PERMANGANATE DECOMPOSITION IN ALKALINE MEDIA[1]

BY R. H. FERGUSON, WM. LERCH AND J. E. DAY

The purpose of this investigation was (a) to measure the effect of hydroxyl-ion concentration and of temperature on the rate of the reaction

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^= + 2H_2O + O_2 \qquad (1)$$
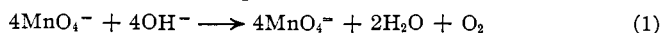
and (b) to study the possible reversibility of this reaction in the absence of extraneous materials other than the reaction medium (water).

One of the authors,[2] when oxidizing ethyl alcohol by potassium permanganate solutions containing potassium hydroxide, observed that the available oxygen values of the strongly alkaline permanganate solutions were measurably lessened if not used promptly. In 1917 Day prepared a solution containing 340.8 g. of stick caustic potash (purified over alcohol), 30.404 g. of potassium permanganate and one liter of water, and kept the mixture at room temperature. By the end of one year the available oxygen had dropped 25%; in four years, 50%; and in ten years, 53%. A portion of this final dark green solution was held at 95°, manganese dioxide appearing and the supernatant liquid becoming colorless in about six days. The potassium permanganate (available oxygen = 98.67% of the theoretical) had not been aged and freed of any probable dioxide.

Preparation of Materials

Unless otherwise stated all filtrations were made through asbestos fiber supported in a Büchner funnel. The fiber was purified by digestion with sodium hydroxide, then with hydrochloric acid, and the product well washed, suspended in dilute sulfuric acid, treated with potassium permanganate solution and finally washed until free from chloride and sulfate ion.

Potassium hydroxide, when prepared by Ruby's[3] method, reduced a permanganate solution, hence the solutions of the two alkalies (potassium and sodium) used in this investigation were obtained by metathesis from purified non-reducing saturated solutions of barium hydroxide and 2 N solutions of the corresponding alkali metal sulfate. After reaction the decanted solutions were freed of the last traces of barium sulfate by

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[2] See Evans and Day, THIS JOURNAL, **38**, 375 (1916); *ibid.*, **41**, 1267 (1919).

[3] Ruby, *ibid.*, **43**, 294 (1921).

filtration in a carbon dioxide-free atmosphere. These solutions were concentrated to approximately 13 N in large loosely covered glass pyrex beakers. The final product was further appropriately treated until it gave negative tests[4] for carbonate, chloride, barium and sulfate ions. Ten-cc. samples acidulated with sulfuric acid did not reduce one drop of 0.1 N potassium permanganate.

A slightly less than saturated solution of **potassium permanganate** was placed in a clear glass-stoppered bottle and aged in ordinary light for five months, then filtered six times, at two-day intervals, through specially prepared[5] asbestos wool. An ultramicroscopic examination of the final solution showed no evidence of colloidal manganese dioxide. The last filter was tested for the presence of manganese dioxide with negative results. The dioxide test was made by first carefully washing the undisturbed filter free from potassium permanganate and then determining the oxidation titer of the filter by the oxalic acid–permanganate method.

A **sodium permanganate** solution was prepared from Kahlbaum's best product in the same manner as was the potassium salt except that because of the relatively greater impureness of the sodium compound, it was allowed to age for a year with six periodic filtrations through asbestos. The sixth filter gave a negative test for manganese dioxide.

These two permanganate solutions were then standardized against sodium oxalate (Bureau of Standards) and kept in stoppered black-coated bottles. The molar concentration of the potassium permanganate solution was 0.1248, this value being an approximate mean of the concentration used in an acid medium in quantitative analysis and that in an alkaline medium in organic oxidation. Because of the reputedly poor keeping quality of sodium permanganate, its concentration was brought down to 0.0680 M.

