for the cases of no branching, single branching and double branching, respectively, but the precise significance of this result is not apparent.

The compressibility of the methanol molecule estimated from bond force-constants is about 1/1000 as large as the observed compressibility. This indicates that it is the space between the molecules which is compressed, rather than the molecules themselves.

The adiabatic compressibility is of interest in thermodynamics. For example, the ratio of isothermal to adiabatic compressibilities is equal to the ratio of specific heats

$$K_{is}/K_{ad} = c_p/c_v = \gamma \qquad (7)$$

The isothermal compressibility can be obtained either from static measurements or from

$$K_{is} = K_{ad} + T\alpha^2/c_p d \qquad (8)$$

where $T$ is the absolute temperature, $\alpha$ the coefficient of thermal expansion, and $c_p$ the heat capacity at constant pressure.

Sufficient data are available[18] in several cases for calculating[19] the ratio of specific heats from equations (7) and (8). The results in Table III show that $\gamma$ decreases slightly as the complexity of the molecule increases, as expected because of the larger number of degrees of freedom.

**Acknowledgments.**—The author is indebted to Dr. G. R. Ringo for many stimulating discussions, to Dr. H. W. Carhart for samples of several of the alcohols, and to The Quaker Oats Company for samples of furfuryl and tetrahydrofurfuryl alcohols.

## Summary

The velocity of sound at 30° has been measured in thirty liquid alcohols, using a one-megacycle ultrasonic interferometer. Densities and refractive indices at 30° are also reported.

To illustrate the applicability of sound velocities in chemical studies, these data have been used to calculate molecular weight, van der Waals $b$, adiabatic compressibility, and the ratio of specific heats. The compressibility has been correlated semi-quantitatively with molecular structure.

The analogy between molar sound velocity and molar refraction has been discussed.

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[18] Shiba, *Sci. Pap. Inst. Phys. Chem. Research (Tokyo)*, **16**, 205 (1931).

[19] It is necessary to avoid using the large body of isothermal compressibility data which has been determined for high pressures, because the excess pressure attained in the ultrasonic interferometer is only a very small fraction of an atmosphere.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Accuracy of Estimation of Hydrogen Peroxide by Potassium Permanganate Titration

BY CHARLES E. HUCKABA[1a] AND FREDERICK G. KEYES[1b]

## Introduction

The usual method for analyzing aqueous solutions of hydrogen peroxide is by titration in acid solution with a standard solution of potassium permanganate. However the complete reliability of this method for very accurate determinations has been questioned, because of some doubt as to the optimum conditions for carrying out the titration.

A search of the literature revealed varying recommendations as to the proper sulfuric acid concentration, and some uncertainty as to the rate of addition of the permanganate to the peroxide solution. For example, if the rate of addition is too great, some manganese dioxide may be formed due to a local depletion of acid in the solution and bring about catalytic decomposition of a portion of the peroxide.

There are three possible methods for carrying out the determinations of hydrogen peroxide: titration, colorimetry and decomposition. Titration methods using the following reagents have been described in the literature[2]: potassium permanganate, ceric sulfate, potassium iodide–sodium thiosulfate, sodium arsenite and titanium trichloride. However in each case there has been observed either disagreement regarding the best procedure for performing the titration, or uncertainty as to the reliability of the method. The colorimetric method is applicable only for detecting a few parts per million of peroxide.

The method based on the decomposition of the peroxide with a suitable catalyst followed by measuring the amount of oxygen evolved would appear in principle to combine simplicity and reliability. The reaction occurs as follows

$$2H_2O_2 \xrightarrow{\text{catalyst}} 2H_2O + O_2$$

There are no known side reactions to introduce error as is present in some of the titration procedures.

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[1] (a) Results recorded in this article are from a thesis submitted as partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at the Massachusetts Institute of Technology; (b) Department of Chemistry, Massachusetts Institute of Technology.

[2] J. S. Reichert, S. A. McNeight and H. W. Rudel, *Ind. Eng. Chem., Anal. Ed.*, **11**, 194 (1939). This paper surveys the titration procedures for peroxide to date.

The inconvenience of the decomposition method in practice would bar it from general use. However there seems to be no doubt that it is an "absolute" method of analysis. Therefore it was concluded that considering the existing confusion concerning other methods, the decomposition procedure was the only completely reliable method with which the titration methods could be compared.

The objective of this investigation involves then the constructing of a suitable apparatus for carrying out the absolute or gasometric analysis by decomposition as a basis for the comparison with the convenient permanganate titration procedure. No record of such a comparison has been found in the literature. The necessity for such a comparison is apparent.

