MANGANESE COMPOUNDS

1. Introduction

Manganese is the twelfth most abundant element in the earth's crust and is the fourth most used metal following iron, aluminum, and copper (see also MANGANESE AND MANGANESE ALLOYS). Manganese use dates back to antiquity where early references relate to the use of manganese in glassmaking. The first useful manganese compound isolated was permanganate discovered by the German chemist, Glauber, in the seventeenth century. The most used manganese compound aps of the early 1990s, outside of the manganese–iron alloy, ferromanganese, used in steelmaking (see STEEL), is manganese dioxide. Use of manganese dioxide had its beginnings in 1868, when Leclanché developed the dry cell battery (see BATTERIES, INTRODUCTION) which uses manganese dioxide as the primary component of the cathode mixture.

Manganese, atomic no. 25, belongs to the first transition series and is the principal member of Group 7 (VIIA). It has nine isotopes (1,2) (Table 1).

Ground-state electronic configuration is $1s^22s^22p^63s^23p^63d^54s^2$. Manganese compounds are known to exist in oxidation states ranging from -3 to $+7$ (Table 2). Both the lower and higher oxidation states are stabilized by complex formation. In its lower valence, manganese resembles its first row neighbors chromium and especially iron in the Periodic Table. Commercially the most important valances are Mn^{2+}, Mn^{4+}, or Mn^{7+}.

As the oxidation state of manganese increases, the basicity declines, eg, from MnO to Mn_2O_7. Oxyanions are more readily formed in the higher valence states. Another characteristic of higher valence-state manganese chemistry is the abundance of disproportionation reactions.

$$2\ Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+}$$
$$2\ Mn^{5+} \longrightarrow Mn^{4+} + Mn^{6+}$$
$$3\ Mn^{6+} \longrightarrow Mn^{4+} + 2\ Mn^{7+}$$

Thermodynamic data (4) for selected manganese compounds is given in Table 3; standard electrode potentials are given in Table 4. A pH–potential diagram for aqueous manganese compounds at 25°C is shown in Figure 1 (9).

There are approximately 250 known manganese minerals. The primary ores which typically have a Mn content >35%, usually occur as oxides or hydrated oxides, or to a lesser extent as silicates or carbonates. Table 5 lists the manganese-containing minerals of economic significance (10). Battery-grade manganese dioxide ores are composed predominately of nsutite, cryptomelane, and todorokite.

Worldwide refinery amounts of manganese ore are estimated (ca 2003) at 23.2×10^6 t. The world's supply of commercial manganese ore comes from Australia, Brazil, China Gabon, India and the Republic of South Africa (11).

Deep-sea manganese nodules represent a significant potential mineral resource. Whereas the principal constituent of these deposits is manganese, the primary interest has come from the associated metals that the nodules can also contain (see OCEAN RAW MATERIALS). For example, metals can range from

0.01–2.0% nickel, 0.01–2.0% copper, and 0.01–2.25% cobalt (12). Recovery is considered an economic potential in the northwestern equatorial Pacific, and to a lesser degree in the southern and western Pacific and Indian Oceans (13–18).

United States resources of manganese ores are estimated at over 70×10^6 metric tons. These are, however, low grade deposits having manganese contents ranging from 0.6–12% and U.S. manganese production from domestic ore stopped in 1970. The United States depends on imports for its manganese needs and maintains sizable stockpiles for emergencies.

Whereas hydrogen does not react with manganese to form a hydride, hydrogen is soluble to some extent in manganese metal. Exposure of manganese to oxygen leads to the ready formation of manganese oxides, especially at higher temperatures. Nitrogen above 740°C forms solid solutions, as well as several nitrides such as, MnN [36678-21-4], Mn_6N_5 [64886-63-1], Mn_3N_2 [12033-03-3], Mn_2N [12163-53-0], and Mn_4N [12033-07-7]. Manganese nitrides are used in steelmaking as nitrogen-containing intermediate alloys (19) (see NITRIDES).

Carbon reacts with molten manganese forming various carbides including $Mn_{23}C_6$ [12266-65-8], Mn_3C [12121-90-3], Mn_7C_3 [12076-37-8], Mn_2C_7 [75718-05-7], and $Mn_{15}C_4$ [12364-85-1]. Manganese tricarbide [75718-05-7] reacts with water to yield about 75% H_2, 12–15% CH_4, and 6–8% ethylene. It is an important factor in a fuel–alloy process designed to produce liquid Hydrocarbons (qv) (19,20). In steel and other ferrous alloys, Carbides, Survey (qv) achieve the desired mechanical properties. With silicon, manganese forms a series of silicides, eg, Mn_3Si [12163-59-6], Mn_5Si_3 [12033-10-2], MnSi [12032-85-8], and $MnSi_{1.7}$. Manganese silicides have excellent heat-resisting properties. Manganese forms compounds only with a limited number of metals, ie, Au, Be, Zn, Al, In, Ti, Ge, Sn, As, Sb, Bi, Ni, and Pd. In the commercially important iron–manganese system, no compounds are formed.

Manganese metal reacts with many compounds (21). Although Mn is fairly stable against water at room temperature, a slow reaction accompanied by the evolution of hydrogen takes place at 100°C. Most dilute acids dissolve manganese at a fast rate. At 350–875°C, anhydrous ammonia converts Mn into nitrides. Concentrated alkalies, eg, KOH and NaOH, dissolve Mn metal at their boiling temperatures to form hydrogen and manganese(II) hydroxide.

2. Low Valent Manganese Compounds

A family of highly reduced metal Metal Carbonyls (qv) based on the anion $Mn(CO)_4^{3-}$ which contains manganese(−III), is obtained by the reduction of $Mn_2(CO)_{10}$ in the presence of sodium metal in hexamethylphosphoramide (22). A further example of −3 valent manganese is $Mn(NO)_3CO$ [14951-98-5], the volatile green crystals, mp 27°C, obtained by treating $Mn(CO)_5I$ [14896-42-6] with NO. The −2 oxidation state is represented by an anionic complex of Mn with phthalocyanine which can be made by reducing manganese(II) phthalocyanine [14325-24-7] with lithium in tetrahydrofuran (23). Manganese pentacarbonyl anion, $Mn(CO)_5^-$, which contains −1− valent Mn, is prepared by treatment of dimanganese decacarbonyl [101070-69-1] with sodium amalgam in tetrahydrofuran or with alcoholic potassium hydroxide.

The manganese(0) compound, $Mn_2(CO)_{10}$, has yellow crystals, mp 154–155°C, and sublimes *in vacuo* (24). The metal–metal bond is 29.3 pm and has an estimated strength of 142 kJ/mol (34 kcal/mol). This compound is obtained from the monovalent methylcyclopentadienylmanganese tricarbonyl [12108-13-3] (MMT), $C_9H_7Mn(CO)_3$, by reduction with sodium in diglyme in the presence of CO under pressure. Manganese carbonyl is the parent compound for a large family of manganese carbonyl compounds.

Compounds having manganese in the univalent positive state exist only as complexes. Reduction of sodium or potassium manganese(II) cyanides, eg, $K_4(Mn(CN)_6)$, in the presence of aluminum powder in alkaline solution under hydrogen, yields octahedral sodium or potassium manganese(I) cyanide, $M_5(Mn(CN)_6)$. The manganese(I) species have also been formed by electrolytic reduction of the manganese(II) cyanides. These colorless alkali metal salts are strong reducing agents. Sodium manganese(I) hexacyanide [75535-10-3] generates hydrogen from hot water. Monovalent Mn–cyanide complexes may also contain carbonyl or nitrosyl groups. The monovalent nitrate complex $MnONO_2(CO)_5$ [14488-62-1] can be obtained by the action of N_2O_4 on $Mn_2(CO)_{10}$. In the manufacture of MMT, methylcyclopentadienyl dimer is gradually added to a mixture of molten sodium metal and diethylene glycol dimethyl ether at 185–190°C to form methylcyclopentadienylsodium. After completion of this reaction, anhydrous flaked manganese chloride is added to the reaction mixture which is kept agitated at 165°C. The product formed, bis(methylcyclopentadienylmanganese), is subsequently treated with carbon monoxide at 4.3 MPa (625 psi) or 4.5 MPa (650 psi) at 193°C. The product is isolated from the reaction mixture by vacuum distillation (25). The complex MMT is a light amber liquid, mp 1.5°C, bp 233°C, having a density of 139 g/cm^3 at 20°C.

3. Divalent Manganese

Divalent manganese compounds are stable in acidic solutions but are readily oxidized under alkaline conditions. Most soluble forms of manganese that occur in nature are of the divalent state. Manganese(II) compounds are characteristically pink to colorless, with the exception of MnO and MnS which are green, and $Mn(OH)_2$, which is white. The physical properties of selected manganese(II) compounds are given in Table 6.

In neutral and acidic aqueous solution, the Mn^{2+} cation occurs as the pale pink hexaaqua complex $[Mn(H_2O)_6]^{2+}$. The rate of oxidation of dissolved divalent Mn cation to insoluble higher valent oxide hydrates accelerates with increasing hydroxyl ion concentration (see Fig. 1). Strong oxidizing agents such as permanganate, ozone, or hydrogen peroxide accomplish the oxidation at a lower pH than molecular oxygen, which requires a pH of 9.3–10, eg,

$$3\ Mn^{2+} + 2\ MnO_4^- + 2\ H2O \longrightarrow 5\ MnO_2(s) + 4H^+$$

The dependence of the oxidizability of Mn^{2+} on the degree of alkalinity is an important factor in some processes for the removal of manganese from water and wastewater. Manganese(II) compounds are fairly stable, although the hydroxide and carbonate precipitated from alkaline solution tend to oxidize to MnO(OH).

In neutral solutions, the manganese salts of more common acids show very little hydrolysis, although hydrolysis may occur over a period of time. Slow precipitation of the hydroxide, which in turn oxidizes, occurs resulting in a brown precipitate being formed in the solutions. Manganese sulfate, $MnSO_4 \cdot xH_2O$ where $x = 7$, 5, 4, 2, or 1, is the most stable common divalent manganese salt. The color of the manganese ion is considered pink, although some solutions containing it are almost colorless. Many simple manganese salts can be obtained as hydrates, containing the pale pink cation $[Mn(H_2O)_6]^{2+}$. These hydrates are water soluble. Manganese(II) chlorides, nitrates, and sulfates are soluble in water, but the carbonates, hydroxides, and oxides are only sparingly soluble. A number of industrial processes require the purification of Mn(II) salt solutions, particularly those that have been prepared from gangue-bearing manganese ores. A useful technique employs the property that most other heavy-metal hydroxides, such as Fe(III) and Al, precipitate at lower pH than $Mn(OH)_2$ which precipitates at pH 8.3. Furthermore, in the presence of S^{2-} and OH^- ions, the sulfides of most other heavy metals precipitate at lower alkalinities than does manganese monosulfide [18820-29-6], MnS.