Experimental

All reactions were carried out in flasks (Fig. 1) kept in a constant temperature bath. A is a pyrex Kjeldahl flask constricted at the top. The pyrex cup E is sealed into the rubber stopper B by means of plaster of Paris, C. The collection, in the cup, of condensed steam from the reaction mixture was practically avoided by keeping the cup nearly filled with mercury, D, when the inverted 30-cm. glass condenser was in position. Care was always exercised in preventing the mercury from getting into the flask contents. The condenser was equipped with a guard tube filled with soda lime and cotton. A strip of blotting paper fastened around the condenser just above the cup E prevented condensed water vapor from the thermostat from getting into the reaction mixture by the route of

Fig. 1.

the mercury seal when samples were withdrawn. The water-bath thermostat[6] was electrically heated and was controlled to within 0.1°.

In each reaction mixture the initial strength of the potassium permanganate was 0.156 mole and that of the sodium permanganate was 0.085 mole of available oxygen per liter. Two hundred cc. of the permanganate solution of the necessary concentration was placed in the reaction flask and a like volume of the alkali solution of the desired concentration in another flask. The two solutions were then brought to the desired
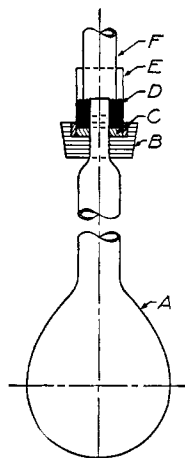
[4] Commonly accepted wet methods.

[5] Cheishvili, *J. Russ. Phys.-Chem. Soc.*, **42**, 856 (1911).

[6] Day and Ferguson, "A Constant Temperature Bath," This Laboratory, 1927, unpublished.

temperature and the alkali solution added to the permanganate solution at a sufficiently slow rate to avoid entirely the precipitation[7] of any of the permanganate. After vigorous shaking for several minutes the reaction mixture was placed in the thermostat and the flask-condenser connection made as in Fig. 1. The progress of each reaction was determined by periodically measuring the amount of available oxygen in a 10-cc. portion of the reaction mixture. The reaction in the sample was stopped by the addition to the sample of a measured quantity (65 cc. for the potassium and 35 cc. for the sodium series) of a sulfuric acid solution of standard oxalic acid and this then back-titrated for the oxygen titer with standard potassium permanganate. For the 75 and 95° series the sampling pipet was brought to about the temperature of the reaction mixture to avoid volume errors.

The identity of oxygen as an evolved product from the reaction mixtures was established by the glowing splint test and also by absorption in a hydrochloric acid solution of cuprous chloride.[8] Samples of the reaction mixture after the available oxygen titer became constant were examined under the ultramicroscope for colloidal manganese dioxide.

Results and Discussion

The use of a mechanical stirrer in the reaction apparatus, described above and partially shown in Fig. 1, added greatly to the tediousness of sample withdrawal. A modified form of this apparatus, consisting of an 18-cm. glass condenser sealed to a short-necked pyrex flask, was equipped with a mechanical stirrer. In Table I is shown the relative effect of slow (60 r. p. m.) stirring (Col. 1) and no stirring (Col. 2) upon the water medium

TABLE I

COMPARATIVE DATA

Time, hours	Available oxygen, mole per liter	
	Col. 1	Col. 2
0	0.156	0.156
12	.151	.152
48	.149	.149
96	.143	.145
144	.142	.143
192	.139	.142

reaction between 12.4 N potassium hydroxide and 0.634 N potassium permanganate at 50°. The velocity of the reaction was increased slightly but the extent was practically the same. Because of the difficulty in effecting condensation of the water with the 18-cm. condenser as well as the added manipulation in the removal of samples for analysis, the use of this apparatus was discontinued.

The effect of four concentrations of potassium hydroxide and of three temperatures on the conversion of potassium permanganate into a manganese compound, or compounds, of lower manganese valence is shown in Figs. 2, 3 and 4. The molar ratios (before mixing) of permanganate to alkali are approximately 1:45, 57, 76 and 99. The behavior of sodium

[7] Sackur and Taegener, Z. Elektrochem., 18, 718 (1912).