### The Gasometric Method

An apparatus was assembled as shown in the drawing for carrying out the analysis by decomposition. It consisted chiefly of a reaction vessel of two sections connected by a ground glass joint, a moisture trap, a Töpler pump, a volumometer, a manometer, a thermometer and a McLeod pressure gage.

The mercury levels in the Töpler pump and the volumometer were controlled by applying either pressure or vacuum to the steel mercury containers. Very accurate control of mercury introduction was attained through the use of steel needle valves. For the volumometer extremely fine adjustment of the mercury levels was afforded by a small piston-type injector.

Small monel metal bellows were placed between the steel tubing from the mercury containers and the glass of both the Töpler pump and the volumometer to absorb any shocks that might occur.

A mixture of Dry Ice and methyl alcohol ($t$ = 78.5°) was used as the refrigerant around the moisture trap, and proved to be adequate. The thermometer was strapped to the outside of the volumometer with asbestos tape. Vacuum for the system was furnished by a mercury diffusion pump capable of producing a high vacuum.

The volumometer was calibrated by weighing the amount of mercury needed to fill the space between the three pointers and the top. The following results were obtained:

| Top of volumometer to | Volume, cc. | Precision |
|---|---|---|
| Top pointer | 34.038 | 1:3000 |
| Middle pointer | 100.341 | 1:2500 |
| Bottom pointer | 202.041 | 1:3500 |

The following procedure was used in making a run with the decomposition apparatus:

The manometer, volumometer and Töpler pump were evacuated and closed off from the remainder of the system. The mercury level in the volumometer was adjusted to a point just below the delivery tube from the Töpler pump to seal the manometer off from the volumometer. An 8-10 cc. sample of 2 to 3% hydrogen peroxide was weighed out in the top part of the reaction vessel, which had previously been cleaned with hot fuming sulfuric acid to prevent premature decomposition of the peroxide. After this part of the reaction vessel had been attached, the remainder of the apparatus was evacuated. With the reaction vessel closed off from the rest of the system, the peroxide was transferred to the cooled (−78°) lower part of the vessel. This was followed by two portions of distilled water of approximately 10 cc. each to rinse all of the peroxide into the lower vessel. Next a great excess of liquid catalyst was introduced in the same manner exercising great precaution not to let air leak into the bottom vessel. The dissolved air in the rinse water and liquid catalyst was removed by applying a vacuum in the top part of the reaction vessel prior to admission of the liquid.

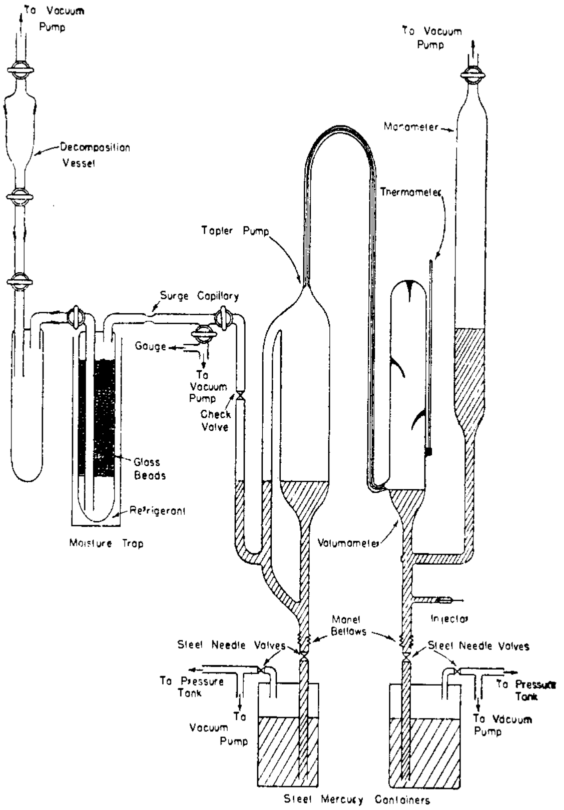

Fig. 1.—Decomposition apparatus.

As the peroxide thawed, the decomposition started and it was allowed to go to completion. Tests made by adding huge excesses of several catalysts to the residues proved that the reaction was in truth complete.

The evolved oxygen was transferred to the volumometer by means of the Töpler pump. About eight passes with the Töpler pump which has a volume of about 600 cc. was sufficient to complete the transfer. Completeness of transfer was evidenced by a pressure reading of about $10^{-4}$ mm. of mercury in the pump, and by the fact that no appreciable amount of gas was transferred by the last pass with the pump.