There are two manganese(II) sulfides, MnS and MnS_2. Manganese(II) disulfide contains a S–S bond and has a pyrite structure. When a solution of a manganous salt is treated with ammonium sulfide, a flesh-colored hydrated precipitate is formed which is comprised of MnS and $Mn(II)S_2$. This mixture very slowly changes to the more stable green-black MnS.

A number of complexes containing the manganese(II) ion are known. Acetoacetic ester, acetonedicarboxylic ester, salicylaldehyde, benzoyl acetone, and ethylenediaminetetraacetate (EDTA) are included among the number of compounds that form such complexes. All are pale pink or yellow solids insoluble in water, but soluble in organic solvents. Manganese(II) forms complex cyanides of the general type $M_4(Mn(CN)_6)$, where M is monovalent, that are similar to the ferrocyanides. These are readily soluble in water, but hydrolyze fairly rapidly. They also are readily oxidized to the trivalent complex $M_3^+(Mn^{3+}(CN)_6)$, which corresponds to the ferricyanides.

3.1. Manganese Carbonate.

Manganese carbonate [589-62-9] occurs in nature as rhodochrosite, a reddish white to brown hexagonal–rhombohedral mineral having a specific gravity of 3.70. Pure manganese carbonate is a pink-white powder that is relatively insoluble. Rhodochrosite is the main constituent of the manganese ores used as the raw material for a portion of Japan's electrolytic manganese dioxide (EMD) production (see ELECTROCHEMICAL PROCESSING, INORGANIC).

Synthetic manganese carbonate is made from a water-soluble Mn(II) salt, usually the sulfate, by precipitation with an alkali or ammonium carbonate. The desired degree of product purity determines the quality of manganese sulfate and the form of carbonate to be used. For electronic-grade material, where the content of K_2O and Na_2O cannot exceed 0.1% each, the $MnSO_4$ is specially prepared from manganese metal, and ammonium bicarbonate is used (26) (see ELECTRONIC MATERIALS). After precipitation, the $MnCO_3$ is filtered, washed free of excess carbonate, and then, to avoid undesirable oxidation by O_2, dried carefully at a maximum temperature of 120°C.

3.2. Halides.

The Mn^{2+} ion combines with each of the halogens to make compounds of the type MnX_2. The halides, except for the fluorides, are quite soluble, as are the corresponding hydrates. The chloride has hydrates of 2, 4, 6, and 8 waters and these are normally obtained by the action of hydrochloric acid on the oxides or carbonates, followed by crystallization and, if desired, dehydration. Complete dehydration is difficult to accomplish, but the anhydrous salt can be made directly by the action of HCl gas on heated manganese metal or Mn^{2+} oxide. Hydrochloric acid also reacts with higher valent manganese oxides to produce manganous chloride, but in this case chlorine is also generated. The bromide is similar to the chloride and forms the same series of hydrates. The iodide forms hydrates having 1, 2, 4, 6, or 9 waters and is very hygroscopic. These can only be dehydrated under vacuum because they lose iodine above 80°C. The fluoride is only slightly soluble. It may be prepared by action of hydrogen fluoride on metallic manganese or Mn^{2+} oxide. A cyanide,$Mn(CN)_2$, is known, but this material is rapidly oxidized and has never been obtained in a pure state.

There are a number of complex chlorides of three general types: $M(MnCl_3)$, $M_2(MnCl_4)$, and $M_4(MnCl_6)$. M is monovalent in each case. Fluorine forms only $9M(MnF_3)$ and the only complex bromine compound reported is $Ca(MnBr_4){\cdot}4H_2O$. There are no iodide complexes. The anhydrous salt, $MnCl_2$, forms cubic pink crystals, and three well-defined hydrates exist. Aqueous solubilities of the tetrahydrate and dihydrate are given in Table 7.

$$MnCl_2 \cdot 6\,H_2O \overset{-2°C}{\rightleftarrows} MnCl_2 \cdot 4\,H_2O \overset{58°C}{\rightleftarrows} MnCl_2 \cdot 2\,H_2O \overset{198°C}{\rightleftarrows} MnCl_2$$

In the presence of moist air, $MnCl_2$ vapor decomposes into hydrochloric acid and manganese oxides.

Manganese chloride can be prepared from the carbonate or oxide by dissolving it in hydrochloric acid. Heavy-metal contamination can be removed by precipitation through the addition of manganese carbonate which increases the pH. Following filtration, the solution can be concentrated and upon cooling, crystals of $MnCl_2{\cdot}4H_2O$ are collected. If an anhydrous product is desired, dehydration in a rotary dryer to a final temperature of 220°C is required. Anhydrous manganese chloride can also be made by reaction of manganese metal, carbonate or oxide, and dry hydrochloric acid.

Manganese chloride is manufactured by Chemetals Corp. using a process in which manganese(II) oxide is leached with hydrochloric acid. Manganese carbonate is added after completion of initial reaction to precipitate the heavy-metal impurities. Following filtration of the impurities, the solution is concentrated and cooled and the manganese chloride is isolated. Gradual heating in a rotary dryer above 200°C gives anhydrous manganese chloride (27,28).

For top quality $MnCl_2{\cdot}xH_2O$ grades, the starting material is manganese metal or high purity MnO. To make anhydrous $MnCl_2$ directly, manganese metal or ferromanganese is chlorinated at 700–1000°C. Any $FeCl_3$ initially present in the product is removed by sublimation (29).

3.3. Manganese Nitrate. Manganese nitrate [10377-66-9] is prepared from manganese(II) oxide or carbonate using dilute nitric acid, or from MnO_2 and a mixture of nitrous and nitric acids. $Mn(NO_3)_2$ exists as the anhydrous salt [10377-66-9]; the monohydrate [3228-81-9]; trihydrate [55802-19-2], mp 35.5°C; tetrahydrate [20694-39-7]; and hexahydrate [17141-63-8], deliquescent needles having mp 25.8°C. Manganese nitrate is very soluble in water and decomposes at 180°C yielding manganese dioxide and oxides of nitrogen. The commercial product consists of 61 and 70% solutions.

3.4. Manganese(II) Oxide. The MnO found in nature as manganosite can be prepared by the reduction of higher valent manganese oxides by either thermal means or by the use of a reducing agent such as CO, H_2, or carbon at elevated temperatures. Manganese oxide, insoluble in water, readily dissolves in mineral acids. Manganese(II) oxide is bright green in color and is moderately stable in air. Manganese monoxide absorbs oxygen and the oxidation state of the manganese changes progressively according to the increased oxygen absorption to Mn_2O_3 (30). The activity of manganese oxide toward oxygen absorption is enhanced by low temperatures employed in its formation. Manganese(II) oxide is an important precursor of such manganese compounds as $MnSO_4$, $MnCl_2$, and EMD, as well as being an ingredient in fertilizer and feedstuff formulations (see FERTILIZERS; FEEDS AND FEED ADDITIVES, NONRUMINANT FEEDS). It is made from manganese dioxide ores through a reductive roasting process (31–33).

The Chemetals process (34) uses a stationary bed of crushed (particle size <10 mm) manganese ore which is continuously replenished from the top and into which a reducing gas, eg, CH_4 and air, is introduced from the bottom. The MnO is formed from the MnO_2 in a reaction zone immediately beneath the top layer where the temperature is controlled to 760–1040°C to avoid sintering. The manganese oxide moves downward and finally passes through an inert atmosphere cooling zone before it is ground to <74 μm. A significant portion of the MnO_2 is already thermally decomposed to Mn_2O_3 before it comes in contact with the reducing gas, thus economizing on fuel.

Other processes use rotary kilns for the reduction step. Before roasting, the finely ground MnO_2 ore is mixed with the reducing agent, such as hydrogen, carbon monoxide producer gas, or heavy (Bunker C) oil. Thus, in order to obtain better manganese yields (98–99%), the roasting temperature is kept at 800°C, even though some of the iron is also reduced to the acid-soluble FeO (35).

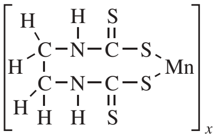
3.5. Manganese Hydroxide. Manganese hydroxide [18933-05-6] is a weakly amphoteric base having low solubility in water. $Mn(OH)_2$ crystals are reported to be almost pure white and darken on exposure to air. Manganese dihydroxide occurs in nature as the mineral pyrochroite and can also be prepared synthetically by reaction of manganese chloride and potassium hydroxide that is scrupulously free of oxygen. The entire reaction is conducted under reducing conditions (36).

3.6. Manganese Sulfate. Manganese sulfate [7785-87-5] is made by dissolving manganese carbonate ore (rhodochrosite) or manganese(II) oxide in sulfuric acid. The solubility of manganese sulfate in water is given in Table 8. The tetrahydrate readily converts into the monohydrate upon gentle heating;

$MnSO_4{\cdot}H_2O$ [31746-59-5] is stable up to 280°C. Manganese sulfate may also be produced by treating finely ground manganese dioxide with sulfuric acid and a reducing agent:

$$2\,MnO_2 + 2\,H_2SO_4 + C \xrightarrow{air} MnSO_4 \cdot H_2O + CO_2$$

3.7. Manganese Ethylenebis(thiocarbamate). Maneb [12427-38-2], $(C_4H_6MnN_2S_4)_x$ (**1**), is a yellow powder used as a leaf and soil fungicide (see FUNGICIDES, AGRICULTURAL). Maneb is obtained by treating disodium ethylenebis-(dithiocarbamate) with an aqueous solution of maganese(II) sulfate (37).



(**1**)

4. Trivalent Manganese

The Mn^{3+} ion is so unstable that it scarcely exists in aqueous solution. In acidic aqueous solution, manganic compounds readily disproportionate to form Mn^{2+} ions and hydrated manganese(IV) oxide, $MnO_2{\cdot}2H_2O$; in basic solution these compounds hydrolyze to hydrous manganese(III) oxide, MnO(OH). Sulfuric acid concentrations of about 400–450 g/L are required to stabilize the noncomplexed Mn^{3+} ion in aqueous solutions.

In the solid phase the most stable forms of Mn(III) are manganese sesquioxide [1317-34-6], Mn_2O_3, and its hydrate $Mn_2O_3{\cdot}nH_2O$, and manganese oxide, Mn_3O_4, which is thermally the most stable manganese oxide. Physical properties of manganese(III) compounds are given in Table 9.