[8] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, 1922, p. 380.

permanganate in the presence of sodium hydroxide under conditions similar to those for the two potassium compounds is presented in Figs. 5,
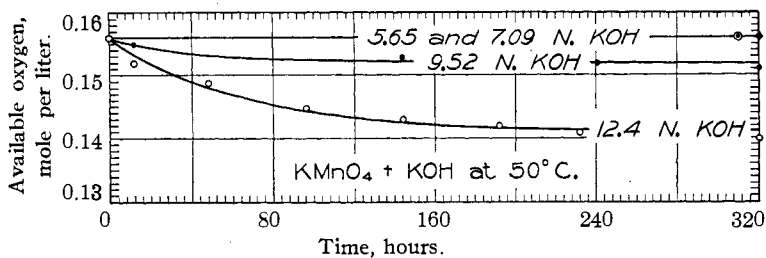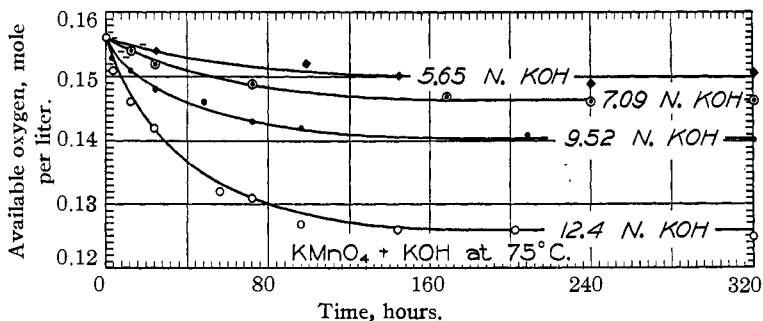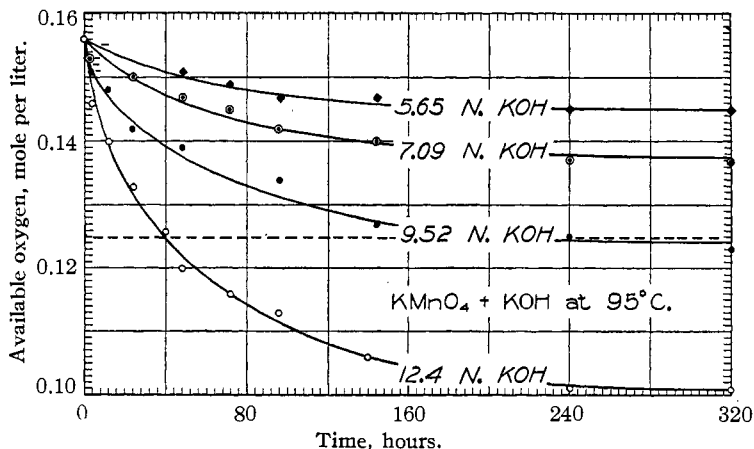

Fig. 2.

Fig. 3.

Fig. 4.

6 and 7.   In the case of this permanganate, and the corresponding hydroxide, the integral molar ratios are 1:46, 60, 97 and 169.   The available oxygen value is that calculated on the basis of normal solutions for oxidation–reduction in acid media.

Whether or not the dissolved glass from the extensive action of the strong alkali upon the reaction flasks at 95° may have influenced these reactions catalytically or otherwise was not studied.

Figures 2–7, inclusive, show that the extent of the loss of available oxygen is a function both of the concentration of the hydroxide and also
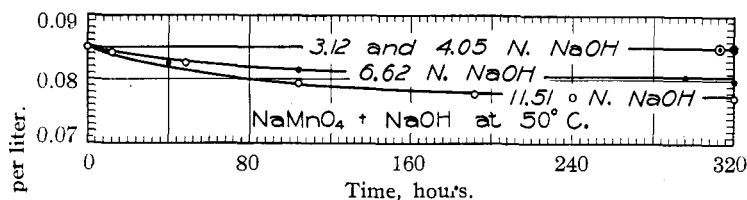

