The tetryl side of the curve, with data

TNT, %	10.0	20.0	40.0
Equil. temp., °C.	120.8	112.2	90.8
t	7.92	16.52	37.92

gave the equation $y = 0.72 + 0.65x + 0.007x^2$. From this, taking the value of S when x is zero, L_f of tetryl = 6237 and w = 21.7.

Guia[8] has published an incomplete freezing-point-solubility curve for this system, showing the formation of a molecular compound but not identifying it. The same criticism applied to his study of the system, trinitrotoluene-picric acid was found to apply here, his equilibrium temperatures being too low, as shown by Taylor and Rinkenbach.[4] For this reason, his data cannot be used for the calculation of heats of fusion.

Summary

A summary of the values obtained for the heats of fusion of trinitrotoluene, picric acid and tetryl is as follows.

	Heat of fusion in gram-calories per gram of substance			Heat of fusion in gram-calories per gram molecule of substance		
	TNT	Picric acid	Tetryl	TNT	Picric acid	Tetryl
TNT-Picric	18.3	18.7	..	4163	4282	..
Tetryl-picric	..	22.1	22.6	..	5041	6482
TNT-Tetryl	22.1	..	21.7	5025	..	6237
Av.	20.2	20.4	22.2	4594	4662	6360

The results are of the same order, as is to be expected because of the similarity of the compounds and the average results are in the same general ratio as their molecular weights.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A NEW ABSORBENT FOR OXYGEN IN GAS ANALYSIS

BY LOUIS F. FIESER

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On dissolving in dilute alkali a mixture of sodium anthraquinone-β-sulfonate and sodium hyposulfite in large molar excess, a deep red solution is obtained which absorbs oxygen with great rapidity. This paper reports a brief investigation of the suitability of this reagent as an absorbent for oxygen in gas analysis.

Since sodium hyposulfite has itself been recommended for this purpose,[1]

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[8] Guia, *Z. ges. Schiess. und Sprengstoffw.*, **10,** 111 (1915).

[1] (a) Franzen, *Ber.*, **39,** 2069 (1906). (b) Durig, *Biochem. Z.*, **4,** 65 (1907). See also (c) Tobiesen, *Skand. Arch. Physiol.*, **6,** 278 (1895). Pettersson and Högland, *Ber.*, **22,** 3324 (1889). Descamps, *J. Chem. Soc.*, **112,** ii, 216 (1917).

it was necessary to determine at the outset whether the presence of a small amount of anthrahydroquinone sulfonate which, of course, is immediately formed by reduction of the quinone, has any effect on the velocity with which hyposulfite reacts with oxygen. The rates of absorption were consequently compared, use being made of the method described by Jones and Meighan,[2] which consists in observing the decrease in pressure in a closed vessel in which the absorbing solution is shaken with air. Their apparatus was slightly modified.

A 330cc. three-neck Wolff bottle served as the absorption vessel and was attached to a mechanically driven piston which slid the bottle back and forth in a pan of water at the uniform rate of 210 25mm. strokes per minute. A thermometer was fitted into the first neck; the second was connected by means of a short length of vacuum tubing to a stopcock to which a manometer was sealed; and into the third was inserted the main tube of a capillary three-way stopcock. One of the two tubes of this stopcock was a short upright tube connected to a vacuum pump with rubber tubing; to the other was sealed a 50cc. cup into which the absorbing solution could be measured. In carrying out an experiment the stopcock of the manometer was closed and the vessel evacuated. A quantity of solution, usually 30 cc., was measured into the cup and quickly introduced into the bottle without allowing any air to follow it. Mechanical shaking and adjustment of the temperature of the water-bath soon brought the contents of the bottle to a temperature of 25 ± 1°. The three-way stopcock was then turned so as to admit air by way of the cup, the manometer stopcock was opened and, the gas within the bottle being at atmospheric pressure, the three-way stopcock was closed and shaking started. After definite intervals of time the stopcock of the manometer was closed and the pressure read without interrupting the shaking.

Each reagent was prepared and kept in an atmosphere of illuminating gas until needed. A potassium pyrogallate solution, used for purposes of comparison, was of the composition recommended by Benedict[3] and was prepared by mixing a solution of 15 g. of pyrogallol in 15 cc. of water with 135 cc. of potassium hydroxide solution of specific gravity 1.55. The composition of the chief hyposulfite solutions employed is indicated in Table I together with data descriptive of solutions to be discussed later.

