the surface tension of a single liquid, only the difference in density between the two fluids (liquid and vapor), and not the ratio of the two, appears, the relations might well be different at the interface between two liquids, where the density of the lighter phase becomes relatively more important. All that can now be said in this connection is that the work of Harkins and Humphery indicates that for values of r/a between 0.5 and 0.7, and of $r/V^{1/3}$ between 0.5 and 0.65, the most convenient range for the measurement of the interfacial tension of water and liquids lighter than water, the interfacial correction curve is practically identical with that presented in this paper. Whether further work over a larger range will show that the densities of the liquids enter as two variables instead of as one, is not yet known, but is under investigation in this laboratory. Even with our present knowledge the drop-weight method is undoubtedly the most accurate and the most convenient of those now in use for the determination of interfacial tension, where the principal defect of the capillary height method, the uncertainty as to the angle of contact, becomes more apparent. The corrections presented in this paper should be used in works in interfacial tension, in the place of those given by Harkins and Humphery.

16. It has recently been suggested to one of the writers that by bubbling air upward through a liquid the surface tension might be determined without the use of our factors of correction, but they are involved by a bubble-volume method, the principal difference being that in the application of such a method the diameter of the tip is made small, to prevent the liquid from running down into it, so the value of r/a is small. While this has the apparent advantage that the correction factor $f(r/a)$ or $\psi(r/V^{1/3})$ comes much closer to the value one, it has the much greater disadvantage that the slope of the correction curve becomes at the same time considerable, thus introducing a greater uncertainty as to the exact correction to be applied.

The writers wish to extend their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for the funds used in securing the tips employed in this work.

CHICAGO, ILLINOIS.

THE DETERMINATION OF NITROUS ACID AND NITRITES.

BY J. S. LAIRD AND T. C. SIMPSON.

Received November 26, 1918.

In a recent article by Fox[1] entitled "The Chemical Control of Ammonia Oxidation," there is advocated the use of an alkaline solution of hydrogen peroxide as a reagent for the absorption and determination of nitrous gases, the excess of standard peroxide being titrated with potas-

---

[1] Fox, *J. Ind. Eng. Chem.*, 9, 737–43 (1917).

sium permanganate. This method is also recommended by Taylor and Davis,[1] though they point out that according to Carpenter[2] the oxidation of nitrous gases by hydrogen peroxide is incomplete in alkaline solution.

In connection with some work involving a large number of determinations of nitrous acid and sodium nitrite we attempted to use this method, as it has some obvious advantages, particularly in the rapidity and sharpness with which peroxide can be titrated at ordinary temperatures. In testing the method on standard solutions we obtained very discordant results, which led to a study of the various methods suggested for the determination of nitrites. This investigation has shown that the peroxide method is inaccurate, probably on account of catalytic decomposition of the peroxide. Potassium permanganate can, however, be used as oxidizing agent and made the basis of a rapid, accurate method, if used strictly in accordance with the well known principles of permanganate titration.

Preparation of Standard Solutions.

Lunge[3] and Mason[4] recommend the use of carefully prepared silver nitrite in preparing a standard nitrite solution. Such a solution was prepared by dissolving in hot water 7.695 grams of silver nitrite, twice recrystallized from hot water and dried in a vacuum desiccator in the dark. A slight excess of pure sodium chloride was added to precipitate the silver, and after being allowed to settle the precipitate was filtered off and carefully washed, and the filtrate and washings made up to one liter with water. The solution so prepared gave on titration with permanganate a value about one per cent. weaker than that calculated, indicating that silver nitrite was not a reliable standard, a conclusion which has been confirmed by determinations which will be given later.

To avoid this difficulty, a solution of pure sodium nitrite was prepared, and standardized according to the gravimetric method worked out by Busvold.[5] 100 cc. of the solution was added to 1.5 grams of recrystallized silver bromate dissolved in 200 cc. of normal acetic acid in a flask. 30 cc. of 1 : 4 sulfuric acid was added, and the flask was shaken and warmed to coagulate the yellow precipitate of silver bromide formed. The precipitate was filtered on a Gooch crucible, washed and dried at 130°. The factor for conversion is 1.1022. The results of careful determinations by this method show excellent agreement and are believed to be quite accurate. Based on such determinations our solution had a concentration of 0.0977 *N*.