Fig. 5.
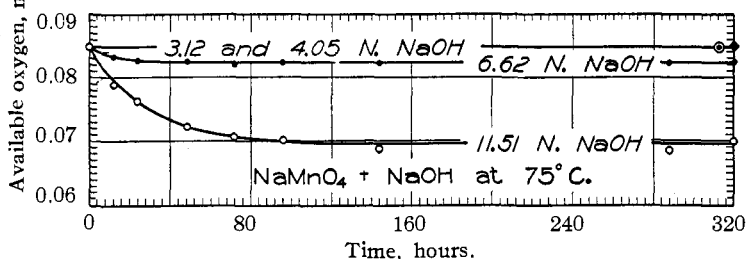
Fig. 6.
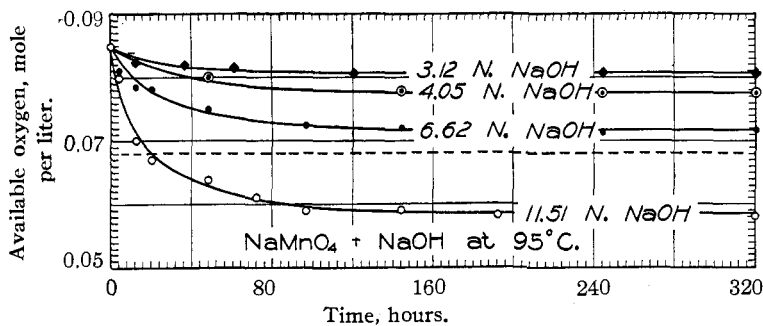
Fig. 7.

of the temperature. There is, for each temperature, a minimum concentration of alkali necessary for a depreciation of the available oxygen in the reaction mixture. This alkali value may be roughly estimated from Figs. 2, 5 and 6. For certain alkalinities, there was either no reaction or else it was not measurable by the method used. An experiment with potassium permanganate and 12.4 N potassium hydroxide at room temperature (about 30°) for 240 hours gave no measurable loss of available oxygen.

The color changes as identified by the naked eye in ordinary daylight through a north window for the potassium permanganate–potassium

hydroxide reactions are given in Table II. Aliquot portions of the final and also of several of the intermediate reaction mixtures of the 9.52

TABLE II
COLOR CHANGES

| Temp., °C.	Alkalinity			
	5.65 N	7.09 N	9.52 N	12.4 N
50	Purple	Purple	Almost black	Black
75	Purple	Darker purple	Green	Green
95	Darker but not green		Purple ⟶ black ⟶ green	

and 12.4 N potassium hydroxide series at 95° were filtered through asbestos and the filters examined for any precipitate with negative results. Under the ultramicroscope samples of the intermediates showed no suspension; samples of the finals, when cooled and exposed to the air, seemingly underwent some decomposition with the formation of a suspension, hence a positive decision was impossible. A second aliquot of each of these two final solutions when diluted (1–5) with water changed in color to a pink accompanied by residue formation presumably in accordance with

$$3MnO_4^= + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^- \quad [9] \qquad (2)$$
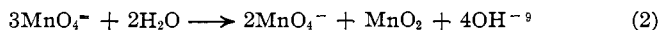
A third aliquot of the hot 12.4 N potassium hydroxide final mixture was heated with a concentrated solution of potassium hydroxide and rapidly cooled; a fourth portion was treated with the concentrated alkali and evaporated isothermally at 95°—neither procedure giving uniform results, even on repetition. In a few cases a crystalline product separated out from the cooled samples, whereas a mixture of manganese dioxide and a crystalline substance usually separated from the evaporated sample. The crystalline product from both procedures was of a dark green color and had the following crystallographic properties.

The crystals were imperfect rhombohedrons, pseudo hexagonal, striated vertically, almost opaque, showed no pleochroism and no color change under the Nicol prism of the polarizing microscope. They were always contaminated with manganese dioxide and alkali, and usually permanganate crystals could also be detected. Purification of them was difficult as a drop of water would give a dark green solution which upon dilution turned pink with the precipitation of manganese dioxide.

These crystallographic data show these crystals to be identical with potassium manganate.[10] Gorgeu[11] by a slightly different procedure obtained the double salt $KMnO_4 \cdot K_2MnO_4$ crystallizing in the monoclinic system. The above experimental data, however, warrant the conclusion that potassium manganate and not a double salt is the product of the reaction.

