1 mg./100 cc.) in the movable cup is matched at intervals with the fading solution.

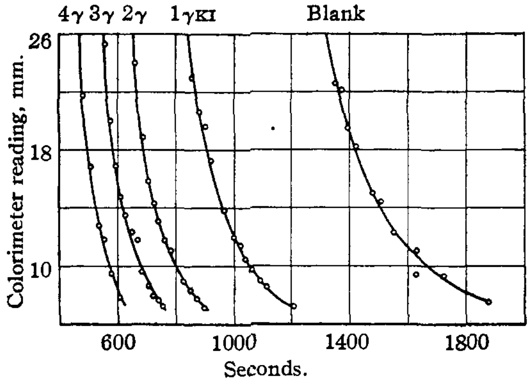

Fig. 2.

When the readings of the standard l_s are plotted against the corresponding times, t, the set of curves in Fig. 2 is obtained for the lowest range of iodine detected by the catalytic system. When the logarithm of the readings is plotted against the reciprocal of the respective times, the straight lines shown in Fig. 3 are obtained. Accordingly, the decoloration of methylene blue can be represented by the equation

$$l/t = k \log l_s + K \qquad (1)$$

but according to Beer's law when the intensities of the two beams are equal the reading of the standard l_s is proportional to the concentration of the methylene blue in the fading solution or

$$l/t = k' \log c + K \qquad (2)$$

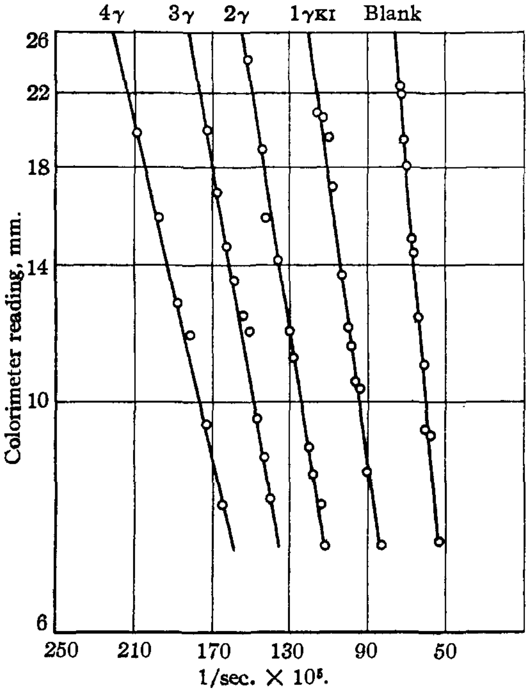

Fig. 3.

B. With the Photoelectric Cell.—According to Beer's law

$$C = \frac{\log I_0/I_e}{K'} \qquad (3)$$

where I_0 is the intensity of light before passing through the solution and I_e the intensity of the light which has escaped absorption at depth e and C is the concentration of the solution. On substitution of 3 in 2, the following equation is obtained

$$l/t = k' \log \frac{\log I_0/I_e}{K'} + K \qquad (4)$$

$$= k' \log \log \frac{I_0}{I_e} + K'' \qquad (5)$$

This equation expresses the relation between time and intensity of light of the fading solution as measured by the photoelectric cell. The curves obtained by plotting log log microamperage against the reciprocal of time are straight lines within limits of experimental error. Figure 4 is the curve obtained using the photoelectric cell

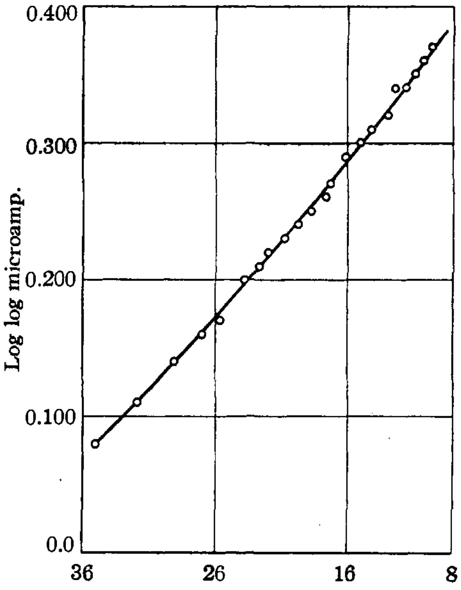

Fig. 4.

when 4 micrograms of iodine was present in the reaction solution.