---

[1] Taylor and Davis, *J. Ind. Eng. Chem.*, **9**, 1106–10 (1917).

[2] Carpenter, *J. Soc. Chem. Ind.*, **5**, 287 (1886).

[3] Lunge, *Ber.*, **10**, 1073 (1877).

[4] Mason, "Examination of Water."

[5] Busvold, *Chem. Ztg.*, **38**, 28 (1914).

The potassium permanganate solution was prepared by dissolving 80 grams of pure crystals in 5 liters of distilled water. The solution was boiled under a reflux condenser for two days, allowed to settle and filtered through a Gooch crucible. It was standardized according to the method of Sorensen[1] against a freshly prepared solution of very pure sodium oxalate. In this standardization, as indeed throughout the whole investigation, the solutions were measured by means of standardized pipets and weight burets.

The hydrogen peroxide solution was prepared from Merck's 30% "Perhydrol," or for part of the work, where noted, from commercial peroxide. Ferrous sulfate was dissolved in normal sulfuric acid, and titrated the day used, as was also the peroxide.

The Hydrogen Peroxide Method.—Oxidation by means of peroxide was tested in both acid and alkaline solutions as follows: 25 cc. nitrite solution was run into a flask, and excess peroxide was added. The solution was then made distinctly acid with sulfuric acid or alkaline with potassium hydroxide. After permitting the reaction to go on for 5–15 minutes with frequent shaking the excess peroxide was titrated with permanganate, after acidifying with 5–10 cc. 1 : 1 sulfuric acid.

In these titrations the end-point was never satisfactory, fading colors being produced with the addition of the last few drops of permanganate. This suggested the presence of nitrite unoxidized by the peroxide, which was confirmed by Griess' reagent even in solutions which had been boiled for ten minutes to expel the excess of peroxide. Though permanganate was used in oxidizing this nitrite, less permanganate was required in titrating back than was theoretically necessary, indicating loss of peroxide, probably by catalytic decomposition. This decomposition seemed to be as great in acid as in alkaline solutions as shown in Table I. In this table as in those which follow the volumes of solutions used are recalculated to equivalent volumes of exactly tenth normal solutions.

TABLE I.—OXIDATION BY PEROXIDE.

Taken: 24.42 cc. $NaNO_2$; 48.81 cc. H_2O_2. Calculated $KMnO_4$, 24.34 cc.

Reaction of solutions.	Required 0.1 N $KMnO_4$. Cc.	Error. Cc.
Alkaline	22.79	—1.60
	22.44	—1.95
	22.81	—1.58
Acid	23.07	—1.32
	23.04	—1.35
	22.05	—2.34

In these tests on an average 3.46% of the hydrogen peroxide added has decomposed, and the experimental error by this method may be as much as 5%.

[1] Sorensen, *Z. anal. Chem.*, 42, 352 (1903).

Method of Lunge.—According to Lunge[1] nitrous acid can be determined accurately by means of permanganate if the nitrite is run slowly into warm acid permanganate instead of the reverse. The reaction goes very slowly towards the end, especially if the solution is not warm enough, and it is very easy to overstep the end-point. If the solution is too warm a precipitate of manganese dioxide is formed which makes the end-point almost impossible to determine.

Three determinations were made by this method using in each case 16.55 cc. 0.1 *N* $KMnO_4$ in a volume of about 200 cc., containing 10 cc. sulfuric acid, at a temperature of 30–40° C. In the three determinations 0.28 cc., 0.25 cc., and 0.24 cc. less nitrite solution than theoretically necessary were required. It is probable that with sufficient care accurate results can be obtained by this method, but as has been pointed out by Raschig,[2] it is too slow and uncertain to be satisfactory.

Method of Scott.—According to Scott[3] nitrite can be oxidized in acid solution by excess permanganate solution, and the excess titrated back with sodium oxalate solution, the titration being carried out in hot solution, 60–90°. This is contrary to accepted practice, which demands that the permanganate be added slowly to the oxalate solution and not the reverse. In our tests a precipitate of MnO_2 was formed in each case, the end-point was very uncertain, and the results most unreliable as shown by the following:

TABLE II.—METHOD OF SCOTT.