[9] Cf. (a) Dieffenbach, German Patent 195,523 (1867), and (b) Ruby, THIS JOURNAL, **43**, 294 (1921).

[10] (a) Mitscherlich, Pogg. Ann., **25**, 287 (1832); (b) Retgers, Z. physik. Chem., **8**, 6 (1891).

[11] Gorgeu, Compt. rend., **110**, 1134 (1890).

The color changes for the corresponding sodium permanganate–sodium hydroxide reactions are given in Table III.   Most of the efforts to obtain a crystalline product from the 6.62 and 11.51 N sodium hydroxide series at

TABLE III
COLOR CHANGES

Temp., °C.	Alkalinity			
	3.12 N	4.05 N	6.62 N	11.51 N
50	Purple	Purple	Dark purple	Greenish
75	Purple	Purple	Green	Greenish
95	Purple	Dark purple	Greenish	Green

95° were unsuccessful, as the crystals generally disappeared or decomposed in the course of their isolation and purification.   If a little water or dilute alkali was brought in contact with them a dark green mass resulted which upon being dried was found to be mainly manganese dioxide.   The few which were secured were so contaminated with alkali that it was impossible to purify them for crystallographic analysis.   Finally, by allowing a dark green reaction mixture to stand for twenty-four hours after treatment with concentrated sodium hydroxide, and then cooling somewhat, a good crop of well-formed dark green (almost black) crystals was obtained. A few of these upon treatment with a drop or two of water gave a dark green solution and on further dilution gradually turned pink.   The remainder was dried by a short contact with blotting paper and then over sulfuric acid, and examined under the polarizing microscope.

They consisted of orthorhombic prisms striated vertically with cleavage parallel to the side pinacoid and gave a very dark purple color upon fresh fracture which quickly tarnished to a brown.   The crystals rapidly decomposed in the air.   Their color was so dark that no interference figures were observable with polarized light.

These crystals may have been either sodium manganate or the hydrated form.[12]   The evidence favors some form of sodium manganate as a product of the reaction between sodium permanganate and sodium hydroxide.

At 95° with both the potassium and sodium series of reactions, a gas (identified as oxygen) was very slowly but visibly given off.   There was no *visible* gaseous evolution in the 50 and 75° series.

The available oxygen titer is a measure of either the permanganate or manganate ions, hence any intermediate titer does not give the measure of either ion when both are present.   Obviously then no conclusive calculations of the velocity constants are possible.   For indicative purposes only, the authors calculated the approximate velocity constants using the commonly accepted integrated equations for first- and second-order reactions and also the differential equation

$$-\frac{d(MnO_4^-)}{dt} = 4\frac{d(O_2)}{dt} = K_2(MnO_4^-)^2 \tag{3}$$

[12] Auger, *Compt. rend.*, **151**, 69 (1910).

for a second order reaction and found that these values favored a reaction of the second order with respect to MnO_4^-.

These approximate constants also tend to support the intermediate formation of an hydrated ion as indicated in the equation

$$MnO_4^- + 4OH^- \longrightarrow MnO_4^-·4OH^- \longrightarrow MnO_4^- + 2H_2O + O_2 \qquad (4)$$
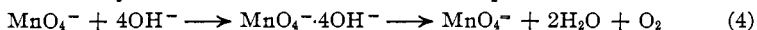
For example, in the 95° $KMnO_4$–KOH series, the constants (from the integrated bimolecular equation) for the alkalinities 5.65, 7.09, 9.52 and 12.4 N were substantially the same at 48, 96, 144 and 240 hours, respectively.