TABLE I

ABSORBING SOLUTIONS

	Weight in g. of materials dissolved in 100 cc. of water				
	No. 1	No. 2	No. 3	No. 4	No. 5
$Na_2S_2O_4$ (86.7%)[4]	16	16	16	16	16
NaOH (stick)	13.3	13.3	6.6	3.3	2
Anthraquinone-β-sulfonate (95%)	2	4	2	2	2

The results of a series of experiments are given graphically in Fig. 1. The quantities of sodium hyposulfite and anthraquinone sulfonate indi-

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[2] Jones and Meighan, *J. Ind. Eng. Chem.*, **11**, 311 (1919).

[3] Benedict, "The Composition of the Atmosphere," *Carnegie Inst. Pub.*, **166**, 80 (1912).

[4] Kindly supplied by the Merrimac Chemical Co. through the courtesy of Mr. A. L. Bump.

cated in describing Curves 1–4 represent the amounts of impure materials taken per 100 cc. of water, the concentration of alkali being in each case that of Solutions 1 and 2. The percentage absorption was calculated from the reading of the manometer at any time as compared with the reading when it had finally become constant. Each curve represents the average of two or more determinations with fresh solutions, the figures being reproducible to about 5%. In the experiments of Curve 2, a 60cc. sample was employed, while in every other case 30 cc. of solution was used.

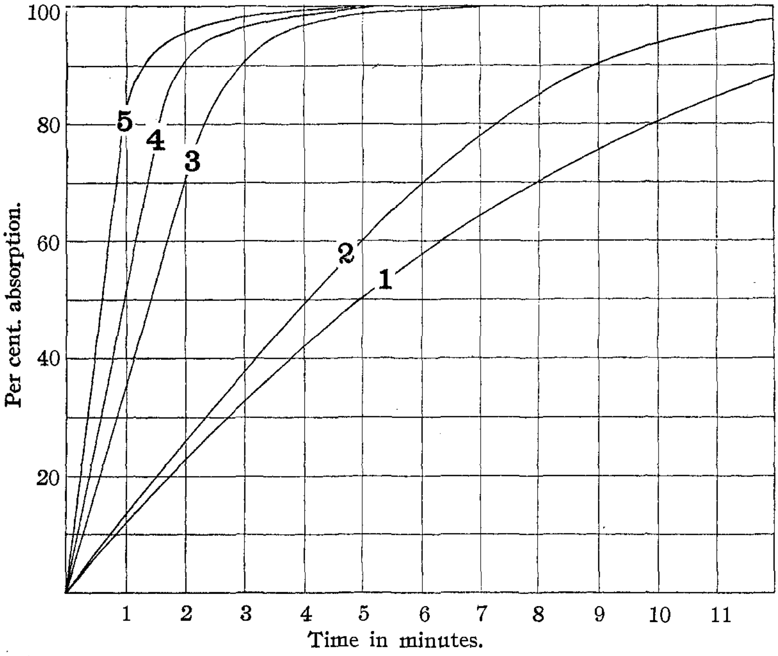
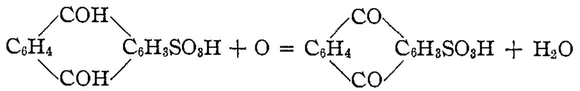
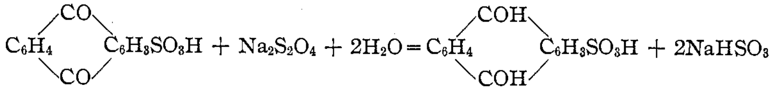


Fig. 1.—Relative rates of absorption curves: 1, 16 g. $Na_2S_2O_4$ per 100 cc.; 2, 16 g. $Na_2S_2O_4$ per 100 cc. (double quantity of solution); 3, 2 g. anthraquinone sulfonate, 8–16 g. $Na_2S_2O_4$ per 100 cc. (of Solution No. 1); 4, 4 g. anthraquinone sulfonate, 16 g. $Na_2S_2O_4$ per 100 cc. (Solution No. 2); 5, pyrogallol.

It is quite evident that sodium hyposulfite absorbs oxygen much more slowly than the hyposulfite-anthraquinone sulfonate reagent even when twice as much solution is employed. The velocity with which the latter reagent reacts is, within limits, apparently independent of the concentration of hyposulfite; but an increase in the concentration of the anthrahydroquinone sulfonate increases the rate of absorption. Since the amount of anthrahydroquinone sulfonate present was insufficient to absorb all of the oxygen, its action must be catalytic. Thus the operation of the reagent may be described by the equations,



$$C_6H_4\left\langle\begin{matrix}COH\\COH\end{matrix}\right\rangle C_6H_3SO_3H + O = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3SO_3H + H_2O \quad (1)$$



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3SO_3H + Na_2S_2O_4 + 2H_2O = C_6H_4\left\langle\begin{matrix}COH\\COH\end{matrix}\right\rangle C_6H_3SO_3H + 2NaHSO_3 \quad (2)$$

the net result being, $Na_2S_2O_4 + H_2O + O = 2NaHSO_3$ (3)

Some oxygen is probably absorbed directly according to Equation 3, though the first reaction appears to be much the faster of the two. Reaction 2 must also be fairly rapid in order to maintain the more active reducing agent at an efficient concentration. Thus sodium sulfide cannot be substituted for hyposulfite, for its action is too tardy.