Compounds of trivalent manganese can be made either by oxidation of corresponding manganous compounds or by reduction of the more highly oxidized compounds. The color of Mn(III) compounds in the solid state can vary from red to green. The corresponding aqueous solutions mostly have a reddish purple, almost permanganate-like appearance. Simple cationic Mn(III) compounds are olive green $MnPO_4{\cdot}H_2O$ [14986-93-7], dark green $Mn_2(SO_4)_3$ [13444-72-9], and reddish purple MnF_3.

Manganese(III) fluoride, MnF_3, a red salt, can be made by reaction of fluorine and manganese(II) iodide. The dihydrate, $MnF_3{\cdot}2H_2O$, can be made by dissolving manganese(III) oxide, Mn_2O_3, or preferably the hydrated MnO(OH), in hydrofluoric acid. Manganese(III) chloride, a brown salt giving a green solution in organic solvents, is only stable below −40°C, above which it decomposes to $MnCl_2$ and chlorine. It is formed by treatment of a suspension of MnO_2 in ether with HCl gas below −70°C and precipitating with carbon tetrachloride. The bromide and iodide, even as complexes, are not known.

The brown crystalline manganese(III) acetate dihydrate is of considerable commercial importance because it is often used as the source material for other trivalent manganese compounds. It can be made by oxidation of manganese(II) acetate using chlorine or potassium permanganate, or by reaction of manganese(II) nitrate and acetic anhydride.

Although the manganese(III) ion is more acidic than the manganese(II), and hence forms fewer stable simple salts, Mn(III) has a greater tendency to form stable complex compounds. Complex chlorides, chloromanganates of the type $M_2(MnCl_5)$ where M is a monovalent cation, are dark red and rather easily prepared, either by reduction of permanganate and addition of alkaline chloride, or from Mn_2O_3 and an alkaline chloride in aqueous HCl at 0°C. In water these complexes hydrolyze. Complex fluorides are of the type $M(MnF_4)$ and $M_2(MnF_5)$. These are obtained as dark red crystals by adding alkali fluorides to a solution of MnF_3.

Complex phosphates of two types, $MH_2(Mn(PO_4)_2)$ and $M_3(Mn\ (HPO_4)(OH)_2)H_2O$, are known. The complex with pyrophosphate $(Mn_2(H_2P_2\ O_7)_3)^{3-}$ is the stable product in the potentiometric determination of manganese. Manganese(III) does not coordinate with amines or nitro complexes, but it does make manganicyanides of the types $M_3(Mn(CN)_6)$ and $M_3(Mn(CN)_5(OH))$, which are similar to the ferricyanides. The K^+, Na^+, Li^+ and $NH^+{}_4$ manganicyanides have been prepared and slowly hydrolyze in water to MnO(OH).

4.1. Manganese(III) Oxides. The sesquioxide, Mn_2O_3, exists in dimorphic forms. The α-Mn_2O_3 exists in nature as the mineral bixbyite. Synthetic α-Mn_2O_3 is prepared by the thermal decomposition of the nitrate, dioxide, carbonate, oxalate, or chloride in air in the temperature range of 500–800°C. Heating above 940°C, it is reduced to Mn_3O_4. Higher temperatures or the presence of reducing agents allow the reduction to continue to MnO. The gamma form is unstable and thus does not occur in nature. γ-Mn_2O_3 may be synthesized by the dehydration of the precipitated hydrated form at 250°C in vacuum.

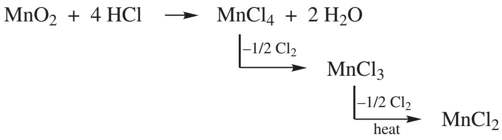
The mixed valent oxide Mn_3O_4 occurs in nature as the mineral hasumannite. The structure of this ferromagnetic material has been the subject of much dispute. Mn_3O_4 is the most stable of the manganese oxides, and is formed when any of the other oxides or hydroxides are heated in air above 940–1000°C. The oxidation of aqueous solutions of $Mn(OH)_2$ can also lead to the formation of Mn_3O_4.

As seen in some iron oxides, both γ-Mn_2O_3 and Mn_3O_4 have pseudo-spinel structure and tetragonal symmetry. Because of the close similarities between the structures of these two oxides the x-ray diffraction patterns are nearly identical. Both oxides can be represented by the general formula $Mn^{II}Mn^{III}{}_2O_4$ where the Mn(II) ions occupy tetrahedral sites and the Mn(III) ions occupy the octahedral sites of the spinel (38). Upon heating Mn_3O_4 above 1170°C, a reversible transition from the tetragonal to a cubic structure occurs. The weakly acidic manganese sequioxide forms oxo anions with alkali metal hydroxides. Thus potassium manganate(III) [12142-17-5], $KMnO_2$, is prepared by heating Mn_2O_3 in the presence of KOH. Needle-shaped gray crystals that are readily oxidized by O_2 to higher alkali manganates are formed (39).

5. Tetravalent Manganese

By far the most significant manganese(IV) compound is the dioxide [1313-13-9] MnO_2, found in nature as pyrolusite, a black mineral. There is also a hydrated form approximating $MnO_2{\cdot}2H_2O$ which is formed by precipitation from solutions. The dioxide is a reasonably good conductor. Its specific conductance is $0.16\Omega^{-1}$ at 0°C. Manganese dioxide is seldom stoichiometric and is insoluble in water. This lack of aqueous solubility is responsible for much of its stability, because the Mn(IV) ion is unstable in solution. Physical properties of manganese(IV) compounds are given in Table 10.

In acid solution, MnO_2 is an oxidizing agent, and is used as such in industry. The classic example is the oxidation of chloride in HCl, which has been a convenient means of chlorine generation, both in the laboratory and in the old Weldon process for the manufacture of chlorine.



$$MnO_2 + 4\,HCl \longrightarrow MnCl_4 + 2\,H_2O \xrightarrow{-1/2\,Cl_2} MnCl_3 \xrightarrow[\text{heat}]{-1/2\,Cl_2} MnCl_2$$

Most of the simple halides, MnX_4, are unknown except for blue manganese tetrafluoride [15195-58-1]. Manganese(IV) is amphoteric, appearing as the cation in salts and as an anion in compounds known as manganites, M_2MnO_3, where M is monovalent. The manganites are salts of the very weak manganous acid, H_2MnO_3, or hydrated dioxide, $MnO_2{\cdot}2H_2O$, which can be obtained by reduction of potassium permanganate in slightly alkaline solutions, then dissolved in concentrated alkalies to give the manganites. The manganites may also be prepared by fusing MnO_2 and the oxide of the desired cation.

The principal complexes of Mn^{4+} are of the type K_2MnX_6, where X may be fluoride, chloride, cyanide, or iodate, and as a group these materials are readily hydrolyzed. The hexafluoride, K_2MnF_6, a yellow hexagonal crystal, can be formed by treating either a manganate(V) or (VI) with concentrated HF. The chlorides, M_2MnCl_6, M monovalent, have dark red crystals, and are formed by reaction between permanganate and HCl gas in glacial acetic acid. A similar cyanide complex, $K_2Mn(CN)_6$, is said to be made by treatment of potassium permanganate using potassium cyanide in a saturated aqueous solution.

A triperoxymanganate(IV), $K_2H_2MnO(O_2)_2$, is said to be formed (40) when $KMnO_4$ in 30% KOH is treated with H_2O_2 at −18°C. It is a dark red-brown crystalline compound, which in water slowly evolves O_2 and precipitates MnO_2. In the dry state this material is explosive above 0°C, but under acetone at −60°C, it is stable for several days.

The oxidation of Mn(II) to MnO_2 using oxygen can be accelerated by certain microorganisms such as *Pedomicrobium manganicum* or *Hyphomicrobium manganoxydans*. This biochemical oxidation can occur in the pH range of 5.5–7.5, in contrast to the pH range of 8.5–10 normally required for the chemical oxidation of Mn(II) by O_2. Microbial action is assumed to have been involved in the genesis of some manganese ore deposits and could also contribute to the clogging of water distribution systems with manganese dioxide deposits (41).

Water purification chemistry depends on the oxidation of Mn(II) by a suitable oxidant, eg, O_2 at pH >9, or at lower pH potassium permanganate or ozone, resulting in the formation of hydrous manganese dioxide. The colloidal properties of hydrous manganese oxide have been studied (42) and exploited in the treatment of potable water. As shown in Figure 2 (43), the surface of a hydrous MnO_2 particle in a colloid solution has an outer layer of exposed OH groups capable of adsorbing charged species, such as H^+, OH^- and metal ions. Hydrous manganese dioxide is amphoteric and can participate in surface–solution exchanges of H^+ and H^-. The zero point of charge for hydrous manganese dioxide is in the range of pH 2.8–4.5. In the absence of other ions, the overall surface charge is largely determined by the pH of the solution. The sorptive and ion-exchange characteristics of MnO_2 solutions, as well as the parameters controlling coagulation, have been studied in some detail (44).

5.1. Manganese Oxides.

Manganese(IV) dioxide rarely corresponds to the expected stoichiometric composition of MnO_2, but is more realistically represented by the formula $MnO_{1.7-2.0}$, because invariably contains varying percentages of lower valent manganese. It also exists in a number of different crystal forms, in various states of hydration, and with a variety of contents of foreign ions.

The structure of manganese dioxide can be described as being composed of MnO_6 octahedra where each manganese ion is coordinated to the six nearest oxygen atoms, each of which is located at the vertex of an octahedron. The solid structure is then composed of MnO_6 octahedra, which form chains by sharing edges and cavities or tunnels. The various chains are cross-linked by sharing corners (vertices). Thus a hierarchy can be constructed based on increased complexity of crystal structure. Examples of natural and synthetic manganese dioxides are listed in Table 11. Structures are shown in Figure 3.

α-MnO_2 is isostructural to the minerals hollandite [12008-99-0], psilomelane [12322-95-1], cryptomelane [12260-01-4], and coronadite [12414-82-3]. Its 2×2 tunnel structure is thought to require stabilization at the centers by large cations. Typically, compounds having the general formula MnO_x, x ranges from 1.88–1.95 are found, but x can be as low as 1.6 for the psilomelane family (47). A highly crystalline α-MnO_2 has been prepared from Li_2MnO_3 by a high (ca 90°C) temperature acid leaching process (48).

The mineral pyrolusite (*8*) is the primary example of β-MnO_2, having the general formula MnO_x where x ranges from 1.95–2.00. This mineral is characterized by a high degree of crystallinity and an almost perfect stoichiometric composition. The beta group can be visualized as being composed of single chains of edge-shared MnO_6 octahedra, cross-linked to neighboring chains, through corner sharing of oxygen atoms (Fig. 3).

The crystal structure of ramsdellite [12032-73-4] is similar to that of β-MnO_2 except that double of MnO_6 octahedra are cross-linked to adjacent double chains through the sharing of oxygen atoms located at the corners. Ramsdellite and pyrolusite are the only manganese dioxide phases where the composition approaches the stoichiometric MnO_2 formula. Heating ramsdellite to 250°C transforms it to pyrolusite.