The mercury level in the volumometer was adjusted until it was only a few millimeters below the bottom pointer. The temperature of the gas was then allowed to reach equilibrium with that of the surroundings, as evidenced by constancy of the mercury level in the manometer. The mercury level in the volumometer was finally adjusted by means of the injector until it just made contact with the bottom pointer. The mirror nature of the mercury surface made adjustment to a fine point very accurate (±0.001 mm.).

The difference in mercury levels in the volumometer and manometer were read with a Geneva cathetometer. The cathetometer, of special construction, consists of two telescopes which are mounted on a vertical invar metal bar and each telescope eyepiece is equipped with a micrometer cross-hair arrangement which allows the mercury levels to be read to 0.002 mm. The brass scale used with this cathetometer was calibrated by the Bureau of Standards and found to be accurate to about three parts in 100,000.

The space above the mercury in the manometer was evacuated, and therefore the difference in mercury levels corrected for capillarity was the absolute pressure of the gas in the volumometer. The temperature was read from the thermometer attached to the volumometer.

The gas in the volumometer was the oxygen produced from the decomposed peroxide plus the dissolved air in the sample of peroxide.

It was first attempted to remove this dissolved air by alternate freezing, and pumping away the air. However, it was discovered that the peroxide decomposed during the thawing operation.

Since the removal of air from the peroxide was impractical, it was decided to apply a correction for the dissolved air. To determine the value of the correction, several blank runs were made using a sample of water which had been stored under similar conditions to the peroxide. It was assumed that the amount of air dissolved in 3% hydrogen peroxide is the same as that in water.

The procedure used in the blank runs was exactly the same as that employed in the runs with peroxide. The average value obtained was 0.022 cc.[3] of air at standard temperature and pressure per gram of water at 25°. The value given is somewhat higher than will be found in the literature and this is due to the fact that the number corresponds to a measurement made using the exact procedure where two quantities of pumped rinse water were used. This value was used to correct the observed volumes of gas evolved from the decomposition.

Calculation of the weight of oxygen was carried out by using a simplified approximation of the Beattie–Bridgeman equation of state for oxygen as follows[4]

$$v = (2.5644T/P) + B_0$$

$$B_0 = \left(1.445 - \frac{1447}{2.5644T} - \frac{1.5 \times 10^6}{T^3}\right)$$

where

$v$ is the specific volume of oxygen in cc. per gram,
$P$ = pressure in normal atmospheres
$T = 273.16 + t$ (°C.)

The total volume of oxygen was divided by the specific volume to obtain the weight of oxygen, from which the percentage by weight of hydrogen peroxide in the original solution was calculated.

## The Titration with Potassium Permanganate

A survey of the literature was conducted to obtain the available information pertaining to all phases of the titration of hydrogen peroxide with permanganate. General agreement was found concerning procedures for the preparation and storage of the permanganate solution. The following procedure was actually used.

Permanganate of potassium of high purity was dissolved in hot distilled water which had been boiled for about fifteen minutes and the solution allowed to stand in a stoppered bottle for a week. The precipitated manganese dioxide was removed by filtering the solution through the sintered glass plate of a funnel. The solution was then stored in a pyrex bottle which had been covered with a coat of black paint. The bottle was fitted with a siphon having a stopcock in the line for convenient withdrawal of the solution. During withdrawal of the solution air entered the bottle through a fiber glass filter to remove air-borne dust.

If proper care is taken in its preparation and storage, a solution of potassium permanganate is quite stable. The results of several studies reported by Bruhns,[5] Halverson and Bergeim,[6] Kato[7] and others substantiated this fact, and show that no great deterioration occurs in as much as one to three years. However for very accurate work the solution should be standardized about once a month. The solution prepared for this investigation dropped in concentration about one part in a thousand in approximately six weeks.

The standardization of the permanganate solution can be carried out by using sodium oxalate, arsenious acid, iron, potassium dichromate and other primary standards. Of these, sodium oxalate is probably the most convenient and thus the most widely used. The confusion concerning the best procedure for carrying out the standardization with sodium oxalate was cleared up by the work of Fowler and Bright[8] at the National Bureau

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[3] The reproducibility of the blank measurements was such that the maximum error in the corrected volume of oxygen was not greater than a part in 4000.

[4] J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928).

[5] G. Bruhns, *Chem. Ztg.*, **47**, 613 (1923).

[6] J. O. Halverson and O. Bergeim, *Ind. Eng. Chem.*, **10**, 119 (1918).

