ity, is less than in the nitrogen pentoxide experiments, it will be sufficient to show that for nitrogen pentoxide the energy used in communicating velocity is only a small fraction of that used in overcoming viscous resistance. If the pressure at the low pressure end be taken as 0.1 mm., the velocity will be such as to use up less than 0.3% of the 51-mm. pressure drop. This figure is an upper limit to this error.

Conclusions

An experimental arrangement for measuring viscosities of corrosive gases is described.

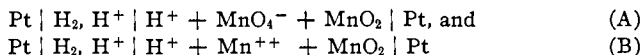The molecular diameter of nitrogen pentoxide is found to be 8.53×10^{-8} cm.

OXIDATION–REDUCTION POTENTIALS. II. THE MANGANESE DIOXIDE ELECTRODES

BY STEPHEN POPOFF, J. A. RIDDICK AND W. W. BECKER

The standard oxidation–reduction potential of the permanganate–hydrogen–manganous ion electrode is of considerable importance both from the point of view of reliable electromotive force constants and from its use in making suitable predictions. Since it is not possible to measure directly the foregoing potential, one must resort to calculations involving electromotive force measurements of the cells

$$\text{Pt} \mid \text{H}_2, \text{H}^+ \mid \text{H}^+ + \text{MnO}_4^- + \text{MnO}_2 \mid \text{Pt, and} \qquad \text{(A)}$$
$$\text{Pt} \mid \text{H}_2, \text{H}^+ \mid \text{H}^+ + \text{Mn}^{++} + \text{MnO}_2 \mid \text{Pt} \qquad \text{(B)}$$

If E_A and E_B represent the standard oxidation–reduction potentials of Cells A and B, respectively, then the standard oxidation–reduction potential (E_C) of the cell

$$\text{Pt} \mid \text{H}_2, \text{H}^+ \mid \text{H}^+ + \text{Mn}^{++} + \text{MnO}_4^- \mid \text{Pt} \qquad \text{(C)}$$

can be calculated from the equation $(3E_A + 2E_B)/5 = E_C$. This calculation was made using the value of E_A obtained by Brown and Tefft,[1] and the value of E_B obtained by Tower.[2] It was noted, however, that Brown and Tefft employed chemically prepared manganese dioxide which analyzed over 99%, while Tower employed electrolytically prepared manganese dioxide whose analysis was not given. It was further observed that the potentials with electrolytic manganese dioxide varied according to the current density employed in its preparation and that the values in the literature for the potential of the manganese dioxide–permanganate electrode differed by more than 0.1 volt.

[1] Brown and Tefft, THIS JOURNAL, **48**, 1128 (1926).

[2] Tower, Z. physik. Chem., **32**, 566 (1900).

It was therefore deemed necessary to determine the potentials of the cells A and B employing the same kind of manganese dioxide and making a critical analysis of all the constituents entering into the reactions.   As a result of this study one is led to conclude that cells involving the use of chemically pure manganese dioxide render themselves incapable of recording accurate electromotive forces because manganese dioxide reduces the permanganate ions, and the electrodes are irreversible in the presence of manganous and hydrogen ions.   The foregoing conclusion becomes almost inevitable when one considers that the materials employed were purified using "atomic weight" technique and that two entirely different methods of analysis were resorted to in the analysis of the important constituents.

Experimental

A. Preparation of Materials

1. **Potassium permanganate** was twice recrystallized from the best quality salt and a solution of the salt was made in redistilled water. After standing for several weeks the clear solution was siphoned off and kept in a bottle painted with black auto enamel.

2. **Water** employed in this investigation was redistilled from alkaline permanganate solution.

3. **Manganese Dioxide.**—Two kinds of manganese dioxide were prepared. One is called chemical, the other electrolytic, for the sake of differentiation.

a. **Chemical.**—Brown and Tefft[1] prepared manganese dioxide by heating manganese nitrate at 160°. They state that their product was over 99% pure but they give no explanation as to the composition of the remaining one per cent. Several attempts to make pure manganese dioxide were made before arriving at the following procedure. Manganous nitrate was prepared by a method similar to that used by Baxter and Hines[3] to prepare manganous bromide for use in the atomic weight of manganese. The manganous nitrate solution was evaporated until a considerable amount of a pasty mass of manganese dioxide had separated out, then poured into a large volume of cold water. The product thus obtained was very finely divided. After suitable washing, the manganese dioxide was dried, ground and then heated about a dozen times with concentrated nitric acid, each treatment being followed by heating to 160°. The product was also ground several times together with dilute nitric acid and the resulting solution decanted. The final product was heated for twenty-four hours at 160°. Analysis gave 99.62% of manganese dioxide and 0.41% of water.