The thermal transitions of the manganese dioxides can be illustrated by the beta phase which undergoes successive reductions and corresponding loss of oxygen as the temperature is increased (49).

$$\beta\text{−}\mathrm{MnO_2} \xrightarrow{600\text{−}700^\circ\mathrm{C}} \alpha\text{−}\mathrm{Mn_2O_3} \xrightarrow{900\text{−}1000^\circ\mathrm{C}} \mathrm{Mn_3O_4} \xrightarrow{>1250^\circ\mathrm{C}} \mathrm{MnO}$$

Manganese dioxides typically lose adsorbed water between 25–105°C. The complete removal of interlayer water, which results in collapse of the crystal lattice, can, however, require temperatures as high as 150–250°C. In the γ-$\mathrm{MnO_2}$ phase the condensation of OH groups occurs in the temperature range of 105–500°C, resulting in the release of this most tightly bound water and collapse of the crystal lattice. The various manganese dioxide phases eventually transform into β-$\mathrm{MnO_2}$, as shown in Figure 4, suggesting the relative thermodynamic stability of the beta phase (50).

The term γ-manganese dioxide is applied to a series of hydrated manganese dioxides of moderate crystallinity that are suitable for battery purposes. These occur in nature as the mineral nsutite and have optimum activity for use in dry cell batteries. The gamma group can be visualized as being composed of irregular structural combinations of β-$\mathrm{MnO_2}$ (single-chain) and ramsdellite (double-chain) components.

The electrochemically active phases of manganese dioxide, ie, gamma and rho, typically contain approximately 4% by weight chemically bonded or structural water. The chemical and electrochemical reactivity of manganese dioxide has been shown to result from the presence of cation (51) vacancies in the manganese dioxide crystal lattice. The cation vacancy model suggests the general formula for this type of manganese dioxide to be $\mathrm{Mn^{4+}}_{(1-x-y)}\cdot\mathrm{Mn^{3+}}_{y}\cdot\mathrm{O^{2-}}_{(2-4x-y)}\cdot\mathrm{OH}_{-(4x+y)}$ where x is the fraction of $\mathrm{Mn^{4+}}$ ions missing in the crystal lattice, and y, the fraction of $\mathrm{Mn^{4+}}$ ions replaced by $\mathrm{Mn^{3+}}$ in the crystal lattice. Each vacant $\mathrm{Mn^{4+}}$ site is coordinated to four groups present in the lattice as $\mathrm{OH^-}$ ions that have replaced $\mathrm{O^{2-}}$ in the crystal lattice. Additional replacement of $\mathrm{O^{2-}}$ in the crystal lattice is caused by the charge compensation determined by the fraction of $\mathrm{Mn^{4+}}$ that has been replaced by $\mathrm{Mn^{3+}}$. Substitution of $\mathrm{Mn^{4+}}$, having radius, r (=53 pm) by $\mathrm{Mn^{3+}}$ ($r = 64.5$ pm) leads to lattice expansion. The model suggests that electrochemical reactivity is caused by manganese lattice vacancies and a corresponding water content that provides the initial concentration of protons for the transfer process.

The delta phase is generally applied to characterize a group of amorphous essentially noncrystalline hydrous manganese dioxides. Typical minerals belonging to the δ-manganese dioxide group include birnessite [1244-32-5], ranceite, takanelite, toddorokite, woodruffite, chalcophanite, and lithioporite. This phase is often labeled as hydrated manganese dioxide because it typically contains 5–40% of chemically bound water. These dioxides have values of x in the range of 1.7–2.0 for the general formula MnO_x and often also contain $\mathrm{Na^+}$, $\mathrm{Ca^{2+}}$ or $\mathrm{Ba^{2+}}$.

The oxidation of divalent manganese, or the reduction of potassium permanganate, leads to the formation of δ-manganese dioxide. These manganites generally follow the composition $\mathrm{M_2O\cdot 4MnO_2}$, where M is an alkali metal cation.

This alkali metal cation is exchangeable with other metal cations. The absorption of alkaline-earth cations by δ-manganese dioxide is shown to be similar to that reported for colloidal hydrous manganese dioxides (52). Absorption capacity increases in the series $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. Absorption has been explained by an ion-exchange mechanism (Fig. 5) involving the manganese dioxide surface and hydrated divalent cations in the bulk solution. The electrostatic attraction between the solid surface and the cations is expected to increase as the radius of the hydrated cations decreases. For the alkaline-earth cations, the increase occurs as the ionic radius decreases (Table 12) (53). Transition metals were found to exhibit the highest degree of absorption on δ-manganese dioxides. Selectivity increased in the series $Co \geq Mn > Zn > Ni > Ba > Sr > Ca > Mg$ (54). The interaction of metal ions with the hydrous manganese dioxide involves the release of a proton from the surface.

Hydrous manganese oxides of composition $MnO_{1.9-1.95}$ having x-ray diffraction patterns suggesting a low degree of crystallinity characteristic of δ-MnO_2, were found to remain colloidally dispersed for several months, and to exhibit Mn(II) absorption (55) in the range of 0.2−0.3 mol/mol MnO_2 in the pH range of 5−7. This value increased to an excess of 0.5 mol Mn(II) per mol MnO_2 in the slightly alkaline range. δ-Manganese dioxides can be oxidized under alkaline conditions to potassium manganate.

The effect H^+ and OH^- ions exert on a manganese dioxide surface can be summarized by the pH at which there is zero surface charge (pH_{pzc}). This point of zero charge (pzc) for the various manganese dioxide phases increases in the series $\delta\text{-}MnO_2 < \alpha\text{-}MnO_2 \approx \beta\text{-}MnO_2 < \gamma\text{-}MnO_2$. Values of pH_{pzc} are 1.5–3.0, 4.5, 4.6, and 3.3−5.0, respectively (56–58).

Synthetic active manganese dioxides, prepared by the reduction of permanganate or the pyrolysis of lower valent manganese salts, have been used as mild, selective, heterogeneous oxidation reagents. The amorphous manganese dioxides are mild enough to be used for the oxidation of α,β-unsaturated alcohols and unsaturated polyene alcohols into the corresponding α,β-unsaturated carbonyl compounds; the oxidation of benzylic alcohols into the corresponding Aldehydes (qv) and Ketones (qv); and the oxidative coupling of phenols (59).

Manganese dioxide, in combination with other metal oxides, forms a series of active catalysts (60) that participate in a variety of environmentally important oxidation and decomposition reactions. The manganese-based catalysts for these applications exhibit a long life and high catalytic activity. At moderately elevated temperatures, manganese dioxide catalysts (61,62) are used for the complete oxidative degradation of many organic compounds. These catalysts are particularly effective for oxygenated compounds such as alcohols, acetates, and ketones. At a contact time of ca 0.24 s, 95% hydrocarbon destruction efficiency is achieved for ethanol at 204°C; ethyl acetate, 218°C; propanol, 216°C; propyl acetate, 238°C; 2-butanone, 224°C; toluene, 216°C; and heptane, 316°C. Carbon monoxide oxidation occurs at ambient temperatures when no H_2O is present. A contact time of ca 0.36 s gives >95% destruction efficiency. Ozone decomposition, at ambient temperatures, that is >99% efficient requires a contact time of ca 0.72 s. Manganese dioxide also catalyzes the decomposition of H_2O_2 at room temperature and of alkali metal chlorates at about 270°C.

Manufacture of manganese metal or compound requires the manganese dioxide of the natural ores to be reduced to lower oxides, principally MnO or other Mn(II) salts. This reduction is usually carried out at 600–900°C by roasting finely powdered MnO_2 mixed with ground coal or heavy oil. Alternatively, the presence of gaseous reductants such as carbon monoxide or hydrogen is employed. Reduction to the Mn(II) state and conversion of the oxide to the desired salt can also be performed in the liquid phase, in a single step, by employing acids which have reducing properties. Hydrochloric acid forms $MnCl_2$ and Cl_2, sulfurous acid gives $MnSO_4$ and MnS_2O_6 [13568-72-4], and NO_2 gives $Mn(NO_3)_2$ [10377-66-9].

Oxidation of manganese dioxide to higher valence states takes place in the fusion process of MnO_2 and KOH. A tetravalent manganese salt identified as K_2MnO_3 [12142-27-7] (63) which disproportionates spontaneously is formed.

$$2\,K_2MnO_3 \longrightarrow KMnO_2 + K_3MnO_4$$

Both of these manganates can be further oxidized. K_2MnO_3 is black and has a density of 3.071 g/cm^3.

Synthetic Manganese Dioxides. Chemical manganese dioxide (CMD) can be prepared by various methods including the thermal decomposition of manganese salts such as $MnCO_3$ or $Mn(NO_3)_2$ under oxidizing conditions. CMD can also result from the reduction of higher valent manganese compounds, eg, those containing the MnO_4^-ion.

A commercially practiced process (64) for the recovery of high purity manganese dioxide based on thermal decomposition results in a well-defined crystalline manganese dioxide exhibiting a purity greater than 99.5%. The process involves adjusting the pH of an aqueous manganese nitrate solution using manganese oxide to a pH of 4.8–5.0. The mixture is heated to 105°C, filtered, and combined with a previously prepared manganese dioxide. The manganese nitrate decomposition occurs between 135–146°C under vigorous agitation and controlled at a rate of 0.24–0.61 kg of manganese dioxide product per liter of slurry per day.

$$Mn(NO_3)_2 \longrightarrow MnO_2 + 2\,NO_2$$

The NO_2 generated can be recycled by reaction with water:

$$NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

The acid formed then reacts with low grade manganese dioxide ore (65) forming a slurry of impure manganese nitrate to feed the process.

$$HNO_2 + HNO_3 + MnO_2 \longrightarrow Mn(NO_3)_2 + H_2O$$

In another commercial process, finely ground manganese dioxide ore is reduced to manganese(II) oxide using H_2 or CO (66). The MnO is then leached with sulfuric acid and the manganese sulfate solution neutralized (pH 4–6) and filtered to remove impurities. The addition of $(NH_4)_2CO_3$ precipitates manganese(II) carbonate which is recovered by filtration. The $MnCO_3$ is heated in air at about 450°C resulting in 80% conversion to MnO_2:

$$MnCO_3 + 1/2\ O_2 \longrightarrow MnO_2 + CO_2$$

The manganese dioxide and manganese carbonate mixture is further leached with sulfuric acid and oxidized with $NaClO_3$. Following washing and drying, the product is found to have a manganese content of approximately 60%, 90% as MnO_2. This CMD contains approximately 90% MnO_2, has a surface area of ca 80 m^2/g, an ion-exchange capacity in the range of 1.5–1.6 meq, and a density in the range of 1.3–1.5 g/cm^3. It has been used in magnesium Batteries, Introduction (qv) produced exclusively for military applications, and as a replacement for EMD in Leclanché cells.

