26.98 mm. and for 40.00°, 35.18 mm. The "International Critical Tables"[6] give for these temperatures 15.6, 20.6, 26.9, 34.8. The equation

$$\log_{10} p_s (\text{in mm.}) = 8.5723 - (2200/T) \qquad (5)$$

reproduces our results very accurately, the average deviation corresponding to ±0.04 mm., which is well within the experimental error.

Thermochemical Calculations

Heat of Dissociation.—Representing by ΔH the heat absorbed in the dissociation of a mole of $(HOAc)_2$ into two moles of HOAc, we find from equation (4) for a temperature between 25 and 40°

$$\Delta H = 16{,}400 \text{ cal.} \qquad (6)$$

We judge that this value may be in error by as much as 800 cal.

Heat of Vaporization.—If we assume that the saturated vapor of acetic acid does not deviate much from an ideal gas, we can calculate the latent heat of vaporization of one mole (120 g.) of acid by means of the equation

$$L = -(1 + \alpha)R \frac{\mathrm{d} \log_e p_s}{\mathrm{d}(1/T)} \qquad (7)$$

In view of equation (5), we obtain

$$L = 10{,}060(1 + \alpha) \qquad (8)$$

Inserting in equation (2) the measured values of K_p and of p_s, we find for 25°, $\alpha = 0.093$; for 30°, $\alpha = 0.104$; for 35°, $\alpha = 0.112$ and for 40°, $\alpha = 0.121$. From equation (8) we obtain

L at 25° = 11,000 cal.
L at 30° = 11,110 cal.
L at 35° = 11,190 cal.
L at 40° = 11,270 cal.

Brown[7] obtained by direct measurement at 117.4° a value of 97.05 calories per gram, equivalent to 11,650 calories per 120 g. of the acid.

From Ramsay and Young's[8] measurements of the saturated vapor pressure, p_s, at 100, 110, 120 and 130°, we readily find for 118°, assuming the vapor to be ideal, $L = 9344\ (1 + \alpha)$. Combining this result with that of Brown we infer that at 118° and 1 atm. the value of $(1 + \alpha)$ is 1.247. On the other hand, the value of pV at 118° and 1 atm. obtained by Ramsay and Young[9] is about 0.319 liter-atm. per gram which leads to a value of $(1 + \alpha)$ equal to 1.194. The difference in the calculated values of $(1 + \alpha)$ is probably due to an appreciable departure from ideal behavior when the vapor is saturated.

Summary

1. Values of pV have been determined for the vapor of very pure acetic acid at 25, 30, 35 and 40° and at pressures as low as 3 mm.

2. The equilibrium constant for the reaction: $(HOAc)_2 \rightleftharpoons 2HOAc$, has been determined for 25, 30, 35 and 40°. The heat of dissociation is calculated to be about 16,400 cal.

3. The vapor pressure of acetic acid has been measured at 25, 30, 35 and 40°. The heat of vaporization per 120 g. of acid at these temperatures is calculated to be 11,000, 11,110, 11,190 and 11,270 cal.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 4, 1936

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[6] "International Critical Tables," Vol. III, p. 217.

[7] Brown, *J. Chem. Soc.*, **83**, 987 (1903).

[8] Landolt-Börnstein, "Tabellen," 1912, p. 388.

[9] "International Critical Tables," Vol. III, p. 437.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Use of Chromous Sulfate in the Removal of Oxygen from a Stream of Gas. A Comparison with Other Oxygen Absorbents

BY HOSMER W. STONE

The frequent need of a stream of inert gas of low oxygen content led the author to the observation that not only did the commercial nitrogen contain appreciable quantities of oxygen, but even the gas from the liquid carbon dioxide was contaminated. The usual methods of purifying the nitrogen proved unsatisfactory. This, together with the lack of data on the relative effectiveness of oxygen-absorbing reagents, led to the work reported in this paper.

A cylinder of commercial nitrogen, containing 0.3% oxygen, was chosen for reference. This gas was passed through the apparatus containing the absorbent to be tested, at a constant rate. The time which elapsed before sufficient oxygen escaped the absorbing reagent to color a very sensitive oxygen indicator has been taken as a measure of the effectiveness of that absorbent for removing oxygen from the stream of nitrogen. All of the reagents allowed detectable quantities of oxygen to pass, but in the case of the chromous solution the amount was so small that this reagent was selected as a standard for the comparison of the others. If the time required to color the indicator by the oxygen escaping the chromous sulfate absorbent is taken as 100%, then under the conditions used, none of the other reagents investigated exceeded 4% in their relative efficiency. The work deals with the relative rates of oxygen absorption and makes no attempt to compare the completeness of the reaction at equilibrium conditions.