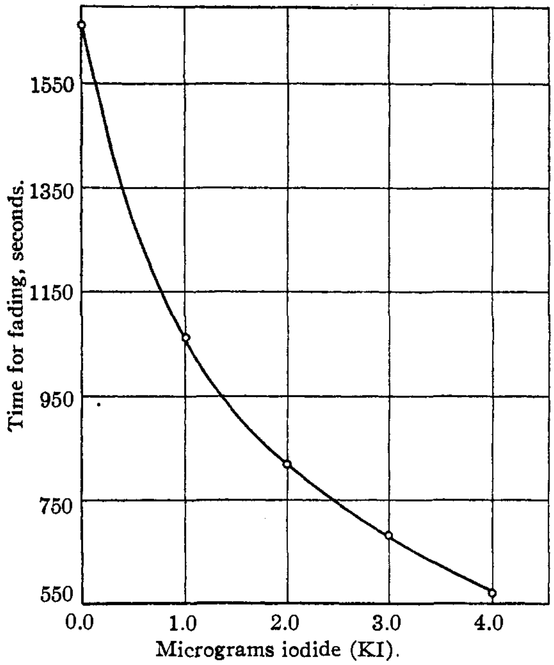

Fig. 5.

The light transmission errors, and errors due to deviation from Beer's law, for practical purposes are therefore negligible and either the colorimeter or the photoelectric cell can be used to measure the fading of methylene blue by the system.

For comparison of times for fading of methylene blue catalyzed by different concentrations of iodine a color intensity equal to 10 mm. of the standard solution of methylene blue (1 mg./100 cc.) in the movable cup of the colorimeter was chosen. When the times to reach this intensity are plotted against the corresponding concentrations of iodine, curve Fig. 5 is obtained. The method of plotting the fading curves as straight lines serves as a method of averaging the colorimetric readings.

A series of analyses carried out using this technique check within 5%.

Summary

A method for determination of iodine in sulfite solutions in concentrations up to 4 micrograms (as potassium iodide) has been devised from considerations of a system of reactions in which iodine acts as a catalyst and sulfite enters into the reaction mechanism. The method is carried out by adding hydrochloric acid and methylene blue to the sulfite solution and measuring the fading as the reaction proceeds in a specially designed apparatus.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

Electric Potentials at Crystal Surfaces, and at Silver Halide Surfaces in Particular

BY I. M. KOLTHOFF AND H. L. SANDERS[1]

With the exception of the glass electrode, very few investigators have studied the thermodynamically reversible potentials which exist at non-metallic surfaces.[2]

For various reasons a study of the potential at the interface of slightly soluble salts in equilibrium with their saturated solutions is of interest. It has been claimed by Haber[3] that this potential, π, is determined by the concentration (or, better, the activity) of the lattice ions in the solution according to the equation

$$\pi = K_c + \frac{RT}{nF} \ln a_c = K_a - \frac{RT}{nF} \ln a_a$$

in which a_c denotes the activity of the cations, and a_a that of the anions in solution. Actually Haber used ion concentrations instead of activities.

Some rough measurements[3] with silver chloride and calomel membranes were in agreement with the above equation. Recently Tendeloo[4] has made measurements with slices of minerals like heavyspar ($BaSO_4$) and fluorite (CaF_2), finding under specified conditions an approximate agreement with the foregoing equations over a limited range of concentrations.

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(2) For a review of R. Beutner's work on the phase-boundary potentials between immiscible liquids see L. Michaelis, "Hydrogen Ion Concentration," Williams and Wilkins, Baltimore, Md., 1926, Chap. 8; also M. Dole, "The Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., Inc., New York, 1935, p. 380; for a review of the work of various other workers in this field see M. Cremer, "Handbuch der normalen und pathologischen Physiologie," Vol. VIII, J. Springer, Berlin, 1928, pp. 999–1053.

(3) F. Haber, *Ann. Physik*, [4] **26**, 927 (1908).

(4) H. J. C. Tendeloo, *Proc. Acad. Science, Amsterdam*, **38**, 434 (1935); *Rec. trav. chim.*, **55**, 227 (1936); *J. Biol. Chem.*, **113**, 333 (1936).