The starting material for activated native ore is a higher quality native MnO_2 ore. It is the objective of the activation process to chemically remove the top layer of the ore particle and to create a new highly porous and chemically active surface. For this purpose, the MnO_2 is first reduced to Mn_2O_3 either thermally, by heating it to 600–800°C in air, or at about 300°C in the presence of a reducing agent. The reduced mass is then treated with hot sulfuric acid and the Mn_2O_3 disproportionates to a highly active γ-MnO_2 and $MnSO_4$:

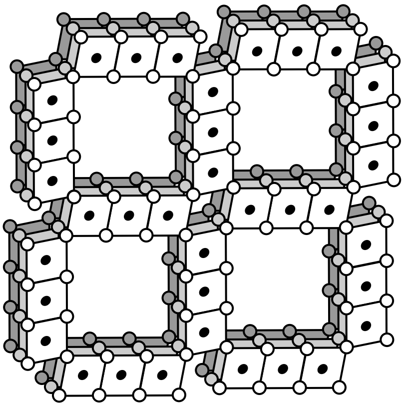
$$Mn_2O_3 + H_2SO_4 \longrightarrow \gamma - MnO_2 + MnSO_4 + H_2O$$

The newly formed γ-MnO_2 actually coats the surfaces of the particles of the solid phase; the $MnSO_4$ dissolves in the liquid phase, along with the majority of the ore impurities. The effective surface area is expanded by the etching action of the sulfuric acid. Following the acid treatment step, the slurry is filtered and the cake is carefully washed and dried at a controlled temperature.

The oxidation of *o*-toluenesulfonamide under alkaline conditions by potassium permanganate results in sulfonbenzimide (saccharin) and a hydrated manganese dioxide. The co-produced chemical manganese dioxide (CMD) can be washed and carefully dried to produce a product containing approximately 79% MnO_2, 5–18% water, and alkali contents of 4–12% as KOH (67). The manganese dioxide powder, Permanox, has been characterized as a poorly crystalline form of δ-MnO_2. Permanox exhibits apparent densities in the range of 0.7–1.1 g/cm^3 and BET surface area at 30 m^2/g.

A thermally stable, pure todorokite has been synthesized by autoclaving a layered structured manganese oxide, initially generated from the reaction of MnO_4^- and Mn^{2+} under alkaline conditions. The synthetic manganese oxide molecular sieve (11) was shown to have a tunnel size, ie, diameter of 690 pm.

This material was thermally stable to 500°C just as natural todorokite is (68).



(11)

Electrolytic Manganese Dioxide. The anodic oxidation of an Mn(II) salt to manganese dioxide dates back to 1830, but the usefulness of electrolytically prepared manganese dioxide for battery purposes was not recognized until 1918 (69). Initial use of electrolytic manganese dioxide (EMD) for battery use was in Japan (70) where usage continues.

The properties of EMD are summarized in Table 13. Historically EMD was assumed to consist essentially of gamma-phase manganese dioxide, but more recent reports suggest the predominance of the epsilon phase (71). EMD is strictly a nonstoichiometric manganese dioxide containing 2–5% lower valent manganese oxides and 3–5% chemically bound water. The Ruetschi vacancy model for EMD assumes a vacancy fraction of 0.06, a Mn^{3+} fraction of 0.08, and a structure intermediate between ramsdellite and ϵ-manganese dioxide. This suggests a true EMD density of 4.55 g/cm^3, a value in agreement with experimental measurements (72).

EMD is prepared from the electrolysis of acidified manganese sulfate solution and can be summarized as follows:

$$\begin{aligned} \textit{Anode}\quad & Mn_{2+} + 2\,H_2O \longrightarrow MnO_2 + 4\,H^+ + 2\,e^- \\ \textit{Cathode}\quad & 2\,H^+ + 2\,e^- \longrightarrow H_2 \\ \textit{Overall}\quad & Mn^{2+} + 2\,H_2O \longrightarrow MnO_2 + 2\,H^+ + H_2 \end{aligned}$$

Deposition of MnO_2 from a solution containing Mn cations on the anode is not considered the primary electrode process. Initially the Mn(III) ion is formed on the anode (73). MnO_2 formation arises from Mn(III) disproportionation:

$$Mn^{3+} + 2\,H_2O \longrightarrow MnO_2 + Mn^{2+} + 4\,H^+$$

At the anode, sulfuric acid is generated. This acid is then recycled into the leaching of $MnCO_3$ or of MnO. Although two side reactions, namely, the evolution of

O_2 and the generation of Mn^{3+}, have been identified, the current efficiency on the anode is greater than 95%. The manganese dioxide formed by electrolysis is generally considered to be of the gamma variety, but at low acid concentration, some β-MnO_2 may be co-produced, and conversely, at high acid concentration, the formation of the α-MnO_2 phase is favored. The steps involved in the manufacture of EMD using either rhodochrosite or manganese dioxide ores are summarized in Figure 6.

The use of rhodochrosite ore is primarily practiced in Japan (74) and involves the use of an ore concentrate, containing about 20–25% Mn, having a particle size of <150 μm. Typical composition of the ore on a wt% basis is $MnCO_3$, 58–68; Mn, 30–35; SiO_2, 15–20; Fe, 2–3; Pb, 0.1–0.2; Zn, 0.2–0.3; Ni, 0.1; and Co, 0.01 (75). The starting material is treated with about 10% excess (100–150 g/L) sulfuric acid at 80–90°C according to the following reaction:

$$MnCO_3 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + CO_2$$

Any divalent iron present in the reaction mixture is oxidized through the addition of finely ground MnO_2. The pH of the slurry is then adjusted to the range of 4–8 using $Ca(OH)_2$ or $CaCO_3$, which results in the precipitation of $Fe(OH)_3$ and other minor impurities such as Pb, Ni, and Co. The majority of the Ca separates as $CaSO_4$ upon cooling. The solids are removed by filtration and the filtrate is added to the cell liquor, displacing an equivalent volume of the electrolyte which is regenerated with $MnCO_3$. The composition of the electrolyte is maintained at about 80–180 g/L $MnSO_4$ and 50–100 g/L H_2SO_4 at 80–88°C. Anodes are composed of Ti, Pb, or graphite and operate at an anode current density of 0.7–1.2 A/dm^2 (see METAL ANODES).

EMD is prepared from manganese dioxide ore containing a minimum of 75% MnO_2. Initially the MnO_2 in the ore is reduced to MnO in rotary kilns, or with natural gas or hydrogen (76) by pile roasting (77), at about 700–900°C. Conditions can be controlled so that MnO_2 is reduced in preference to Fe_2O_3. Following the reduction, the solid mixture is allowed to cool to below 100°C in an inert or reducing atmosphere, to prevent the oxidation of the MnO.

$$MnO_2 + C \longrightarrow MnO + CO$$

The leaching step with H_2SO_4 is essentially identical to the one in use for rhodochrosite, except that owing to the generally higher potassium content in MnO_2 ores an additional purification step or steps may be required. For example, as the sulfuric acid level of the reaction mixture decreases, as a result of the leaching reaction, to approximately 0.1 *M* H_2SO_4, precipitation of potassium jarosite occurs (78).

$$K^+ + 3\,Fe^{3+} + 2\,SO_4^{2-} + 6\,H_2O \longrightarrow KFe_3(SO_4)_2(OH)_6 + 6\,H^+$$

Potassium removal is required because the presence of potassium during electrolysis reportedly promotes the formation of the α-MnO_2 phase which is nonbattery active. Neutralization is continued to a pH of approximately 4.5, which results in the precipitation of additional trace elements and, along with the ore gangue, can be removed by filtration. Final purification of the electrolyte liquor by the addition of sulfide salts results in the precipitation of all nonmanganese transition metals.

The cells are usually rectangular open steel or concrete troughs, lined with a corrosion-resistant nonconductive material such as fiber-reinforced plastic, rubber, concrete, or acid-proof brick. A design of a covered cell (79) has a hermetically sealed top with a rupture disk as a safety feature. The electrodes are flat or corrugated plates, cylindrical rods, or tubes, and the anodes are easily removed for stripping of the EMD deposits. The ratio between the effective anode and cathode areas is about 1:2, the spacing between anode and cathode ranges from 25 to 50 mm. Most cells are equipped with heating devices for the electrolyte.

The anodes can be made of graphite which tolerates high current densities without passivation, but are subject to gradual corrosive attack causing a lowering of its mechanical strength. Graphite anodes are said to be good for about 300 days of operation before they break in the EMD-removal step (80). Titanium is the dominant anode material because of its mechanical stability. This anode is better suited for the use of automated EMD-stripping systems and produces an EMD well suited for alkaline batteries. Titanium anodes have a life of several years, but are expensive. Furthermore, they tend to passivate, if current densities and H_2SO_4 concentrations are not properly controlled. Performance might be improved by application of specific surface coatings.

Cathodes are made from graphite, soft or hard lead, or copper. A production-size cell (81) may contain 44 anode units, each comprising five graphite plate electrodes 25-mm thick, 175-mm wide, and 1100-mm long.

The electrolysis is conducted at 90–95°C and an anode current density of about 50–120 A/m^2 when using lead alloy anodes and lead cathodes. Using graphite electrodes, the current density is from 70–100 A/m^2; using titanium anodes and graphite cathodes, the current density is 50–80 A/m^2 (82).

A layer of oil or paraffin wax is floated on top of the electrolyte to minimize heat and water losses. Cell voltages vary between 1.8 and 2.5 V. In one mode of operation (83) the electrolyte is circulated through the cell at a rate of about 3% of the total volume per minute with the solution usually being introduced at the bottom of the cell. The electrolyte is replenished every one to two hours by drawing off about 10–20% of the total electrolyte volume for treatment with $MnCO_3$ or MnO, followed by filtration, and is then returned to the electrolysis cycle.

In an alternative procedure (84), the electrolyte is pumped through the cells at such a rate that the outlet concentration is 50 g/L $MnSO_4$ and 67 g/L H_2SO_4. This spent electrolyte is then mixed with equal parts of make-up solution containing 150 g/L $MnSO_4$ and the mixture returned to the electrolysis step. The electrolysis is continued over a period of days and terminated when the EMD layer deposited on the anode reaches a specific thickness, usually on the order of 1–3 or 6–8 mm. Following completion of the electrolysis cycle, the entire electrode assembly is removed from the cell for removal of the deposited EMD, either manually or by an automated system (85). The product is repeatedly washed with water to extract the occluded acid (83) and dried at about 85°C in air.