Apparatus and Reagents

The illustration of the apparatus used requires some explanation. A single cylinder of commercial nitrogen, containing 0.3 volume percentage of oxygen, was used throughout the investigation. The flow of gas through the apparatus was maintained at a rate of 300 ml. per minute by the adjustment of a pressure reducing valve at the nitrogen cylinder. A pressure of about eight pounds per square inch (414 mm.) was required to produce the desired rate of gas flow. This rate refers to that which was measured on the flowmeter after the oxygen had been absorbed.

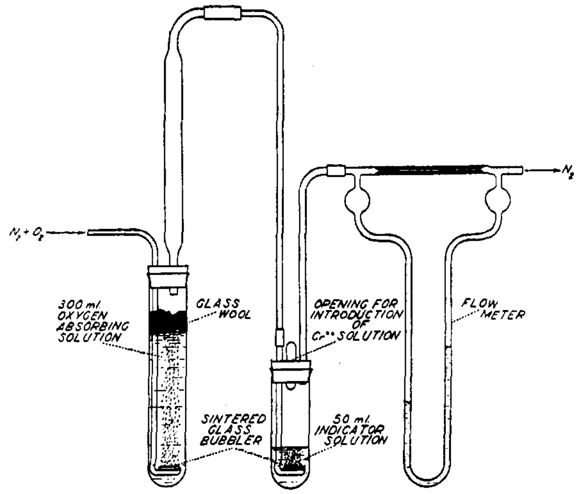

Fig. 1.—Apparatus for the determination of the efficiency of oxygen absorption.

The nitrogen entered the absorbing solution through a sintered glass bubbler. The bubbler, a product of the Jena Glass Works, catalog number 33cG4, was listed as having a pore size to from five to ten microns. The glass wool above the absorbing solution was introduced to overcome the troublesome foaming which occurred when the pyrogallate and the hyposulfite reagents were used as absorbents. The glass wool, together with the tower above it, prevented appreciable amounts of the absorbing solution from being carried into the indicator. The ammoniacal cuprous ammonium chloride reagent liberated so much ammonia gas that it was necessary to introduce a wash bottle containing 2 *N* sulfuric acid between the absorbing solution and the indicator when this reagent was used. When this was not done the basic effect of the ammonia changed the indicator from red to amber at a *p*H of from 6 to 7 and precipitated the hydroxides of the chromium ions.

The Jena glass bubbler in the indicator tube was listed as having pore sizes varying from 100 to 120 microns in diameter. A coarser pore size was used here than in the absorbing tube to reduce the amount of back pressure.

The indicator solution was 0.05 *M* in sulfuric acid and about 0.00025 *M* in the *o*-semidine indicator. The *o*-semidine used in the preparation of the indicator was *o*-amino-*m*-ethoxydiphenylamine and was prepared as described by Jacobsen.[1] A hydrochloric acid solution of this *o*-semidine[1] was oxidized by ferric chloride and the oxidation product recrystallized and thoroughly dried. A stock solution of this oxidation product dissolved in glacial acetic acid was used in making the indicator solution. The properties of this oxidation–reduction indicator were discussed by the author before the Division of Physical and Inorganic Chemistry at the 90th meeting of the American Chemical Society, San Francisco, California, August 19 to 23, 1935. This work has not yet been published.

The indicator was decolorized by the addition of 0.023 *N* chromous sulfate solution. (This chromous sulfate reducing reagent was used to decolorize the indicator in all of the experiments and should not be confused with the chromous reagent used as an oxygen absorbent.) At the end-point of the reaction in which the indicator was reduced by the chromous ion, one drop of the reducing reagent was sufficient to remove the last trace of indicator red and leave a slight excess of unoxidized chromous ion. This excess of chromous ion had to be oxidized by oxygen escaping the absorbing reagent before an indicator color change could appear.

The sensitivity of the indicator was determined by measuring the amount of distilled water, saturated with air, which was required to oxidize the slight excess of chromous ion at the end-point and to produce a distinct color change in the indicator. It required 0.2 ml. of this water which was 0.001 *N* in dissolved oxygen.

Procedure

The following method was used in testing each of the oxygen absorbing reagents. (1) 300 ml. of the reagent to be tested was placed in the absorbing tube. (2) The pressure of the nitrogen gas entering the apparatus was regulated to produce a flow of 300 ml. per minute as indicated on the flow meter. (3) After fifteen minutes of gas flow at this rate and with the gas still flowing the plug in the stopper of the indicator tube was removed and the indicator reduced by a dropwise addition of the 0.023 *N* chromous sulfate solution. Contamination by oxygen of the air during this operation was prevented by the gas which escaped from the opening.