No.	0.1 *N* $NaNO_2$. Cc.	0.1 *N* $KMnO_4$. Cc.	0.1 *N* $Na_2C_2O_4$. Cc.	Error. Cc.
1	29.31	34.66	5.49	—0.14
2	29.31	34.66	5.46	—0.12
3	14.65	41.37	23.89	2.83
4	14.65	41.37	22.45	4.27
5	14.65	41.37	26.18	0.54

Method of Raschig.—The unsatisfactory nature of Lunge's method has been pointed out by Raschig[4] who suggested a modification which is much more accurate. According to his method the nitrite solution is run into about 25% excess neutral permanganate. After two minutes the solution is acidified, 5 cc. 10% KI added to reduce the excess permanganate and the iodine liberated titrated with sodium thiosulfate. One determination was quoted, which agreed with the theoretical to one part in 400, but no details were given as regards standardization of the solutions. Bray and Mackay[5] have shown that the iodine liberated from

---

[1] Lunge, *Loc. cit.*

[2] Raschig, *Ber.*, 38, 3911 (1905).

[3] Scott, "Standard Method of Chemical Analysis," pp. 521–2.

[4] Raschig, *Loc. cit.*

[5] Bray and Mackay, THIS JOURNAL, 32, 1193 (1910).

potassium iodide by permanganate standardized by sodium oxalate is 0.2–0.3% too low when titrated with thiosulfate standardized against pure potassium iodide or iodine. In this laboratory it has been found almost impossible to procure potassium iodide from which iodine is not set free on acidifying. Iodine is also slowly liberated from potassium iodide in sulfuric acid solutions which contain even small amounts of nitrate such as would be formed during a determination. These errors are not large and might be determined by a blank experiment using exactly the same amount of potassium iodide solution as is used in the regular determination. But any method which requires the use of this expensive and, at the present time, almost unobtainable reagent, cannot be considered satisfactory or convenient.

Method Suggested by the Authors.—The method suggested by the authors differs from that of Raschig in using standard ferrous sulfate, sodium oxalate, or hydrogen peroxide in excess as reducing agent, the excess being titrated with standard permanganate. Excess permanganate is placed in a flask and acidified with 10–20 cc. of 1 : 4 sulfuric acid. The nitrite solution is run in slowly with constant shaking. In this way there is no danger of loss due to decomposition of the nitrite on acidifying. Dilute acid is preferable as it avoids the heating of the solution caused by addition of concentrated acid. Excess of ferrous sulfate, hydrogen peroxide or sodium oxalate solution is then added and the clear solution is titrated with permanganate to a faint pink. If oxalate is used, it is necessary to heat the solution. This is unnecessary when using ferrous sulfate, and in fact the solution should be kept at ordinary temperatures to avoid oxidation of ferrous sulfate by the air. The end-point is quite sharp, showing complete oxidation of the nitrite. The accuracy of the method is shown by the following results:

Table III.—Method of Authors.

Solutions all re-calcd. to 0.1 *N*.

Composition of solution.	$KMnO_4$ solution. Cc.			Composition of solution.	$KMnO_4$ solution. Cc.		
	Calcd.	Required.	Error.		Calcd.	Required.	Error.
24.42 cc. $NaNO_2$ 14.47 cc. $FeSO_4$	38.89	38.91	0.02	19.54 cc. $NaNO_2$ 11.28 cc. $Na_2C_2O_4$	30.82	30.82	0.00
"	"	38.90	0.01	"	"	30.75	—0.07
"	"	38.94	0.05	"	"	30.82	0.00
"	"	38.94	0.05	"	"	30.80	—0.02
"	"	38.92	0.03	"	"	30.77	—0.05
"	"	38.91	0.02	"	"	30.80	—0.02
24.42 cc. $NaNO_2$ 28.94 cc. $FeSO_4$	53.36	53.34	—0.02	23.52 cc. $NaNO_2$ 18.83 cc. H_2O_2	42.35	42.41	0.06
"	"	53.38	0.02	"	"	42.34	—0.01
"	"	53.33	—0.03	"	"	42.52	0.17[2]
23.52 cc. $NaNO_2$ 20.14 cc. H_2O_2 [1]	43.66	43.80	0.14	"	"	42.37	0.02
"	"	43.75	0.09	"	"	42.40	0.05
"	"	43.67	0.01	"	"	42.31	—0.04

[1] Acidified with HNO_3 instead of H_2SO_4.