The current efficiency in the electrolysis step is 90–95%, making the energy requirements on the order of 0.45 kWh/kg of EMD. Oxygen is generated at the anode as the principal by-product. This can become significant in electrolytes having high sulfuric acid concentration. At the cathode, a mole of hydrogen is generated for each mole of EMD produced.

The main disadvantage of producing EMD in the form of a solid deposit on the anode is that the process must be interrupted to remove the anodes from the cells. Stripping the MnO_2 is a labor-intensive operation. A number of continuous processes have been devised to generate the MnO_2 as a precipitate that collects at the bottom of the cell where it can be removed without interruption of the electrolysis (86–89).

Newer technology, the suspension-bath process, allows small manganese dioxide particles to adsorb on the electrode surface, thus allowing for higher current densities to be used during electrolysis (90). The resulting manganese dioxide has a macroporous structure, even though some of the micropore area (BET surface are $= 10–25\ m^2/g$) is lost (82).

6. Manganese(V) Compounds

Manganese(V) appears to exist only as the oxyanion $MnO_4{}^{3-}$ and is generally referred to as manganate(V); occasionally the term hypomanganate is used. The pentavalency of manganese was only recognized in the 1940s (91). Historically, the compounds were considered mixtures of Mn^{4+} and Mn^{6+}. Selected manganese(V) compounds and their physical properties are given in Table 14.

The alkali manganates(V) in strongly alkaline solution (45–50% at 0°C) are all blue. In water these manganate(V) compounds instantly disproportionate into manganate(VI) and MnO_2. Lithium manganate(V), prepared by reaction of $LiMnO_4$ and excess LiOH at 124°C, is an exception. This compound is relatively stable in 3% LiOH solution at 0°C and in absolute methyl alcohol.

The most important manganese(V) compound is K_3MnO_4, a key intermediate in the manufacture of potassium permanganate. Potassium manganate(V) is an easily crystallized salt obtained by reduction of potassium permanganate using sodium sulfite in strong sodium hydroxide solution. This was the first compound to be recognized as exclusively pentavalent.

In the early days of $KMnO_4$ manufacture, the yield was only two-thirds of the theoretical; the yield of $NaMnO_4$ never exceeded one-half theoretical. It is now known that the formation of manganate(VI) from MnO_2 passes through a manganate(V) step.

$$2\ MnO_2 + 6\ KOH + 1/2\ O_2 \longrightarrow 2\ K_3MnO_4 + 3\ H_2O$$
$$2\ K_3MnO_4 + H_2O + 1/2\ O_2 \longrightarrow 2\ K_2MnO_4 + 2\ KOH$$
$$MnO_2 + 2\ KOH + 1/2\ O_2 \longrightarrow K_2MnO_4 + H_2O$$

The reaction conditions favoring the formation of manganate(V) do not favor the oxidation of K_3MnO_4 to K_2MnO_4. This latter requires a lower temperature, lower KOH concentration, and higher H_2O concentration.

Although sodium manganate(V) can be made from NaOH and MnO_2 in an oxidizing melt, it is not possible to oxidize Na_3MnO_4 to Na_2MnO_4 using oxygen. Extracting a Na_3MnO_4 melt with water results in disproportionation to Na_2MnO_4 and manganese dioxide.

The intermediate formed in the oxidation of alkenes by permanganate ion is considered a cyclic manganate(V) ester (92). Investigations have suggested that manganate(V) intermediates play a significant role in virtually all permanganate oxidation reactions. It is therefore the further reactions of the manganate(V) intermediates, either oxidation or disproportionation, that are responsible for the dependence of the reaction rates and product composition based on basicity of the system (93). Additionally, a manganese(V) peroxo complex, considered to be a faster oxidizing agent than permanganate, is postulated as an intermediary in the photochemical decomposition of permanganate ion in solution (94).

7. Manganese(VI) Compounds

The hexavalent state of manganese is represented by a few alkali metal and alkaline-earth metal salts of manganic acid [54065-28-0], H_2MnO_4, which is known only through its sodium, potassium, rubidium, cesium, barium, and strontium salts. Properties of a few of these salts are given in Table 15. In the laboratory, manganate(IV) salts are prepared by heating an aqueous solution of alkali metal permanganate in the presence of an excess of strong alkali, excluding carbon dioxide (95).

$$4\ KMnO_4 + 4\ KOH \xrightarrow{\text{reflux}} 4\ K_2MnO_4 + 2\ H_2O + 2\ O_2$$

In a similar fashion, Na_2MnO_4 is made from $NaMnO_4$ and NaOH. Rubidium manganate(VI) [25583-21-5] and cesium manganate(VI) [25583-22-6] are prepared by mixing a solution of Na_2MnO_4 and a concentrated solution of RbOH or CsOH, respectively, whereby the less soluble Rb and Cs salts precipitate. The practically insoluble barium manganate(VI) can be made by decomposition of $KMnO_4$ in $Ba(OH)_2$ solution, or by adding $BaCl_2$ to a solution of K_2MnO_4, leading to the precipitation of $BaMnO_4$.

Potassium manganate(VI), precursor of potassium permanganate, is made commercially in either a one- or two-stage fusion reaction, or by anodic oxidation of manganese metal or ferromanganese in KOH. X-ray crystallographic studies on potassium manganate(VI) obtained from the reduction of potassium permanganate suggest the manganate(VI) forms orthorhombic crystals having the Pnma space group. There are four molecules in the unit cell. Cell dimensions are $a = 766.7$ pm, $b = 589.5$pm, and $c = 1035.9$ pm. The average Mn–O bond distance is 165.9 ± 0.8 pm and the O–Mn–O bond angle is $109.5 \pm 0.7^\circ$, suggesting that the structure is of a regular tetrahedron. The increase in the Mn–O bond length of approximately 3.0 pm over the permanganate ion is consistent with the molecular orbital view of the manganate ion (96), where the extra electrons are considered to occupy an antibonding orbital.

In aqueous solution, K_2MnO_4 is stable when the KOH concentration is >1 M $[OH^-]$ and in a less alkaline environment, disproportionation (97) occurs according to the following:

$$3\,MnO_4^{2-} + 2\,H_2O \longrightarrow 2\,MnO_4^- + MnO_2 + 4\,OH^-$$

This disproportionation is slow under less than molar alkaline conditions, and instantaneous under neutral or acidic conditions. The equilibrium constant, K_{eq}, for the reaction at 25°C, is as follows (98):

$$K_{eq} = [MnO_4^-]^2[OH^-]^4/[MnO_4^{2-}]^3 = \text{ca } 16$$

The solubility of K_2MnO_4 in 2 M potassium hydroxide at 20°C is 225 g/L and decreases with increasing alkali concentration (99). Potassium manganate is insoluble in organic solvents. Pure potassium manganate(VI) is thermally stable to 600°C. Manganate(VI) can be converted to manganate(VII) by either disproportionation or by oxidation using hypochlorite, ozone, or anodic oxidation.

Alkali manganate(VI) salts are used as oxidants in synthetic organic reactions (100) and their reactions have been observed to be similar to permanganate, except that manganate(VI) exhibits lower reactivity. Additionally, solid $BaMnO_4$ in methylene chloride has been reported to achieve high yields for the oxidation of diols to dialdehydes (101).

8. Manganese(VII) Compounds

Permanganic acid [13465-41-3], $HMnO_4$, is conveniently prepared in the laboratory from barium permanganate and sulfuric acid, or by anodic oxidation of ferromanganese in a divided cell using H_2SO_4 as the electrolyte. The acidity of $HMnO_4$ is comparable to that of HNO_3. Aqueous solutions up to 20% are relatively stable and dilute solutions can be heated to boiling without decomposition. Solutions of permanganic acid can be distilled. This acid is assumed to undergo vapor-phase dissociation into Mn_2O_7 and H_2O. Anhydrous $HMnO_4$ and the dihydrate have been isolated (102), but the monohydrate does not appear to be stable, even at low temperatures and pressures. Anhydrous permanganic acid is hygroscopic and soluble in water, slightly soluble in perfluorodecalin, and insoluble in carbon tetrachloride and chloroform. Anhydrous $HMnO_4$ is a powerful oxidant decomposing violently at 3°C; $HMnO_4{\cdot}2H_2O$ [24653-70-1] decomposes at 18°C. Aqueous solutions of permanganic acid below a concentration of 3 wt % are stable over time, whereas in the concentration range of 5–15% $HMnO_4$, the decomposition rate increases with increasing initial solution concentration at room temperature (103).

The anhydride of permanganic acid, manganese heptoxide [12057-92-0], Mn_2O_7, is a viscous oil which looks metallic green in reflected light and red in transmitted light (Table 16). It is prepared by titrating solid potassium permanganate with concentrated sulfuric acid at 25–35°C. Manganese heptoxide is hygroscopic and forms $HMnO_4$ with water. This anhydride is hazardous. Its sensitivity to shock and temperature is comparable to that of mercury fulminate [628-86-4] (see MECRURY COMPOUNDS). Manganese heptoxide reacts with many oxidizable materials such as alcohol, ether, sulfur, and phosphorus with explosive force.

Manganese(VII) compounds containing the cationic permanganyl ion, MnO_3^+, are known. For example, permanganyl fluoride [15586-97-7], MnO_3F, is obtained as a green vapor when $KMnO_4$ reacts with anhydrous HF. The highly unstable gaseous green-violet permanganyl chloride [15605-27-3], MnO_3Cl, is prepared by passing dry HCl gas through a solution of $KMnO_4$ in concentrated sulfuric acid at −50°C (104).

The purple permanganate ion [14333-13-2], $MnO_6{}^-$ can be obtained from lower valent manganese compounds by a wide variety of reactions, eg, from manganese metal by anodic oxidation; from Mn(II) solution by oxidants such as ozone, periodate, bismuthate, and persulfate (using Ag^+ as catalyst), lead peroxide in acid, or chlorine in base; or from MnO_4^{2-} by disproportionation, or chemical or electrochemical oxidation.

The overall decomposition of solid potassium permanganate in the temperature range of 250–300°C leads to the formation of a delta-manganese dioxide (shown in brackets) and can be represented as follows:

$$10\ KMnO_4 \xrightarrow{250-300^\circ C} 2.65\ K_2MnO_4 + [2.35\ K_2O{\cdot}7.35\ MnO_{2.05}] + 6\ O_2$$

The enthalpy of decomposition has been determined to be approximately 10 kJ/mol (2.4 kcal/mol) of $KMnO_4$ (105). The decomposition has been shown to occur in two stages. In the first stage essentially all of the $KMnO_4$ decomposes into $K_3(MnO_4)_2$ and δ-MnO_2 accompanied by the release of oxygen; in the second stage the $K_3(MnO_4)_2$ decomposes forming additional δ-MnO_2 and oxygen.