(4) The opening in the stopper of the indicator tube was then closed and the gas allowed to flow through the system until the oxygen escaping the absorbing reagent was sufficient to produce a faint color change in the indicator. This first faint color change was the starting point in all of the runs at which the recorded number of

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[1] Paul Jacobsen, *Ann.*, **287**, 145 (1895); *ibid.*, **427**, 76 (1922).

drops of the reducing agent were added to the indicator solution. The desired number of drops of the 0.023 *N* chromous sulfate reagent were then added to the indicator and the time interval before the first faint color appeared in the indicator determined. From this observation, the time required to color the indicator, per drop of chromous reagent, was calculated.

(5) The indicator was again decolorized by the addition of a recorded number of drops of the chromous reducing agent and the time interval again determined. This operation was repeated until a nearly constant time interval was obtained. It usually required at least forty-five minutes of gas flow at 300 ml. per minute before this nearly constant value was reached. Up to this time, the intervals were shorter, due to the necessity of removing the air from the system. The data reported represent successive experiments on a single solution of the reagent, obtained after the nearly constant interval had been reached.

The potassium pyrogallate solution which was tested was prepared according to the specifications of Wolf and Krause,[2] who recommend a solution containing 18% potassium hydroxide, 15% pyrogallol and 67% water as absorbing oxygen most rapidly. The reagent containing 50% potassium hydroxide is the approved reagent for absorbing oxygen because it yields less carbon monoxide during its oxidation, even though it is slower in its absorption of oxygen.

The pyrogallate solutions gave trouble by foaming, by forming a precipitate in the glass filter plates, and by yielding a gaseous decomposition product which modified the indicator change. The foaming was overcome by the use of the glass wool. The clogging of the filter plate and the resulting diminution in the flow of gas was taken care of by increasing the nitrogen pressure. The undesirable effect of the decomposition gases on the indicator was minimized by using freshly prepared pyrogallate solution.

The interval of time required to bring back the color to the indicator was 0.30, 0.325, 0.325, 0.28, 0.33, 0.30, 0.28, 0.28 minute per drop of 0.023 *N* chromous sulfate solution. These values represent successive determinations on the same solution after the time interval had become nearly constant.

The oxygen-absorbing sodium hyposulfite reagent recommended by L. F. Fieser[3] consisted of 48 g. of sodium hyposulfite, 12 g. of β-anthraquinone–sodium sulfonate, 40 g. of sodium hydroxide and 300 ml. of water. He states that a train of three Friedrichs bottles containing this solution removed all traces of oxygen gas, even when the velocity was at its maximum. He also reported that, in a bubbling pipet, the absorption of oxygen by this reagent was more rapid than by the pyrogallate reagent.

This reagent, as the oxygen absorbent in a series of successive experiments on the same solution and using from six to fifteen drops of 0.023 *N* chromous reagent, showed the following time intervals in minutes per drop: 0.50, 0.50, 0.50 and 0.47.

The ammoniacal cuprous ammonium chloride reagent used to absorb the oxygen was prepared as directed by Badger.[4]

Five hundred ml. of 15 *N* ammonium hydroxide was mixed with an equal volume of ammonium chloride solution saturated at 23°. Sixty grams of copper ribbon (0.1 by 1 mm.) was immersed in the solution and air blown through the reagent until it became a dark blue in color. Nitrogen was then bubbled through the mixture for several hours so that much of the cupric ammonium complex was reduced to the cuprous form. This solution was siphoned into the absorption tube of the apparatus and the capacity of the absorbing reagent determined by titration against an acidified solution of potassium permanganate.

In experiments with this absorbent, the drops of 0.023 *N* chromous reagent added to the indicator solution varied from eleven to thirty. The minutes required to return the color to the indicator solution per drop of chromous reducing agent were 0.49, 0.36, 0.55, 0.57, 0.40, 0.55, 0.59. As in the other cases these data represent a series of successive experiments where the rate of nitrogen flow was 300 ml. per minute.

The chromous sulfate–sulfuric acid absorption solution was prepared in accordance with the recommendations of Stone and Beeson.[5] In this method the chromous sulfate is obtained by reducing a sulfuric acid solution of violet chrome alum with zinc amalgam in a Jones reductor.