b. **Electrolytic.**—Most of the literature on the electrolytic deposition of manganese dioxide deals with attempts to deposit manganese quantitatively from solution; no attempts have been made to deposit pure manganese dioxide. The adhering deposit was usually ignited to Mn_3O_4 and weighed as such; all investigators found that the product deposited does not have the formula MnO_2 In this investigation a platinum dish (100 cc.) and disk (5 cm. in diameter) served as the cathode and anode, respectively. The current density, temperature and the concentration of nitric acid were varied.   The highest percentage of manganese dioxide found by the electrolytic method was about 92%, the rest being water and lower oxide of manganese.   The analysis was made after the product of electrolysis was washed, dried at 160°, ground and again heated to 160° for one hour.

[3] Baxter and Hines, THIS JOURNAL, **28,** 1560 (1906).

4. **Perchloric Acid.**—G. Frederick Smith's 72% perchloric acid was redistilled under reduced pressure in an all-glass distillation apparatus, rejecting the first and the last quarter portion. From the redistilled portions the dilute acids were prepared.

5. **Manganous perchlorate** was prepared by a method similar to that used in the preparation of manganous nitrate.

B. Apparatus

The electrode vessels, the potentiometric equipment, etc., employed were those used in an earlier investigation by Popoff and Kunz.[4] About 2 g. of manganese dioxide was placed in chamber A. This was sufficient partly to cover the platinum foil.

C. Analytical Methods

1. **The potassium permanganate** solutions were standardized against Bureau of Standards sodium oxalate using McBride's[5] conditions but employing weight burets and electrometric methods of obtaining the end-points.

2. **Perchloric acid** was standardized against a sodium hydroxide solution (free from carbonates) which had been in turn standardized against constant-boiling hydrochloric acid and benzoic acid. The maximum deviations were never more than 0.05%. The total acidity of the permanganate solutions as well as that of the standard acids was checked employing the electrometric method described by Popoff and McHenry.[6]

3. **The water** content of the manganese dioxide was determined by heating the products in a fused silica combustion tube to 900° in a current of dry oxygen and absorbing the water in a suitable bottle containing dehydrite.

4. **The manganese dioxide** was analyzed by the following methods.

a. **The ferrous sulfate method** consisted in adding an excess of the acidified reagent to the manganese dioxide, heating until all of the manganese dioxide had dissolved and then titrating the excess with standard permanganate solution. This method was found convenient for determining the oxidizing power of the electrolytic but not of the chemically prepared manganese dioxide. The latter required heating from thirty to forty-five minutes near the boiling point in order to accomplish the complete reduction. Duplicates failed to agree either among themselves or against the sodium oxalate method when employing the chemical manganese dioxide. Good agreements, however, were found when employing the electrolytic manganese dioxide.

b. **The sodium oxalate** method consisted in adding an excess of sodium oxalate to 50 cc. of 9 N sulfuric acid containing about 0.1 g. of manganese dioxide. then keeping the solution at about 90° (for about five minutes) until reduction was complete. Finally, after diluting to 250 cc., the excess sodium oxalate was titrated with standard permanganate solution. In the actual analysis it was deemed necessary to employ about 0.5 g. of manganese dioxide and after suitable dilution to titrate an aliquot portion. A sample of Bureau of Standards pyrolusite containing an oxidizing equivalent of 87.53% in terms of MnO_2 was found by the foregoing method to be 87.74%. Considering that the sample contained iron, copper and about 5% of insoluble matter, which were not removed, the sodium oxalate method gave good results.

c. **The Pyrophosphate Method.**—The dioxide was dissolved in hydrochloric acid, the solution was heated to the boiling point, then about 2 g. of monoammonium phosphate were added, followed by freshly distilled ammonia until the solution smelled of ammonia. The solution was continually stirred until the precipitate had been converted to the silky form. This was followed by digestion for about two hours. After cooling, the

[4] Popoff and Kunz, THIS JOURNAL, **51**, 382 (1929).

[5] McBride, *ibid.*, **34**, 393 (1912).

[6] Popoff and McHenry, *Ind. Eng. Chem.*, **20**, 534 (1928).

precipitate was filtered, washed with water and finally heated at about 800° to constant weight. The filtrate was evaporated to a small volume and the manganese was determined colorimetrically after oxidation to permanganate by potassium periodate, following the usual procedure. By this latter procedure a correction was made for the solubility of the manganese ammonium phosphate—thus rendering the method precise and accurate.