Aqueous potassium permanganate solutions are not perfectly thermodynamically stable at 25°C, because MnO_2, not $MnO_4{}^-$, is the thermodynamically stable form of manganese in water. Thus permanganate tends to oxidize water with the evolution of oxygen and the deposition of manganese dioxide, which acts to further catalyze the reaction.

$$4\ MnO_4^- + 4\ H^+ \longrightarrow 4\ MnO_2 + 2\ H_2O + 3\ O_2\ (g)$$

The kinetics of the reaction are relatively slow and permanganate solutions exhibit greatest stability around a neutral pH. The decomposition rates increase below pH 3 or above pH 10. Potassium permanganate solutions are stable at elevated temperatures, up to approximately 3 *N* sodium hydroxide, above which decomposition into manganate occurs.

The density of the alkali metal permanganate salts increases with the atomic number of the Group 1 (IA) cation, whereas the corresponding aqueous solubility decreases (106). At room temperature aqueous solubility decreases from about 900 g/L for $NaMnO_4$ to 60 g/L for $KMnO_4$, and to 2.5 g/L for $CsMnO_4$. The solubility of potassium permanganate in water as a function of temperature is as follows:

Temperature, °C	Solubility of $KMnO_4$ g/L	Temperature, °C	Solubility of $KMnO_4$ g/L
0	27.81	40	125.16
10	43.93	53	182.37
20	64.95	63	225.83
30	90.55	70	286.36

The aqueous solubility of $KMnO_4$ in g/Lg/L at various solution temperatures in °C can be estimated by

$$\text{solubility}_{KMnO_4} = 30.55 + 0.796\,T + 0.0392\,T^2$$

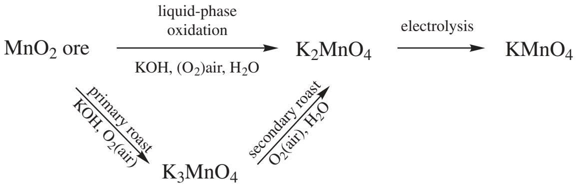
The heat of dissolution of potassium permanganate in water varies between 41.84 kJ/mol (10.62 kcal/mol) in dilute solution to 38.5 kJ/mol (9.20 kcal/mol) as saturation is approached (107). The rate of dissolution is primarily controlled by temperature, particle size distribution of the crystalline potassium permanganate, the amount of energy supplied as agitation, and the final degree of saturation of the resulting solution.

The solubility of potassium permanganate in aqueous potassium hydroxide (108) is shown in Figure 7. Permanganates are soluble in certain nonaqueous solvents such as liquid NH_3, but not in liquid SO_2. Organic solvents such as glacial acetic acid, acetone, acetonitrile, *tert*-butyl alcohol, benzonitrile, pyridine, and trifluoroacetic acid, among others, dissolve $KMnO_4$ to some extent, but the resulting solutions are of limited stability because of the attack by the permanganate ion on the solvent.

Tetraphenylphosphonium permanganate [34209-26-2], $(C_6H_5)_4PMnO_4$, and tetraphenylarsonium permanganate [4312-28-1], $(C_6H_5)_4AsMnO_4$, are nearly insoluble in water, but soluble in organic solvents, thus allowing permanganate oxidations of water-insoluble substrates to be carried out in the homogeneous phase. These salts are obtained when water-soluble forms of the quaternary onium salts, typically the chloride or the bromide, are treated with permanganates.

Crystallographic studies on potassium permanganate suggest that in the solid phase it has an orthorhombic crystal structure, space group Pnma, and four molecules per unit cell. Cell dimensions are $a = 910.5$ pm, $b = 572.0$ pm, and $c = 742.5$ pm. The average Mn–O bond distance in the permanganate ion is 162.9±0.8 pm and the average O–Mn–O bond angle is 109.4±0.7°. Thus the permanganate ion can be visualized as a manganese atom surrounded by four oxygen atoms at the corners of a regular tetrahedron (109).

8.1. Manufacture of Potassium Permanganate. Potassium permanganate may be manufactured by the one-step electrolytic conversion of ferromanganese to permanganate, or by a two-step process involving the thermal oxidation of manganese(IV) dioxide of a naturally occurring ore into potassium manganate(VI), followed by electrolytic oxidation to permanganate:



Depending on the means of conversion of manganate(V) to (VI), the process may be classified as a roasting or liquid-phase process (Fig. 8). The roasting process employs a solid reaction mixture having a molar ratio between MnO_2 and KOH in the range of 1:2 to 1:3. In contrast, the liquid-phase route operates at a higher (°1:5) molar ratio between MnO_2 and KOH.

The roasting process, or variations of it, are most common. Liquid-phase processes are in operation, however, both in the United States and the former USSR. The former USSR is the only place where $KMnO_4$ was produced by anodic oxidation of ferromanganese.

Liquid-Phase Oxidation. In the early 1960s, both Carus Chemical Co. (La Salle, Illinois) and a plant in the Soviet Union started to operate modernized liquid-phase oxidation processes.

The USSR process (118–120) is discontinuous, uses turbine-agitated, low pressure reactors having a volume of 4 m^3 each, and processes 2000–2500 L/batch. Preconcentrated molten potassium hydroxide (70–80%) is added to the reactor with a quantity of 78–80% MnO_2 ore (<0.1–mm particle size) resulting in a 1:5 molar ratio of MnO_2:KOH. Air, or O_2, is introduced below the liquid level by a sparging device at such a rate that a positive pressure of 186–216 kPa (1.9–2.2 atm) is maintained. The temperature is kept at 250–320°C for the duration of the reaction, which requires approximately 4–6 h for completion. The reaction mixture, which reportedly remains fluid during the entire time, is then emptied through a siphon. Conversion of MnO_2 to K_2MnO_4 ranges from 87–94%. To isolate the potassium manganate from the melt, recycle KOH of 10–12% concentration is added until the overall caustic potash concentration is about 450–550 g/L. Upon cooling to 30–40°C, the K_2MnO_4 settles and is separated by centrifugation for use in the preparation of the electrolyte. This process is reported to work well, even with high (up to 11%) silica ores.

The Carus liquid-phase oxidation process is similar in principle; however, it is operated continuously, its oxidation reaction vessels are of a much larger scale, and the separation of the manganate intermediate from the caustic melt is accomplished without dilution by means of filtration (qv) (121–123).

Roasting Processes. The first step in roasting processes is the formation of K_3MnO_4 from MnO_2 ore. This is promoted by high temperature and high KOH and low H_2O concentration. The second step oxidizes Mn(V) to Mn(VI). A lower temperature and control of moisture in the air is used.

In a typical procedure, a slurry of 50% potassium hydroxide solution and finely ground manganese dioxide ore (MnO_2:KOH = 1:2.3–2.7) is sprayed into an atmosphere of preheated (390–420°C) air contained in a rotary kiln or a spray chamber. Formation of K_3MnO_4 occurs almost instantly, ie, within one minute or less. The rate-determining step is the removal of the water from the melt (124), but the specific reactivity of the ore also can be a factor. The material is ground in a ball mill and then transferred to another rotary kiln or a fluidized-bed reactor kept at 180–220°C. Controlled amounts of water are added in a fine spray bringing the average water content of the air to about 300 g/m^3. The retention time in the secondary reactor may be up to 3–4 h for preground roast, and probably on the order of 20 h for unground material. Conversion of the MnO_2 in the ore to K_2MnO_4 ranges from 85–90%.

The rotary kilns used in manganate production in Bitterfeld, Germany, are 5.5 m long and have a diameter of 1.75 m (125). For primary roasting, these are internally heated by hydrogen-fueled burners which minimize the problem of crust formation on the inner walls of the kiln. The use of hydrogen also reduces the amount of K_2CO_3 formed in the course of the roasting process. A total of eight kilns are available.

Newer manganate roasters are said to be significantly larger having diameters of about 2 m and lengths of 10 m. Larger dimensions permit distribution of the $KOH–H_2O/MnO_2$ spray over a wider area, and thus prevent undesirable agglomeration of the roast. Figure 9 shows a typical kiln arrangement.

Electrolysis. Although the oxidation of manganate(VI) to permanganate can be accomplished by chlorination, ozonation, or disproportionation (126), electrolysis is the preferred method. Reactions are as follows:

$$\textit{Anode}\quad MnO_4^{2-} \longrightarrow MnO_4^- + e^-$$

$$\textit{Cathode}\quad H_2O + e^- \longrightarrow 1/2\ H_2 + OH^-$$

$$\textit{Overall}\quad MnO_4^{2-} + H_2O \longrightarrow MnO_4^- + 1/2\ H_2 + OH^-$$

The primary side reaction at the anode is the oxidation of hydroxyl ion to oxygen. In an undivided cell, a side reaction takes place also at the cathode, ie, the unwanted reduction of $MnO_4{}^{2-}$ and $MnO_4{}^-$ to lower valent manganese species.

Anode metals include nickel, Monel, stainless steel, and mild steel; cathode metal is practically always mild steel. Most cell designs do not have diaphragms and undesirable reductive effects at the cathode are minimized by making the cathode area very small in comparison to the anode area. Diaphragms, if employed, are made of Asbestos (qv) sheet or plastic-impregnated fabric. Permanganate cells are mostly monopolar, ie, all anodes on the one hand, and all cathodes on the other hand, are connected in parallel. Bipolar designs are used occasionally. To prevent depletion of manganate ion at the anode, the electrolyte in the cell must be well agitated. Built-in agitators, bubbling gas through the electrolyte, or gravity or pumped electrolyte flow through the cell is used. In batch-type cells, the $KMnO_4$ is allowed to crystallize in the cell and is collected in the usually conical-shaped bottom section. Batch-type cells are frequently run using unfiltered electrolyte containing substantial concentrations of suspended solids, largely consisting of ore gangue and precipitated MnO_2. In continuously operated cells, the permanganate is crystallized outside of the cells in crystallizers specially designed for that purpose. These cells are operated only on filtered electrolyte. The operating temperature of permanganate cells is 40–60°C and cell voltage is between 2.3 and 3.0 V. For undivided cells, anode current densities range from 50–1500 A/m^2 and cathode current densities are 500–5000 A/m^2 or higher. Current efficiencies are in the range of 60–80%.

Manganate(VI) formed in the initial oxidation process must first be dissolved in a dilute solution of potassium hydroxide. The concentrations depend on the type of electrolytic cell employed. For example, the continuous Carus cell uses 120–150 g/L KOH and 50–60 g/L K_2MnO_4; the batch-operated Bitterfeld cell starts out with KOH concentrations of 150–160 g/L KOH and 200–220 g/L K_2MnO_4. These concentration parameters minimize the disproportionation of the K_2MnO_4 and control the solubility of the $KMnO_4$ formed in the course of electrolysis.