Two series of determinations were made with this reagent in the absorbing tube. One series was carried out before any of the other reagents were tested and another series, with a fresh solution, after the other oxygen absorbents had been evaluated. The two series served as a check on the constancy of the technique used in conducting the experiments. The time interval required to color the indicator per drop of chromous reagent added was so long that only this one drop was used in these experiments. The series of experiments carried out before the other reagents were tested gave values of 13, 12, 12.5 minutes per drop of chromous to coloration of the indicator. The runs on the second solution, made after the other absorbents had been tested, gave 11.5, 13, 13.5, 14.25 minutes per drop.

The data obtained with the various reagents tested are summed up in the table.

A COMPARISON OF THE EFFICIENCIES OF VARIOUS OXYGEN ABSORBENTS, USING 300 ML. OF THE ABSORBING REAGENT, AND A RATE OF FLOW OF GAS OF 300 ML. PER MINUTE

Absorbent used	Normal capacity	Average drops of Cr^{++}	Average min. to coloration	Minutes per drop
Potassium pyrogallate	6.3	13.2	3.97	0.30
Quinone hyposulfite	4.8	10.2	5.0	.49
Cuprous chloride	1.2	19.3	9.39	.49
Chromous sulfate	0.4	1.0	12.82	12.82

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(2) Otto Wolf and Arthur Krause, *Arch. Warmenwirt*, **10**, 19–21 (1929).

(3) L. F. Fieser, THIS JOURNAL, **46**, 2639–2647 (1924).

(4) W. L. Badger, *Ind. Eng. Chem.*, **12**, 161–164 (1920).

(5) H. W. Stone and C. Beeson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 188–190 (1936).

The values under the heading "Normal Capacity" in the table present the maximum concentration in equivalents per liter with respect to the reaction with oxygen. For the pyrogallate solution, the normality is based on von Kovács-Zorkoczy's[6] statement as to the capacity of pyrogallol and the quantity of this reagent used. The concentration of the hyposulfite reagent is based on a determination of the purity of the reagent and the amount used. The ammoniacal cuprous ammonium chloride was titrated with permanganate before and after the data were taken and found to change from 1.16 to 0.98 *N*. The chromous sulfate value is based on the amount of chrome alum used in preparing the reagent, though titration before and after one series of runs showed a variation from 0.31 to 0.12 *N* during the experiment.

Discussion

A comparison of the values set forth in the last column of the table shows that, under these conditions, chromous sulfate is at least twenty-five times more rapid in absorbing oxygen than any of the other reagents used.

No difference was found between Fieser's reagent and the ammoniacal copper chloride. The difference between these reagents and the pyrogallate is sufficient to prove that pyrogallate solutions are slower in their absorption of oxygen. Moreover, this superiority of the hyposulfite reagent over the pyrogallate is in agreement with the work of Fieser which has been quoted previously.

No data are given concerning the precise changes in the concentrations of the absorbing agents during the time that their relative efficiencies were determined. This is because variations in the concentration were found to have no effect on the results within the limits of the experimental observations. 0.3 *N* chromous sulfate was no more effective in absorbing oxygen in the apparatus than a 0.1 *N* solution. In either case the reaction appeared to be as rapid as one between ions.

Experiments in this Laboratory[7] showed that the rate of absorption of oxygen by chromous sulfate solutions, in an apparatus such as Fieser used, is too rapid to be measured. The concentration of the chromous sulfate was varied from 0.4 to 0.01 *N* and the concentration of the sulfuric acid from 3.0 to 0.12 without obtaining any measurable change in rate of absorption.

Since each of the reagents used in a particular series of determinations yielded a nearly constant interval of time for coloring the indicator, rather than a decreasing interval, it is clear that the change in concentration of the reagent, due to oxygen absorbed, did not affect the data presented.

It is the writer's opinion that the rate of reaction of the dissolved oxygen with the absorbent is so much greater than the rate at which the oxygen is dissolved by the bubbling process that the former factor can be neglected entirely. This opinion leads one to conclude that the high relative efficiency of the chromous reagent, as compared to the other absorbents, may be at least partially explained by the fact that the physical properties of the chromous solution favor a more rapid solution of the oxygen in the chromous reagent than in the other solutions.

In addition to the advantage of absorbing the oxygen at a much faster rate than the other reagents, the chromous sulfate may be used to reduce the oxygen content of carbon dioxide and other acid gases which could not be treated by the reagents which are basic. The liberation of ammonia gas by the ammoniacal cuprous chloride, the clogging of the filter plate pores by the pyrogallate and hyposulfite reagents, the formation of a troublesome foam, and the evolution of gaseous decomposition products are disadvantages found in working with the other oxygen absorbents which were not met with when using the chromous sulfate.