Jolles[13] prepared potassium manganate in accordance with Equation 1 and reported theoretical yields by using concentrated solutions of alkali and permanganate. Kassner and Keller[14] obtained a green solution but were unable to isolate any of the manganate. Without question, manganese dioxide is formed from the permanganate when reducing agents (particularly organic) are present. In the present investigation no microscopic evidence was found showing the formation of either precipitated or colloidal manganese dioxide. If it was a reaction product, it was present in less than colloidal dimensions or else was consumed in a subsequent or simultaneous reaction. Equation 1 then is substantiated in so far as the dioxide is concerned. Sackur and Taegener[15] found that Equation 1 was not reversed by the addition of atmospheric oxygen. No one has reported the study of the effect of atomic oxygen or ozone. If the non-reversibility of Equation 1 is accepted, then an equilibrium condition in the reactions reported herein cannot be considered. The method used by the authors in estimating the available oxygen is based on

$$4MnO_4^- + 12H^+ \longrightarrow 4Mn^{++} + 6H_2O + 5O_2 \qquad (5)$$
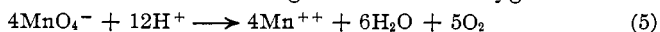
If the reaction indicated in Equation 1 proceeded to completion, only one-fifth of the total available oxygen in a reaction mixture would have been evolved. The initial titer of all of the potassium permanganate reaction mixtures was 0.156 mole of available oxygen. The maximum loss of available oxygen, then, on the basis of Equation 1, would be 0.0312 mole and the lowest possible solution titer would be 0.1248 (0.068, for the $NaMnO_4$ series) mole of oxygen. With the exception of the experiment involving the permanganate and 12.4 N hydroxide (see broken line in Fig. 4 and also Table IV) the oxygen titer in the potassium ion experiments was above 0.1248 mole. In this one exception the oxygen value did not become constant until it reached 0.101 mole or there was an oxygen loss of 35.2%, which is 15.2% more than is required by Equation 1. This extra loss might seem a substantiation of the equation

$$4MnO_4^- + 2H_2O \longrightarrow 4MnO_2 + 4OH^- + 3O_2 \qquad (6)$$
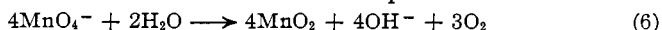
[13] Jolles, *Z. Naturw.*, [4] **5**, 423 (1886).

[14] Kassner and Keller, *Arch. Pharm.*, **239**, 473 (1901).

[15] Sackur and Taegener, *Z. Elektrochem.*, **18**, 718 (1912).

of Sackur and Taegener. Smith[16] assumed the formation of a peroxide from the oxygen which remained in solution. While this or a similar possibility has not been proved, an analogous compound $H_2O_2 \cdot K_2CrO_4$[17] has been isolated. Maksimov,[18] upon dissolving the potassium or sodium permanganate in solutions of their respective hydroxides, obtained the dioxide and oxygen and postulated the presence of the alkali peroxide in the resulting solution. As evolved oxygen was not detected in the reaction mixtures of lower alkalinity in this investigation, it is possible that a portion or all of the oxygen set free in the major reaction may have been consumed in the formation of an alkali peroxide. This, however, is not in harmony with our knowledge of the interactions of alkali peroxides and water. It is more likely that the oxygen was in solution for those reactions at the lower temperatures. For the $NaMnO_4$–$NaOH$ series of reactions the highest percentage loss of available oxygen for each of the temperatures (50, 75 and 95°) was 8.2, 17.6 and 23.5%, respectively.

One gram of manganese dioxide dried at 100° was added to a reaction flask containing 200 cc. of 12.4 N potassium hydroxide and 200 cc. of the potassium permanganate and the reaction allowed to proceed at 95°. The contrast in behavior between this mixture and another containing none of the dioxide is given in Table IV. At about seventy-two hours the reaction mixture turned brown in color and further analysis by the

TABLE IV

EXPERIMENTAL DATA

	Available oxygen, mole per liter	
Time, hours	No MnO_2	1 g. MnO_2 (hydrated)
0	0.156	0.156
4	.146	.137
24	.133	.128
48	.120	.109
72	.116	
140	.106	
240	.101	
320	.101	

procedure previously used became impossible. The manganese dioxide not only increased the speed of the reaction but also brought about complete decomposition. A second experiment in which was used manganese dioxide from another source gave widely different results, except that the rate of decomposition was not apparently changed for the first twenty-four hours, but at the end of this time the brown decomposition resulted as before. These observations with added manganese dioxide confirm

[16] Smith, *J. Soc. Chem. Ind.*, **6**, 260 (1887).