[2] Solution became hot due to use of concentrated H_2SO_4 and heavy precipitate of MnO_2 formed.

There seems little difference in the accuracy of the results obtained with oxalate and ferrous sulfate; peroxide seems slightly less reliable. The use of the oxalate has the disadvantage of requiring heating of the solution, but the reagent is quite stable. Ferrous sulfate must be restandardized frequently but is rather more stable than hydrogen peroxide. In case the use of sulfuric acid had to be avoided, as for example if barium were present, hydrogen peroxide could be used in nitric acid solution. The end-point in nitric acid solution is not quite so sharp, evanescent pink colors being obtained with each drop added towards the end. The results are, however, fairly accurate.

Use of Commercial Hydrogen Peroxide.—Commercial hydrogen peroxide can be used only if it is free from impurities or substances added to prevent decomposition which react slowly with permanganate. There is no reason why a solution which gives a good end-point when titrated should not be satisfactory. This was found to be true of solutions prepared from the commercial hydrogen peroxide used in this laboratory.

Stability of Hydrogen Peroxide Solutions.—Dilute acid hydrogen peroxide solutions are fairly stable. In 1916 0.1 N solutions of peroxide in normal sulfuric and normal nitric acids were prepared and standardized by Dr. H. H. Willard of this laboratory. The solutions have since then been kept in dark glass bottles in a dark cupboard. On restandardizing the results below were obtained.

Acid.	Conc. 5/15/16.	Conc. 10/18/18.	% decrease.
H_2SO_4	0.1189 N	0.1120 N	5.8%
HNO_3	0.1291 N	0.1018 N	21.1%

The sulfuric acid solution of hydrogen peroxide has decreased in strength at the rate of 0.2% a month, the nitric acid solution much more rapidly. Under less favorable circumstances the decrease in strength is more rapid. During the course of these experiments a solution made up in 1% sulfuric acid solution was kept in a clear glass bottle, from which samples were frequently taken. Its strength decreased in two weeks from 0.1255 N to 0.1236 N or on the average of 0.1% a day. The ferrous sulfate solution under similar conditions decreased in 18 days from 0.1437 N to 0.1419 N, or on the average of 0.05% a day. Ferrous sulfate may be made much more stable by keeping a coil of pure aluminum wire in the solution as suggested by Waring.[1]

Determination of Nitrite in Presence of Chlorides or Bromides.—According to Busvold[2] the titration of nitrites with permanganate according to the method of Lunge is inaccurate in the presence of chlorides, and he quoted results which showed that less than the theoretical amount

---

[1] Waring, *Mining Sci. Press*, 117, 193–4 (1918).

[2] Busvold, *Loc. cit.*

of permanganate was required, a result quite contrary to what might be expected.

Experiments were made to determine the effect of chlorides and bromides, by adding known amounts of solutions of sodium chloride or bromide to a 20 cc. sample of the nitrite solution before adding it to the permanganate, and completing the determination as usual. Results are given in Table IV. The concentration of chloride or bromide in Col. 1 are based on titrating in a volume of 150 cc.

TABLE IV.—EFFECT OF CHLORIDES AND BROMIDES.

In each determination 23.52 cc. 0.1 *N* $NaNO_2$ were taken.