Even under the most favorable conditions the reagent here described is not so rapid in its action as Benedict's pyrogallol solution (Curves 4 and 5). Were pyrogallol an ideal absorbent there would be little reason for further discussing the possible utility of a reagent which appears from this test to be inferior to it in one important respect. However, this is not the case. The difficulty in preventing and the error arising from the evolution of carbon monoxide during the oxidation of pyrogallol and the difficulty of handling this viscous reagent in certain types of apparatus are too well known to require comment. Since the hyposulfite-anthraquinone sulfonate reagent appeared to offer certain advantages in these respects, it was investigated further with the following results.

Rate of Absorption in the Richards Pipet[5]

Analyses of the oxygen content of the air were carried out with the Richards constant-volume apparatus[6] with water as the confining liquid. The Hempel buret was used in analyzing an oxygen-air mixture. The average volumes of the air and of the oxygen-air samples were 62 cc. and 50 cc., respectively, at atmospheric pressure and room temperature. The pipet held conveniently about 250 cc. of reagent, Solution 5 being employed. During absorption the pipet was gently rocked back and forth at a uniform rate in such a manner that the walls of the bulb were washed with the solution. Vigorous shaking is unnecessary but does not cause frothing. The results of typical analyses are given in Table II. Readings were made after successive periods of contact of gas and absorbent and complete absorption is indicated by the agreement of successive readings. It appears that shaking for one minute suffices to remove the oxygen from a 62cc. sample of air; with a sample of 90.0% oxygen complete absorption may be obtained by shaking for two minutes. This is sufficiently rapid operation for all ordinary purposes and it is

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[5] Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 273 (1901).

[6] Richards, *ibid.*, **38**, 273 (1902).

much more satisfactory than the performance of hyposulfite solution[1a] alone (Expt. 5).

TABLE II

ANALYSES USING RICHARDS' APPARATUS

	Expt.	Percentage of oxygen found after shaking for					Complete absorption
		Min. $^1/_2$	1	2	3	4	Min.
Air	1	20.4	20.8	20.8	20.8	..	1
	2	19.3	20.9	..	..	20.9	1
	3	..	20.9	20.8	..	..	1
	4	..	20.8	..	20.8	..	1
	5 (Hyposulfite)	..	17.2	20.1	20.8	20.8	3
Oxygen and air	7	..	85.6	90.0	90.0	..	2
	8	..	..	90.0	..	..	...

In Expts. 3 and 4, only 2 g. of sodium hyposulfite per 100 cc. was used, an amount which represents only one-half equivalent in excess of that required to reduce the anthraquinone sulfonate employed. Since no change in the velocity of absorption was detected, it again appears that the rate of the reaction is practically independent of the concentration of hyposulfite. Thus one would expect no decrease in efficiency to occur with the consumption of the reserve of hyposulfite similar to the decrease encountered with those reagents whose action does not depend upon a catalytic process. In other words, the specific absorption[7] should be practically equal to the theoretical absorption. The following experiment was designed to determine whether this is the case.

Efficient Capacity

The efficiency of the reagent was noted at various stages of exhaustion and the amount of oxygen which could be absorbed at the maximum rate compared with the calculated value. In order to exhaust the reagent by causing it to absorb large quantities of oxygen of known volume, it was shaken with successive portions of an oxygen-nitrogen mixture containing 90.0% of oxygen until an appreciable quantity of nitrogen had accumulated in the pipet. The amount of oxygen which had been absorbed could obviously be calculated from the volume of this residual nitrogen and the concentration of nitrogen in the gas mixture. After having thus partially exhausted the reagent an air analysis was made, readings being taken after shaking the pipet for one minute and again after an additional shaking of two minutes. As long as the two results agreed within the experimental error the pipet was rendering its maximum rate of absorption.