The effect of varying the current density and the concentration of nitric acid in the electrolytic method of preparing manganese dioxide is seen from the results given in Table I.

TABLE I

ANALYSIS OF ELECTROLYTIC MANGANESE DIOXIDE

HNO$_3$ added, cc.	MnO$_2$, %		H$_2$O, %	Lower oxides, %	CD$_{100}$	Method of analysis
2	91.49	91.34	5.29	3.30	0.05	Ferrous iron
2	90.85	90.87	5.07	4.08	.03	Ferrous iron
2	90.57	90.79	5.03	4.29	.10	Ferrous iron
5	91.57	91.67	5.00	3.38	.05	Sodium oxalate
10	90.00	89.98	4.72	5.28	.05	Sodium oxalate

The effect of increased temperature, different acids added, such as formic, perchloric, gave manganese dioxide differing in oxidizing power but slightly from the foregoing. Table II gives the comparison as well as the results of analyses of the different kinds of manganese dioxide by two entirely different methods.

TABLE II

ANALYSES OF MANGANESE DIOXIDE BY DIFFERENT METHODS

Kind of MnO$_2$	MnO$_2$ from oxalate, %	MnO$_2$ from Mn$_2$P$_2$O$_7$, %	H$_2$O, %	Total From oxal.	From Mn$_2$P$_2$O$_7$
Commercial	89.55	95.60	..	...	....
	89.73	95.80			
Electrolytic	91.57	97.18	5.00	96.57	102.18
	91.67	97.49	5.00	96.67	102.49
Chemical	99.62	99.59	0.41	100.03	100.00

It is believed that there are no lower oxides of manganese present in our chemically prepared manganese dioxide, as the percentages of manganese dioxide found by two entirely different methods are in excellent agreement.

5. The manganous perchlorate solutions were analyzed by the pyrophosphate method given under manganese dioxide. The mean error was of the order of 0.03%.

D. The Instability of Potassium Permanganate Solutions

The instability of potassium permanganate in perchloric acid solutions in the presence and absence of manganese dioxide is a very significant and important factor in this investigation. It is very evident from Table III that permanganate solutions are decomposed by comparatively dilute perchloric acid solutions either in the presence or absence of pure manganese

dioxide. In the presence of the electrolytic manganese dioxide, a 0.00237 M potassium permanganate solution in 0.025 M perchloric acid became practically colorless in about three days. It is significant to note that a solution (No. 4) identical with the one employed by Brown and Tefft was found to have undergone considerable decomposition, although it gave almost an identical value for the electromotive force of the cell. A solution (No. 5) identical with No. 4 was prepared, sealed in a glass vessel and kept in the constant temperature bath for seven days. This solution also underwent decomposition, thus proving that outside contamination was not responsible for the decomposition.

The instability of potassium permanganate solutions in the presence of sulfuric acid is of about the same order as that found in perchloric acid.

TABLE III

INSTABILITY OF POTASSIUM PERMANGANATE SOLUTIONS

No.	Acid and concn.	Concn. $KMnO_4$ found, per g. of soln.	Loss, mg.	No. of days	
		0.001587	0.022	0	
1	0.5M HClO$_4$	.001575	.034	1	
		.001556	.053	2	
		.001526	.083	3	
		.04938		0	
2	0.025 M HClO$_4$	.04929	.09	1	
		.04923	.15	2	
		.04919	.19	3	
3	0.025 M HClO$_4$ with MnO$_2$, Series I, Cell 1	.001556 .001497	.059	0 8	
4	0.025M HClO$_4$ with MnO$_2$, Series IV, Cell 2	.0003683 .0003342	.034	2	Brown–Tefft soln.
5	0.025M HClO$_4$ with MnO$_2$, sealed	.0003683 .0003162	.052	7	

E.   Electromotive Force Measurements

Electromotive force measurements were made of Cells A and B under varying conditions. It is evident that it is next to impossible to obtain accurate electromotive force data from Cells A (Series I–IV) because of the instability of the potassium permanganate solution. It is interesting to note that the cells in Series IV gave 1.4972 and 1.4977 volts as compared to 1.4975 obtained by Brown and Tefft. These authors state that "the potential of a newly prepared manganese dioxide electrode, when first filled with perchloric acid–permanganate mixture rose at first, then declined, approaching a limiting value after several weeks. According to analysis, this drop in potential was not due to the decomposition of the potassium permanganate." It is significant to note further that Inglis,[7] who employed electrolytic manganese dioxide, states that the coating on

[7] Inglis, Z. Elektrochem., 9, 222 (1903).

the electrode must be very thin in order to obtain reproducible results. The solubility of the electrolytic manganese dioxide is much greater than that of the chemically pure manganese dioxide.   It is doubtful whether or not the solution was saturated with the manganese dioxide when the electrolytic manganese dioxide was employed by former investigators.