[7] T. Kato, *J. Chem. Soc. Japan*, **48**, 17 (1927).

[8] R. M. Fowler and H. A. Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

of Standards. Their investigation showed that McBride's procedure[9] gave results that are about 0.4% too high compared with the results obtained by using arsenious acid, pure iron, and potassium dichromate. Fowler and Bright worked out a procedure that gave results within 0.03%, or within the experimental error of the results obtained by the other methods. The recommended method using sodium oxalate was used in this investigation.

The oxalate used had a purity of about 99.98%. A precision of approximately one part in 3500 was realized in the standardization. The titer of the permanganate was 0.4899% by weight corresponding to a normality of about 0.16.

As stated above, considerable disagreement is expressed in the literature regarding the optimum conditions for carrying out the titration of an aqueous solution of hydrogen peroxide with potassium permanganate. The situation was also confused by the fact that in most cases no reasons for the given procedure were stated.

The various recommendations for the weight ratio of sulfuric acid to hydrogen peroxide ranged from 50/1 to 300/1. No specific recommendations were given as to the correct rate of addition of the permanganate to the peroxide solution. Kolthoff and Stenger[10] state that the results are influenced by this rate of addition, and while the error is almost negligible at slow rates, it is more serious at fast rates. L. J. Heidt[11] also reports the influence of rate of addition on the results.

The following procedure for the titration was used in this investigation: A 10-g. sample of 2–3% peroxide was weighed out in a glass-stoppered flask,[12] and rinsed with approximately 50 cc. of distilled water into a beaker containing 150 cc. of distilled water and 7 cc. of 95% sulfuric acid. The distilled water (conductivity water) had been boiled for fifteen minutes to destroy any organic matter, and then cooled to room temperature before use. The rate of addition of the permanganate solution was approximately 35–40 cc. per minute. The titration was carried out at room temperature and with moderate stirring.

The weight ratio of acid to peroxide in this procedure was about 65/1, which corresponds closely to that recommended in Scott's "Standard Methods of Analysis."[13] However the procedure described, while corresponding in some respects to that given by Scott and others, was used as a point of departure with the thought of introducing alterations as shown by experience to be necessary under comparison with the absolute method by oxygen measurement.

As an aid in achieving accuracy, a weight buret (capacity 500 cc.) instead of the usual volumetric type was used in both the standardization of the permanganate and in the titrations. The permanganate was standardized in terms of per cent. by weight of permanganate in the solution instead of normality. By touching the tip of the buret to the stirring rod, the end-point can be determined within about a third of a drop or about 0.017 g. If it is desired to obtain the end point closer than one-third of a drop, a correction for the amount of permanganate needed to color the solution can be estimated by determining what fraction of a drop of permanganate added to a volume of water equal to that of the solution produces a coloration of equal intensity to that at the end point of the titration. Approximately 100 cc. of 0.4899 weight per cent. permanganate were required in the procedure outlined.

The permanganate titration cannot be used if any organic matter is present in the peroxide solution. Some commercial peroxide contains small amounts of organic compounds added as stabilizers against decomposition. In this case the ceric sulfate titration has been recommended by various authors[2,14,15] since ceric sulfate will not react with organic matter.

## Experimental Results

Using the procedures outlined above, runs were made to compare the permanganate titration with the gasometric method for analyzing hydrogen peroxide solutions. Seven runs were made using osmic acid as the decomposition catalyst, and three were made using lead oxide as the catalyst. Since varying amounts of two different catalysts left the same results unaltered, it was concluded that the catalyst is effective in causing complete decomposition into oxygen and water. The osmic oxide was used in basic solution and the lead oxide in a water suspension.

Table I shows the results of the runs made. The values reported for the gasometric method represent only one trial because the time required for carrying out the procedure was about five hours, and approximately four hours were required to prepare the apparatus for another run as the trap system had to be pumped free of moisture after each run. After this time had elapsed, the peroxide would have changed in concentration sufficiently (about one part in 500) to have made the data therefrom unreliable for comparison with the previous run. The values reported for the titration represent the average of three titrations, with the greatest deviation from the average about one part in 3000 to 4000.

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[9] R. S. McBride, THIS JOURNAL, **34**, 393 (1912).

[10] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1942, p. 175.

[11] Personal communication.

[12] The inside of glass ware can be made anti-catalytic by treating with hot fuming sulfuric acid. If this procedure fails, the surface of the glass probably has catalytic dust particles fused into its surface. We have preferred to construct glass ware from tubing scrupulously cleaned with fuming sulfuric acid, rinsed with the purest distilled water and using air in the glass blowing filtered through fresh medical cotton.