[17] Moissan, *Traité Chim. Min.*, **1**, 275 (1904).

[18] Maksimov, *J. Russ. Phys.-Chem. Soc.*, **57**, 357 (1925).

in a general way the work of Brand and Ramsbottom,[19] although these investigators do not mention total decomposition as having taken place. The previous history then of the dioxide is of importance in this reaction.

The oxides of manganese are good adsorbents of both alkali metal and hydroxyl ions. The gel form of manganese dioxide has been prepared, which suggests that the hydrated sol form may also exist. Hydrated ferric oxide sol is not visible under the ultramicroscope and this invisibility may also hold for the possible hydrated manganese dioxide sol. The dioxide may also have been present as a true solution in the highly alkaline media used in this investigation. The final conclusion is that neither the colloidal nor the precipitated form of manganese dioxide was a reaction product of the reactions recorded in Fig. 2 for the reasons that: (a) the oxygen loss ceased beyond a certain time; (b) manganate was present in the final solutions (see Tables II and III); and (c) added colloidal and precipitated manganese dioxide caused the complete disappearance of the permanganate and manganate from the reactions studied in this and other investigations.

Gorgeu[20] obtained the double salt $KMnO_4 \cdot K_2MnO_4$ [or $(K_{1.5}MnO_4)_2$] from an alkaline solution of the two salts, which was soluble in a 20% potassium hydroxide solution without decomposition. Potassium mangani-manganate having the formula $5K_2O \cdot Mn_5O_{13}$ [or $(K_2MnO_{3.6})_5$] and sodium mangani-manganate having the formula $4Na_2O \cdot Mn_2O_5$ [or $(Na_4MnO_{4.5})_2$], have been described by Sackur[21] and also by Auger.[22] Morawsky and Stingl[23] found potassium in combination with the hydrated oxide or oxides of manganese and assigned to this the formula $Mn_4KH_3O_{10}$ [or $(K_{0.25}MnO_{2.125})_8 \cdot (H_2O)_3$]. In view of the above facts it seems likely that a more or less continuous series of (a) double salts, or (b) double oxides of the alkali metal and manganese existed in the reaction mixtures described in this paper. The identification of the hydrated manganates and not other manganese compounds is still unexplained.

Manganese Dioxide.—The character of the manganese dioxide obtained and observed during these experiments is of interest. A suspension of manganese dioxide formed when a dark green reaction mixture, consisting probably of potassium permanganate, manganate, water and potassium hydroxide, was diluted. The color of this dioxide was almost jet black when wet, which slowly changed to a dark brown upon being washed and dried at 100°. The oxide obtained from different dilutions of the reaction mixture likewise varied in color—brownish-black to light

[19] Brand and Ramsbottom, *J. prakt. Chem.*, [2] **82**, 366 (1910).

[20] Gorgeu, *Compt. rend.*, **110**, 958 (1890).

[21] Sackur, *Ber.*, **43**, 381 and 448 (1910); *ibid.*, **44**, 777 (1911).

[22] Auger, *Compt. rend.*, **150**, 470 (1910); *ibid.*, **151**, 69 (1910).

[23] Morawsky and Stingl, *J. prakt. Chem.*, [2] **18**, 82–83 (1878).

brown—as did the samples obtained from the permanganates of sodium and potassium. One of the authors[24] observed this same sort of color variation when working with alkaline permanganate solutions in the presence of organic reducing agents.

When a 400-cc. dark green alkaline reaction mixture of sodium permanganate and sodium hydroxide was diluted with 100 cc. of distilled water and evaporated over an open flame, a point was reached where a jelly-like precipitate of manganese dioxide was formed. This form and its conversion into a hydro-sol has been described by Witzemann.[25] His procedure for obtaining it varied from the above in that he reduced an alkaline permanganate solution with glucose and other organic material. The jelly obtained in the present investigation when diluted with water and dried at 100° formed a hard wax-like cake, which had a resinous luster upon fresh fracture. Inorganic jellies of this type have been described by Weiser[26] in a comprehensive review, but no mention is made of the jelly form of manganese dioxide. This jelly was quite stable in alkaline solution, but upon dilution changed into the suspensoid form.