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS

Series I, $KMnO_4$, 0.01 M; $HClO_4$, 0.0250 M.   Chemical MnO_2, 99.6%

Time	Volts Cell 1	Cell 2	Remarks
9:00 A.M.	1.5162	1.5141	Plain platinum electrodes in graded seal glass
2:00 P.M.	1.5165	1.5140	
6:00 P.M.	1.5166	1.5141	
10:00 A.M.	1.5175	1.5141	
2:00 P.M.	1.5176	1.5143	
9:00 A.M.	1.5041	1.5000	New electrodes of plain platinum foil, sealed in lead glass
3:00 P.M.	1.5031	1.5038	
10:00 A.M.	....	1.5075	
1:30 P.M.	....	1.5078	
10:00 A.M.	....	1.5096	
3:00 P.M.	....	1.5098	

$KMnO_4$ solution changed from 0.001556 to 0.001497 in eight days.

Series II. Same as Series I, except MnO_2 (chemical) on Pt electrodes

Time	Volts Cell 1	Cell 2	Remarks
10:00 A.M.	1.5029	1.5002	
1:00 P.M.	1.5000	1.5001	MnO_2 electrodes interchanged
7:00 P.M.	1.4979	1.5001	
9:30 A.M.	1.4966	1.4980	
11:30 A.M.	1.4968	1.4986	
4:30 P.M.	1.4968	1.4986	
10:00 A.M.	1.4951	1.4973	E. m. f. lower than in Series I and continually decreasing
1:00 P.M.	1.4951	1.4975	
7:00 P.M.	1.4963	1.4983	
9:00 A.M.	1.4936	1.4959	
1:00 A.M.	1.4938	1.4959	
7:00 P.M.	1.4932	1.4952	

Series III. $KMnO_4$, 0.00237 M; $HClO_4$, 0.025 M; Electrolytic MnO_2

Time	Volts Cell 1	Remarks
10:00 A.M.	1.4735	
1:00 P.M.	1.4747	
7:00 P.M.	1.4737	
7:00 P.M.	1.4569	Three-day interval; the solution became almost colorless
8:00 P.M.	1.4567	
4:00 P.M.	1.4533	
5:00 P.M.	1.4522	

TABLE IV	(*Concluded*)

Series IV.	Same as Series III except Chemical MnO_2, 99.6%

Time	Cell 1	Cell 2	Remarks
7:00 P. M.	1.5068	1.5071	
11:30 A. M.	1.5077	1.5107	
4:00 P. M.	1.5075	1.5089	
8:00 P. M.	1.4815	1.4770	Electrodes cleaned with H_2O_2–H_2SO_4 mixture
10:00 A. M.	1.4896	1.4882	
1:30 P. M.	1.4910	1.4886	
9:00 A. M.	1.4956	1.4949	
1:00 P. M.	1.4966	1.4967	Solution changed (Cell 2) from 0.0003683 to 0.0003342
4:00 P. M.	1.4970	1.4965	
7:00 P. M.	1.4972	1.4977	

Brown and Tefft found 1.4975.

Series V.	$Mn(ClO_4)_2$ in $HClO_4$ soln.	Chemical MnO_2, 97.8%, prepared by the usual method

Date	Time	E. m. f.
1/6	8:34 P. M.	1.1890
	9:10	.8955
1/7	9:15 A. M.	.8845
	11:35	.9219
	7:03 P. M.	.9258
1/9	8:30 A. M.	.9250
	10:20	.9256
	1:20 P. M.	.9252

Series VI.	$Mn(ClO_4)_2$ in $HClO_4$ soln.	Chemical MnO_2, 99.6%

Date	Time	E. m. f.	Remarks
9/1	7:45 P. M.	0.72005	
	7:49	.71563	
	7:54	.71701	
9/3	7:02 P. M.	.66450	
	7:35	.64057	Stirred
	9:05	.63316	
	11:00	.63511	Stirred
9/9	2:55 P. M.	.62416	Stirred
	4:00	.62409	Stirred
	5:18	.63336	
9/10	2:45 P. M.	.69062	Stirred by motor
	4:30	.75642	Stirred by motor
	4:40	.73809	
	4:55	.70818	

Series V and VI give the electromotive forces obtained employing Cell B. When manganese dioxide (97.8%), prepared by the usual method, and containing lower oxides, was used (Series V), a steady potential was obtained in about two days. However, with the pure (99.6%) manganese dioxide the potentials were unsteady and subject to change without any notice.