Solution No. 3 was used, the amounts of materials employed being 2.5 times those indicated in Table I. The alkali used was that required to

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[7] Anderson, *J. Ind. Eng. Chem.*, **7**, 587 (1915).

neutralize the bisulfite formed on oxidation of sodium hyposulfite. The Richards pipet and the Richards constant-volume apparatus were used in making the analyses. The results are given in Table III. Measurements were all made at temperatures and pressures very close to 22° and 760 mm., and the volumes given refer to these conditions.

TABLE III

EFFICIENT CAPACITY OF ABSORBENT

N_2 residue cc.	O_2 absorbed cc.	O_2 total cc.	Percentage of theoretical absorption	Percentage of O_2 in air[8] found after shaking for 1 min.	3 mins.
45.04	404	404	18.2	20.84	20.81
	13	417			
37.40	336	753	34.1	20.83	20.77
	13	766			
33.42	300	1066	48.2	20.80	20.79
	13	1079			
47.17	423	1502	68.0	20.80	20.77
	13	1515			
44.90	403	1918	86.7	20.88	20.86
	13	1931			
19.92	179	2110	95.5	20.85	20.85
	13	2123			
7.41	67	2190	99.2	Turned brown	

Calculated absorption: 2210.

Since the pipet cannot be expected to function efficiently after the anthrahydroquinone begins to be permanently oxidized, the theoretical absorption (vol. at 22° and 760 mm.) was calculated as that equivalent to the pure hyposulfite taken minus that equivalent to the anthraquinone sulfonate used. The last analysis in which absorption was complete in one minute was made after 95.5% of the calculated amount of oxygen had been absorbed. When the theoretical volume had been absorbed the solution became somewhat brown and thick, indicating either the disappearance of alkali or the permanent oxidation of the anthrahydroquinone. The solution was frothy and difficult to handle and a further analysis was not completed.

It is evident that absorption is as rapid when the solution is almost exhausted as when it is fresh. Durig has shown[1b] that with hyposulfite alone the velocity gradually decreases and the solution must be renewed long before it has become exhausted.

[8] The average of these results is 20.83%, a value considerably below the accepted value of 20.98% (for oxygen plus CO_2), and the percentages in the second column are somewhat lower than those in the first. Both of these deviations are probably due to the evolution of oxygen from the confining water, a source of error of more importance in the constant-volume than in the constant-pressure method because the excess of pressure existing when the initial reading is made causes more oxygen to be dissolved, while the reduced pressure after absorption aids the evolution of oxygen to the gas space.

Accuracy and Adaptability to the Orsat Pipet

Solution No. 3 was employed in the analysis of illuminating gas which had been collected after bubbling through strong potassium hydroxide solution to remove carbon dioxide and to which a little oxygen was added. The analyses were made over mercury in a 50cc. Hempel buret with rubber connections, but still with the Richards pipet. Comparison was made with Benedict's pyrogallol solution.[3]

PERCENTAGE OF OXYGEN IN ILLUMINATING GAS

	I	II
New reagent	1.43	1.44
Pyrogallol	1.37	1.44

While its low viscosity renders this reagent admirably adapted to a pipet designed for shaking and constructed of small capillary tubing, this property becomes a distinct disadvantage when the stationary Orsat pipet is employed. Since the viscosity may be increased to a certain extent by increasing the concentration of alkali, a number of solutions were compared in the Orsat pipet in order to establish the most suitable concentration of this material, while the amounts of hyposulfite and of anthraquinone sulfonate employed remained the same as above. The 50cc. Hempel buret with mercury was again employed and the Orsat pipet was of the usual form which is filled with glass tubes to increase the absorbing surface.

TABLE IV

AIR ANALYSES WITH THE SIMPLE ORSAT PIPET

Number of ½ min. passes	Sol. 5 2 g. %	Sol. 4 3.3 g. %	Sol. 3 6.6 g. %	Sol. 1 13.3 g. %	Pyrogallol %
1	6.9	6.8	7.7	9.2	18.5
2	12.7	12.5	14.7	17.3	20.6
3	17.0	17.8	19.4	20.8	20.98
4	19.7	20.2	20.95	20.97	..
5	20.7	20.98	..	..	..
6	20.9	..	..	..	..
7	21.01	..	..	..	..

The gas was rapidly passed into the pipet, allowed to stand there a short time, and returned to the buret in such a way that the complete operation consumed one-half minute. The process was repeated until successive readings were identical, indicating complete absorption. Two or more determinations were made with each of the solutions, and the results given in Table IV are averages of closely agreeing analyses. Haldane's pyrogallol solution, consisting of 1 g. of pyrogallol in 10 cc. of potassium hydroxide solution of 1.55 specific gravity, was employed both because it appears to be one of the most efficient proposed[9] and because it probably evolves no carbon monoxide.

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[9] Ref. 3, p. 114.