The desirability of comparing the rates of oxygen absorption, by these reagents, over a wide range of conditions was recognized early in the work. Many experiments were conducted at widely varying rates of gas flow, with longer absorption columns, and with air in place of the commercial nitrogen. Though the results of these experiments indicated that relative rates similar to those reported in this paper held over a wide range of conditions, satisfactory comparisons were obtained only under the method and system described. Serious difficulties arising from fundamental differences in the properties of the absorption reagents and from the character of the indicator led to the abandonment of further attempts at quantitative comparisons.

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(6) Etelka von Kovács-Zorkoczy, *Biochem. Z.*, **162**, 161 (1925).

(7) Ramsey, King and Klain, unpublished work.

Summary

1. A new oxidation-reduction indicator has been shown to be a satisfactory reagent for the detection of small amounts of oxygen.

2. A method of comparing the rates at which various reagents absorb oxygen from a stream of nitrogen has been described.

3. Chromous sulfate–sulfuric acid solutions have been shown to absorb oxygen from a stream of nitrogen at an unusually high rate under certain conditions. Adopting the results obtained with chromous sulfate reagents, as a standard, the relative oxygen-absorption rates as found in this same apparatus under similar conditions may be expressed as follows: potassium pyrogallate 2.3%, ammoniacal cuprous ammonium chloride 4%, alkaline sodium hyposulfite β-anthraquinone-sodium sulfonate 4%, and chromous sulfate-sulfuric acid reagent 100%.

LOS ANGELES, CALIF. RECEIVED JULY 15, 1936

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF MARYLAND]

A Study of Promoter Action. The Oxidation of Aniline Sulfate by Hot, Concentrated Sulfuric Acid in the Presence of Copper and Mercury Sulfates[1]

BY M. M. HARING AND H. H. KAVELER

Oxidation by hot, concentrated sulfuric acid has many applications, of which one of the more important is the analytical method of Kjeldahl.[2] Numerous modifications of the method have been published, the use of copper and mercuric sulfate catalysts being emphasized. However, only Bredig and Brown[3,4] have made a study of the kinetics of the reaction and of the relation between catalytic effect and amount of the catalyst. They observed, among other things, that mixed copper and mercuric sulfates exhibited a catalytic effect greater than the additive value. However, they published only one set of data on mixed catalysts. It was the primary purpose of this investigation to study a wide range of catalyst ratios and total amounts.

Reagents.—Mercuric oxide was prepared by adding the calculated amount of sodium hydroxide to a solution of C. P. mercuric chloride heated to 70°. The precipitated red oxide was washed free of alkali and chlorides and dried at 100°.

Reagent copper sulfate pentahydrate was used without further purification.

The sulfuric acid used was reagent quality (sp. gr. 1.83–1.84) and was demonstrated to be free of the heavy metals.

The aniline sulfate was the purest obtainable. Analysis by the Kjeldahl method gave 9.77% nitrogen as against 9.86% theoretical.

Apparatus.—The apparatus used was similar to that described by Bredig and Brown.[3,4] The thermostat was modified to accord with modern practice. It maintained the experimental temperature of 275° to ± 0.1°. The reaction vessel and gas measuring apparatus are shown in Fig. 1, the volume of the reaction bulb being about 75 cc.

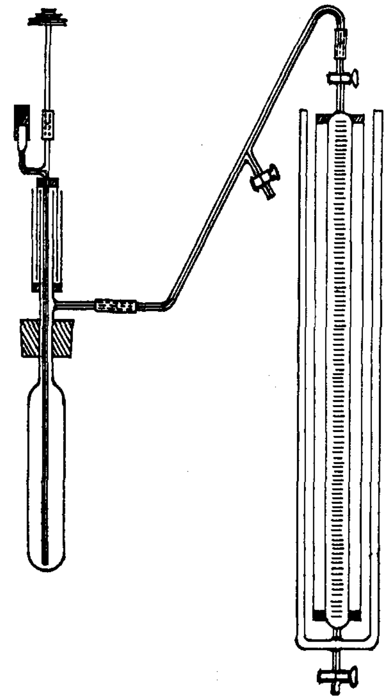

Fig. 1.

All weights and other measuring devices were checked for precision.

Procedure.—The desired quantity of the catalyst was introduced into the reaction flask through a long-stemmed funnel, followed by 50 cc. of sulfuric acid. After insertion in the bath, the mixture was stirred for one hour.

The stirring was stopped and the desired amount of a standard solution of aniline sulfate in sulfuric acid (about

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(1) Abstracted from a thesis submitted by H. H. Kaveler to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Kjeldahl, *Z. anal. Chem.*, **22**, 366 (1883).

(3) Brown, Dissertation, Heidelberg, 1903.

(4) Bredig and Brown, *Z. physik. Chem.*, **46**, 502 (1903).