After presenting this article for publication, opportunity was given to look over and examine the article of Brown and Liebhafsky.[8]   The main argument is the preparation and analysis of the manganese dioxide.   We were not able to prepare pure manganese dioxide until the pasty mass was dropped into cold water, this procedure giving a crystalline product. Two entirely different and specifically stated methods of analysis showed that the manganese dioxide prepared did not contain lower oxides of manganese than that corresponding to MnO_2.   The foregoing authors do not give any details of their method of analysis.   Without modification of the method of the preparation of the manganese dioxide, the product gave a steady potential in a few days as shown in Table IV, Series V.   In Table IV, Series VI, it has been shown that pure manganese dioxide does not give steady potentials even if the electrode solution is stirred and left to stand for a period of nine days.   If one employs the values of E_A and E_B, and calculates E_C, one obtains a value of -1.48 volts.   Brown and Liebhafsky report a value of -1.446 using the new value of E_B rather than that obtained by Tower.   One would expect a much larger difference and in the opposite direction in the calculated values, since Tower used electrolytic manganese dioxide, which everyone admits contains lower oxides of manganese.

It is significant to note that, in general, serious polarization[9] may be expected to take place at electrodes which involve reactions that take place with a change in the oxygen content.   All of the electrode potentials E_A, E_B and E_C certainly involve a change in the oxygen content and therefore one must resort to other means than electromotive force measurements of determining these electrode potentials.

Summary and Conclusions

1.   Pure manganese dioxide (99.6%, rest water) was prepared and analyzed by two entirely different methods.

2.   It was not possible to prepare electrolytically manganese dioxide which did not contain lower oxides of manganese.

3.   Solutions of potassium permanganate containing perchloric acid were found to be unstable either in the presence or absence of manganese dioxide.

4.   Due to the foregoing instability, it was found impossible to measure the potential of the permanganate–hydrogen–manganese dioxide electrode.

5.   When pure manganese dioxide was employed in the manganese dioxide–hydrogen–manganous electrode, the electrode was found to be irreversible.

   [8] Brown and Liebhafsky, THIS JOURNAL, 52, 2595 (1930).
   [9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co. Inc., New York, 1923, p. 388.

6.   It is evident then that the potential of the permanganate–hydrogen–manganous electrode cannot be calculated from the potentials of the manganese dioxide electrodes.

7.   Since the manganese dioxide electrodes involve reactions in which there are changes in the oxygen contents, one would expect polarization to take place at the electrodes.

8.   Specific directions are given for the precise determination of manganese gravimetrically.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

TRANSFERENCE PHENOMENA AND THE EXISTENCE OF COMPLEX IONS AS INTERPRETED BY THEIR MAGNETO-CHEMICAL BEHAVIOR

BY SIMON FREED AND CHARLES KASPER

For our purpose we shall define a molecule as an entity consisting of atoms which are held together by chemical bonds.   By a chemical bond we shall mean a coupling of the spin magnetic moments of a pair of equivalent electrons[1] which are held in common by two atoms.   Sodium chloride, from this point of view, does not consist of molecules in the crystalline state but of sodium ions and chloride ions.   On the other hand, mercuric chloride consists mostly of molecules in both the crystalline state and in solution.   Hydrogen consists of molecules in the gaseous state and in the liquid.[2]

We shall extend this definition to a molecular ion.   It is an ion whose atomic constituents are coupled by means of chemical bonds.   We shall identify complex ions with molecular ions.

Let us consider the familiar example of the ferricyanide ion.   Ferric ion in solution is strongly paramagnetic with a molal susceptibility which corresponds to five Bohr magnetons, that is, it appears to have five unbalanced electrons.   If we add cyanide ion to it there is an immediate drop in its magnetic susceptibility and the resulting ferricyanide ion possesses a susceptibility corresponding to about one Bohr magneton.   The magnetic moments of unbalanced electrons have been neutralized.   It is natural to conclude that a number of chemical bonds have been created, that is, that a true complex (molecular) ion has been formed.   It has long been recog-

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[1] Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1923; Heitler and London, Z. Physik, 44, 455–472 (1927); Heitler, ibid., 47, 835–858 (1928); London, ibid., 46, 455–477 (1928); Naturwiss., 16, 58–59 (1928).

[2] McLennan and McLeod, Nature, 123, 160 (1929).