The agreement between the values found with the two reagents is well within the experimental error both in these air analyses and in the analysis of illuminating gas. The average of 18 determinations of the combined oxygen and carbon dioxide content of the atmosphere was 20.97%, a figure which agrees well with the present accepted value of 20.98%.[9,10] It is safe to conclude that the new reagent may be relied upon to give accurate results, and it should be noted that the accuracy is wholly independent of the concentrations used.

The velocity of absorption appears to increase with the concentration of alkali, but when the reagent was prepared from a solution of 26.6 g. of sodium hydroxide in 100 cc. of water, partial reduction to sodium anthranol sulfonate[11] took place and the decanted solution was valueless as a reagent for oxygen. Conversion to this anthranol derivative has not been observed in the less concentrated solutions described. On the other hand, it is clear from the table that the rate of absorption falls off appreciably with decreasing concentration of alkali. Thus Solution 1 appears to be the most satisfactory of those investigated.

Comparison with the results obtained with pyrogallol shows that absorption is definitely slower with the new reagent than with Haldane's pyrogallol solution in this type of apparatus. The relative rates of absorption, however, appear to be largely dependent upon the construction of the absorption apparatus for, when the bubbling pipet of the type recommended[12] by the Chemists' Committee of the United States Steel Corporation was employed, absorption with the new reagent was found to be somewhat more rapid than with pyrogallol. This is shown in Table V of averages of a series of analyses. A 50cc. sample of air was used in each case. Benedict's pyrogallol solution,[3] freshly prepared, was used for comparison since the more viscous solution of Haldane tends to leave a permanent solid residue and is thus unsuited to the pipet in question. Solution 2 contained twice as much catalyst as No. 1. On bubbling air through these solutions a froth containing precipitated

TABLE V

AIR ANALYSES WITH THE BUBBLING PIPET

Number of 1/2 min. passes	Hyposulfite-anthraquinone sulfonate reagent No. 1 %	No. 2 %	Pyrogallol %
1	15.3	15.5	14.1
2	20.1	20.5	18.8
3	20.9	20.9	20.4
4	..	..	20.8
5	..	..	20.9

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[10] Krogh, *Math. fys. Meddelelser*, **1,** No. 12, 16 (1919).

[11] Battegay and Brandt, *Bull. soc. ind. Mulhouse*, **89,** 365 (1923).

[12] Camp, *Chem. Met. Eng.*, **9,** 303 (1911). For description see Dennis, "Gas Analysis," the Macmillan Co., New York, **1920,** p. 80.

anthraquinone sulfonate formed. This readily dissolved on gently shaking the pipet after the removal of most of the gas, and precipitation did not occur on passing the gas into the pipet a second time. Less material separated in the case of Solution 2. Unless the pipet is so rigidly mounted that the slight motion required is not possible, this behavior presents no serious difficulties.

The relatively lower rate of absorption in the simple Orsat pipet is probably due in part to a lower viscosity than that of pyrogallol and partly to the formation of a protecting film of solid anthraquinone sulfonate. When the gas is intimately mixed with the reagent by shaking or by bubbling it through the liquid neither of these factors is of significance and absorption is very rapid. Thus the Friedrichs spiral gas-washing bottle is a highly efficient apparatus for the absorption of oxygen with this reagent. Unfortunately the spiral pipet of Dennis,[13] which embodies the same principle, could not be obtained for comparison. It has been found, however, that a train of three Friedrichs bottles containing Solution 1 constitutes an efficient and simple means of freeing tank nitrogen from oxygen, all traces of the gas being removed even when the velocity is at a maximum.

On the basis of the foregoing experiments, Solution 3 can be recommended for use in any pipet designed for shaking and No. 1 or, better, No. 2, for use in the bubbling type of absorption pipet or in the Friedrichs gas-washing bottle. The reagent is superior to sodium hyposulfite in speed and efficient capacity and it possesses the distinct advantage over pyrogallol that under no conditions can it evolve carbon monoxide. It is cheaply and easily prepared and the velocity of absorption remains constant until the reagent is exhausted, as indicated by a change in color from blood-red to brown. The reagent has been used with satisfaction in the course in gas analysis at this University.

The writer is indebted to Professor G. P. Baxter for his kind advice and criticism during the course of this work.

Summary

An oxygen absorbent consisting of an alkaline solution of sodium hyposufite containing sodium anthrahydroquinone-β-sulfonate as catalyst has been described and the completeness and rapidity of its action together with its capacity and adaptability to various types of pipets have been investigated.

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[13] Dennis, *J. Ind. Eng. Chem.*, **4**, 898 (1912).