[13] W. W. Scott, "Standard Methods of Chemical Analysis," 5th ed., D. Van Nostrand Co., New York, N. Y., 1939, p. 2181.

[14] N. H. Furman and J. H. Wallace, THIS JOURNAL, **51**, 1449 (1929).

[15] H. H. Willard and P. Young, *ibid.*, **55**, 3260 (1933).

TABLE I

| Run no.[a] | Wt. % $H_2O_2$ by absolute method | Wt. % $H_2O_2$ by titration | Average | Deviation from average |
|---|---|---|---|---|
| 1 | 2.3105 | 2.3032 | 2.3069 | 1:625 |
| 2 | 1.9628 | 1.9638 | 1.9633 | 1:4000 |
| 3 | 1.9196 | 1.9262 | 1.9228 | 1:625 |
| 4 | 1.9066 | 1.9091 | 1.9079 | 1:1450 |
| 5 | 1.8378 | 1.8380 | 1.8379 | 1:18,000 |
| 6 | 1.7652 | 1.8035 | 1.7844 | 1:95 |
| 7 | 2.8004 | 2.7992 | 2.7998 | 1:4700 |
| 8 | 2.8002 | 2.8029 | 2.8015 | 1:2200 |
| 9 | 2.8068 | 2.8076 | 2.8072 | 1:7000 |
| 10 | 2.8095 | 2.8102 | 2.8099 | 1:8000 |

[a] Osmic acid was used as the catalyst in runs 1–7; lead oxide was used as the catalyst in runs 8–10.

The results show a favorable comparison of the permanganate titration with the gasometric method. The average deviation from the average of the two methods is about one part in 5000. It is to be noted that the runs using the osmic acid catalyst and those using the lead oxide catalyst in varying amounts led to the same result. Therefore it is assumed the catalyst ran the reaction to completion.

Run 6 in which there was a part in 95 deviation from the average cannot be explained except by some undetected error in carrying out the procedure.

While it was not the purpose of this investigation to determine the effect of varying all conditions under which the titration may be performed, a few variations were made. The results of these tests indicate that variation in the titration procedure, as outlined above, had little effect on the results. Thus, doubling the acid concentration produced a difference of about one part in 10,000 which is within the experimental error. Tests made at rates of addition of 10 cc. per minute and at 50 cc. per minute differed by about the same amount, which may be taken to indicate that some flexibility can be tolerated in the titration procedure.

## Conclusions

The experimental results show that, even where accurate results are required, the permanganate titration, using the procedure given above, can be used for determining the concentration of aqueous solutions of hydrogen peroxide. The procedure can be modified somewhat as indicated and still give sufficiently accurate results, but just how far modifications can be carried without causing decreased accuracy remains to be determined.

In applying the proposed procedure to more concentrated solutions, it is suggested that a sample containing an equivalent amount of hydrogen peroxide to that contained in 10 g. of 3% solution be used. For instance in analyzing a solution near 90%, 0.33 g. of the solution would contain approximately 0.3 g. of hydrogen peroxide, which in turn is approximately the amount contained in 10 g. of 3% solution. If the size of the sample is varied from that stated, precaution should be exercised that the weight ratio of sulfuric acid to hydrogen peroxide is at least 60–70 to 1. There is no reason to believe that higher ratios are harmful, but they are unnecessary. With lower ratios the chance of manganese dioxide formation increases, and for that reason should be avoided.

The rate of addition of the permanganate should be about 35–40 cc. per minute or slower. Excessively fast rates of addition increase the probability of the formation of manganese dioxide, which as previously stated is highly catalytic toward the decomposition of hydrogen peroxide. The titration should of course be carried out at room temperature, since higher temperatures cause loss by vaporization of the peroxide.

The results also indirectly substantiate the procedure recommended by Fowler and Bright[8] for standardization of potassium permanganate solutions. If the standardization procedure had given erroneous results, the good agreement of the titration values with those of the gasometric method would not have been possible.

The authors express their acknowledgment to the Naval Bureau of Ordnance for the support and release of this work.

## Summary

An apparatus and procedure has been described for carrying out the "gasometric" method by decomposition for determining the concentration of aqueous solutions of hydrogen peroxide. The results obtained by this method were compared with those obtained by titration with potassium permanganate. On the basis of the good agreement between the two methods, a procedure for performing the titration was recommended. Also, the method recommended by Fowler and Bright[6] for the standardization of the potassium permanganate solution against sodium oxalate has been substantiated.

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