Summary

1. Aqueous solutions of potassium and sodium hydroxides were prepared which when acidified with sulfuric acid did not reduce a dilute solution of potassium permanganate.

2. Aqueous solutions of potassium and sodium permanganate were prepared which were free from both precipitate and colloidal-size particles of the oxides of manganese.

3. Studies of the reactions between these permanganates and their corresponding hydroxides at 50, 75 and 95° show that (a) the reactions are very slow; (b) an increase in temperature increases the speed of the reactions with progressive lowering of the available oxygen; (c) beyond a certain minimal concentration of alkali an increase in the alkalinity progressively lowers the available oxygen to constancy with time; (d) potassium manganate and oxygen and sodium manganate and oxygen were isolated and identified as reaction products in their respective reaction series; (e) manganese dioxide either in precipitated or colloidal state was not isolated or identified in these reactions: (f) both series of reactions are probably bimolecular and the equation

$$4MnO_4^- + 4OH^- \longrightarrow 4MnO_4^- + 2H_2O + O_2$$
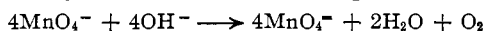
satisfactorily accounts for the reactions at 50 and 75° but not at 95°; (g) at 95° the reaction mixtures for both the Na^+ and K^+ series lost more

[24] J. E. Day, "Dissertation," The Ohio State University, 1919.

[25] Witzemann, THIS JOURNAL, 37, 1079 (1915).

[26] Weiser, "Colloid Symposium Monograph," University of Wisconsin, pp. 38–62 (1923).

available oxygen than is demanded by the equation in (f); and (h) the results obtained are best explained on the assumption that a continuous series of double salts of manganese or double oxides of the alkali metal and manganese were formed in the strongly alkaline solutions.

4.   The initial presence of precipitated manganese dioxide in a reaction mixture brings about an ultimate decomposition of the permanganate to the dioxide in a relatively short time when compared with the time for the reactions summarized in 3 (a).

5.   Slow stirring of a reaction mixture increases the speed slightly without appreciably influencing the point of apparent rest in the reaction.

6.   A new method for the preparation of manganese dioxide gel is described.

COLUMBUS, OHIO

THE ELECTROMOTIVE ACTIVATION OF OXYGEN

BY ARTHUR B. LAMB AND LUCIUS W. ELDER, JR.

The achievement of a fuel cell, in which the free energy of combination of hydrogen or some comparable gaseous fuel with oxygen is converted directly into electric energy, has encountered its most serious difficulties at the oxygen electrode.   Gaseous oxygen establishes its potential sluggishly and imperfectly on inert electrodes at ordinary temperatures, even on open circuit, and an oxygen electrode on closed circuit polarizes at once if any appreciable current is withdrawn.

These difficulties have been overcome to some extent by operating the electrodes in suitable electrolytes at elevated temperatures.[1]   Similarly progress has been made in the electromotive activation of oxygen by the use of catalysts.   These catalysts have been of two types.   In the one type, the catalytic action is confined to the surface of the electrode, the catalyst being either a part of the electrode itself or a reaction product formed upon its surface, which enhances the electromotive activity of the gaseous oxygen.   Electrodes where catalysts of this type are effective are the familiar platinized platinum and similar electrodes, and the electrode of copper immersed in a solution of potassium hydroxide described by K. A. Hofmann.[2]   In the second type the catalytic action takes place throughout the bulk of the electrolyte.   This type of catalyst must be susceptible of rapid oxidation by gaseous oxygen under the conditions in the cell, and its oxidation product must be a rapid depolarizer.

[1] Haber and Bruner, Z. Elektrochem., 10, 712 (1904); Taitelbaum, ibid., 16, 286 (1910); Baur, Treadwell and Trümpler, ibid., 27, 199 (1921); Helv. Chim. Acta, 4, 325 (1921); Rideal and Evans, Trans. Faraday Soc., 17, 466 (1921).

[2] Hofmann, Ber., 51, 1526 (1918); 52, 1185 (1919); 53, 914 (1920).