Conc. chloride or bromide in solution when titrated.	0.1 *N* H_2O_2. Cc.	0.1 *N* $KMnO_4$. Cc.	Error. Cc.	Remarks.
N/75 NaCl......	18.74	42.29	0.03	
N/20 NaCl......	18.74	42.30	0.04	
N/4 NaCl.......	18.74	42.25	—0.01	
N/4 NaCl.......	21.54 ($FeSO_4$)	45.14	0.08	
N/2 NaCl.......	18.66	42.24	0.06	Slight odor of Cl
NaCl...........	18.74	42.58	0.32	Odor of Cl, poor end-point
N/150 NaBr.....	18.63	42.22	0.07	
N/50 NaBr......	18.63	42.62	0.47	Odor of Br, poor end-point

These results show that the titration can be carried out in the presence of chloride as long as the concentration of Cl is not over 0.5 *N* in the solution during titration; in the case of bromide the safe limit is very much lower, about 0.0067 *N*. As has been shown by Barneby,[1] manganese salts greatly decrease the rate of reaction between chlorides or bromides and permanganate. This protective effect can be made use of in this titration when necessary. On the addition of 0.5–1.0 g. manganese sulfate to the permanganate solution before adding the nitrite most of the permanganate is precipitated as manganese dioxide. Under these conditions there is practically no odor of chlorine on titrating even in a 5% chloride solution; or of bromine in a 0.033 *N* bromide solution. The end-point is fugitive, however, and as in the titration of iron under such conditions the first pink color which spreads throughout the solution must be taken as the end-point even though it does not persist for over 5 seconds.

Test of Purity of Silver Nitrite.—Silver nitrite carefully prepared as above was tested for nitrite content according to this method. In some cases the pure crystals were dissolved in hot water, in others were placed directly in the permanganate. In all cases low results were obtained, indicating either that the crystals did not have the composition represented by the formula or that there is partial decomposition on solution. Lunge[2] who prepared standard solutions by dissolving silver nitrite in concentrated sulfuric acid, obtained results 4% too low, which he assumed to

[1] Barneby, THIS JOURNAL, **37**, 1496 (1915).

[2] Lunge, *Loc. cit.*

be due to partial decomposition. Some of the results obtained by us are as follows:

TABLE V.—PURITY OF SILVER NITRITE.

Composition of solution.	0.1 *N* $KMnO_4$ solution. Cc.		
	Calculated.	Required.	Error.
0.3847 g. $AgNO_2$ + 15.00 cc. 0.1 *N* $Na_2C_2O_4$	65.00	63.95	—1.05
		62.87	—2.13
		62.66	—2.34

These results show clearly that silver nitrite is not reliable as a standard in nitrite determinations.

Summary and Conclusions.

1. The volumetric methods described in the literature for the determination of nitrous acid or nitrites are not satisfactory.

2. A method has been devised for determining nitrites which is, briefly stated, oxidation in acid solution with excess permanganate, reduction of the excess permanganate with excess ferrous sulfate, sodium oxalate or hydrogen peroxide and titration of the excess of reducing agent with permanganate. The titration is not interfered with by moderate amounts of chloride, or small amounts of bromide.

3. Silver nitrite is not a satisfactory material for use as a standard in nitrite determinations. A satisfactory standard solution may be made by titrating sodium nitrite solution with potassium permanganate according to the method described above; or sodium nitrite solution may be standardized gravimetrically by the reduction of silver bromate to silver bromide according to the method of Busvold.

UNIVERSITY OF MICHIGAN.

CHEMICAL ACTION PRODUCED BY RADIUM EMANATION. I. THE COMBINATION OF HYDROGEN AND OXYGEN.[1]

BY S. C. LIND.

Received December 30, 1918.

1. Introduction.

In 1903 Ramsay and Soddy[2] reported quantitative data on the decomposition of water in a solution of radium salt. In 1907, Bragg[3] used their data to make the first comparison between the chemical and ionizing effects of α-particles. Although Bragg calculated that the number of molecules of water decomposed was almost exactly equal to the number of ions that would have been produced in air by the emanation employed, he was apparently not impressed by the equality he found, and referred to it as a "curious parallelism in numbers." In 1910 Bergwitz[4] gave the results of

---

[1] Published with permission of the Director of the U. S. Bureau of Mines.

[2] Ramsay and Soddy, *Proc. Roy. Soc.*, 72, 204 (1903).

[3] W. H. Bragg, *Phil. Mag.*, [6] 13, 356 (1907).

[4] Bergwitz, *Physik. Z.*, 11, 273–5 (1910).