The raw potassium manganate(VI) from the secondary roaster or the liquid-phase oxidizer contains a fair amount of insoluble material such as unreacted MnO_2 and ore gangue. In most continuous processes, these insolubles are removed by sedimentation using thickeners or filtration and are disposed of as waste.

The Carus cell is of continuous flow-through bipolar design. The anode side of its rectangular bipolar electrode consists of a Monel screen attached to a steel back plate; the cathode side is mostly covered with a corrosion-resistant plastic material, except for regularly spaced exposed mild steel tips that are also connected to the back plate, and extend through the plastic. A single 4 m^3 volume cell can contain up to 60 electrodes. Cell frames and flow dividers are made of nonconductive materials. Both the electrolyte and the electric current flow are in series. The assembled cell, which contains the electrodes in the horizontal position, is mounted at an incline to allow the electrolyte and the cell gases (H_2 and O_2) to flow in the same direction. Current flow through the cell is 1.2–1.4 kA. Anode current density ranges from 85–100 A/m^2; the cathode current density is estimated to be about 13–15 kA/m^2. Current yields of up to 90% can be obtained .

The monopolar batch-type Bitterfeld cell is circular in shape having a flat bottom. The anodes consist of concentrically arranged Monel sheets; the cathodes, composed of mild steel rods, are placed in the annular space between the anodes. The closed cell has its own agitator consisting of a helix mounted on the vertical shaft and a stirring blade rotating near the bottom of the cell. The crystalline permanganate along with the sludge produced is periodically withdrawn by a bottom-discharge valve. The effective cell volume is about 4 m^3, voltage is 2.2–2.5 V, and the current flow 5000 A. Anode current density is 70 A/m^2; cathode current density is 700 A/m^2. The operating temperature is approximately 45°C, current yield is about 75%, and the energy required for electrolysis is estimated at 0.7 kWh/kg $KMnO_4$.

The electrolyte is unfiltered leach containing 200–250 g/L K_2MnO_4 and 120–150 g/L KOH. It takes about 45 h to bring the K_2MnO_4 concentration down to 20–30 g/L, at which point the electrolysis is terminated.

Crystallization can take place either within the cell container or in separate crystallizers. Using unfiltered electrolyte, the raw product which contains on the order of 90% $KMnO_4$ must still be purified by recrystallization. The crystallizers range from simple agitated tanks equipped with plate coolers or cooling jackets to continuous vacuum crystallizers. The latter, used by Carus Chemical Co., give a product that usually meets the specifications of at least technical-grade $KMnO_4$. Pharmaceutical and reagent-grade are obtained by further recrystallization.

The potassium permanganate crystals are dried at atmospheric pressure below 150°C, cooled, and packaged. Care is taken to prevent heating the product above 200°C during drying to avoid autocatalytic exothermic decomposition of the product.

In the electrolysis of K_2MnO_4, one mole of KOH is coproduced for every mole of $KMnO_4$ generated. This by-product potassium hydroxide must be recovered and utilized. For recycling, it also needs to be purified (130). Alternatively, the KOH can be converted into potassium carbonate by treatment with CO_2 in the red-lye process (131).

Electrolytic Oxidation. Electrolytic oxidation of ferromanganese or manganese metal is a one-stage process that circumvents the problem of ore impurities. Moreover, this procedure can be used with low caustic concentrations at room temperature. This process is based on the following reactions:

$$\begin{aligned} &\textit{Anode} \quad 2\,\mathrm{Mn}^0 + 16\,\mathrm{OH}^- \longrightarrow 2\,\mathrm{MnO}_4^- + 8\,\mathrm{H_2O} + 14\,e^- \\ &\textit{Cathode} \quad 14\,\mathrm{H_2O} + 14\,e^- \longrightarrow 7\,\mathrm{H_2} + 14\,\mathrm{OH}^- \\ &\textit{Overall} \quad 2\,\mathrm{Mn}^0 + 2\,\mathrm{OH}^- + 6\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{MnO}_4^- + 7\,\mathrm{H_2} \end{aligned}$$

The process is most successful using pure manganese metal, but high grade ferromanganese, containing >80% Mn, is more economical. Passivation of the electrodes resulting in higher voltage drops and low current efficiencies can be a problem.

A procedure for industrial-scale (500 t/yr) production of potassium permanganate using this process was adapted for the Rustaw Nitrogen Fertilizer Plant (132). For the casting of anodes, ferromanganese having at least 80%Mn is melted with the addition of cryolite as a flux in an electric furnace. The precast is in the form of a copper coil through which cooling water is passed to keep the cell operating temperature at 20°C. Each cell is operated at 4.5 V and 6500 A. Current densities are 2300 A/m^2 at the anode and 1800 A/m^2 at the cathode. Initially, the electrolyte contains 250 g/L KOH, which gradually decreases to about 30 g/L during the course of the electrolysis. The crystalline $KMnO_4$ generated collects in the bottom of the cone, along with a sludge largely consisting of hydrous iron oxides, manganese dioxide, and SiO_2. The permanganate is separated and purified by recrystallization and the sludge, after drying, is said to have use as a catalyst, a depolarizer in dry cells, or an adsorptive agent for sulfur compounds.

The production of $KMnO_4$ by direct anodic oxidation of ferromanganese is energy intensive. Current efficiencies are on the order of 40% at best, and at the practically required voltages of 4.5 V or higher, the power consumption for the electrolysis alone is estimated to be about 15 kWh/kg $KMnO_4$. Operation at 20°C also requires a significant expense for cooling. This method is attractive under conditions where only low grade Mn ores having high percentages of alkali-soluble impurities (Si, Al) are available, or where those ores can be used to produce ferromanganese.

8.2. Oxidation Reactions. Potassium permanganate is a versatile oxidizing agent characterized by a high standard electrode potential that can be used under a wide range of reaction conditions (100,133–141). The permanganate ion can participate in a reaction in any of three distinct redox couples, depending on the nature of the reducing agent and the pH of the system. Typically permanganate oxidation reactions are conducted in an aqueous environment, or in organic cosolvents, which exhibit some degree of stability toward the oxidant. Solvents include acetone, acetic acid, acetic anhydride, *t*-butanol, ethanol, pyridine, and trifluoroacetic acid. Permanganate oxidizes hydrogen, carbon monoxide, and hydrogen peroxide under a variety of pH conditions, and the halides under acidic conditions.

Under extremely alkaline conditions, $\mathrm{pH} > 12$, potassium permanganate reacts involving a single-electron transfer, resulting in the formation of manganate(VI).

$$\mathrm{MnO_4^-} + e^- \longrightarrow \mathrm{MnO_4^{2-}}$$

In the pH range of 3.5 to 12, and in the presence of most reducing agents, permanganate reactions normally undergo a three-electron exchange resulting in the formation of hydrous manganese dioxide.

$$\mathrm{MnO_4^-} + 2\,\mathrm{H_2O} + 3\,e^- \longrightarrow \mathrm{MnO_2} + 4\,\mathrm{OH^-}$$

Under acidic conditions, $\mathrm{pH} < 3.5$, and in the presence of certain reducing agents, the permanganate ion can undergo a five-electron exchange resulting in the divalent manganese ion.

$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,e^- \longrightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O}$$

The pH has an additional effect on permanganate reactions because the pH can cause a change in the substrate, altering the subtrate's degree of susceptibility toward oxidation. For potassium permanganate, as a general rule (138) for an anion, $\mathrm{Z^{2-}}$, the degree of oxidation follows:

$$\mathrm{Z^{2-}} > \mathrm{HZ^-} > \mathrm{H_2Z} > \mathrm{H_3Z^+}$$

Additionally, the enthalpies of activation (142) for the permanganate oxidation of organic compounds is characteristically low in the range of 21–42 kJ/mol (5.1–10.0 kcal/mol). Figure 10 contains functional groups oxidized by $\mathrm{KMnO_4}$.

One of the most well-known reactions of potassium permanganate is the oxidation of unsaturated compounds. Alkenes are readily oxidized by potassium permanganate under mild conditions which include a pH in the range of 4–8 and ambient temperature. The initial oxidation product is a diol or hydroxyketone, which with additional permanganate is further cleaved into carboxylic acids. The oxidation of alkenes (see Fig. 11) involves the formation of a cyclic manganese ester, which accounts for the observations that the hydroxyl groups are added in a cis fashion and the oxygen atoms come from the permanganate ion.

Primary and secondary alcohols are readily oxidized to aldehydes and ketones under alkaline conditions. Aldehydes, both aliphatic and aromatic, are converted into the corresponding carboxylic acids. Ketones are generally oxidation resistant unless sufficient alkali is present to effect enolization. The enol can be oxidatively cleaved.

Phenols as a compound class are readily oxidized by potassium permanganate and, if sufficient oxidant is added, Phenol (qv) can be completely oxidized into carbon dioxide and water.

$$3\,C_6H_5OH + 28\,KMnO_4 + 5\,H_2O \xrightarrow{\text{pH } 8.5-9.5} 18\,CO_2 + 28\,KOH + 28\,MnO_2$$

Less than stoichiometric amounts of permanganate, added for phenol oxidation, results in ring cleavage and the formation of mesotartaric, formic, and oxalic acids as degradation products (143). Phenols having electron-withdrawing substituents such as halogen or nitro groups are more resistant to permanganate oxidation than phenol or methyl-substituted phenols.

Primary aromatic amines are readily oxidized by neutral or alkaline potassium permanganate, and complete mineralization into carbon dioxide, ammonia, and water can occur if sufficient oxidant is added (144). Aliphatic amines are also rapidly oxidized by neutral or alkaline permanganate, however multiple oxidation products are possible. Oxidation of primary, secondary, or tertiary amines containing hydrogen on carbon bonded to the amine nitrogen, are oxidized rapidly and at high yields by neutral potassium permanganate in aqueous *t*-butanol, at 60–80°C. The corresponding aldehyde or ketone results (145).

Organic sulfur compounds are readily oxidized by permanganate. Permanganate oxidizes aliphatic thiols to disulfides and aromatic thiols to sulfonic acids. Sulfides and sulfoxides are oxidized by permanganate to sulfones. Disulfides are generally resistant to oxidation by permanganate. Organometallic compounds such as tetraethyllead [78-00-2] (146) and tetrabutyltin (147) can be oxidized by potassium permanganate.

Under extreme pH, ie, conditions such as very high acidity, an increase in oxidation rate can result, presumably through the formation of permanganic acid, $HMnO_4$.

Permanganate salts generally exhibit a lack of solubility in the solvents which are suitable for many organic compounds. Phase-transfer reagents such as quaternary ammonium compounds (148) are used to bring the oxidant and the reactant into a common phase. Crown ethers, which complex the cation in the permanganate salt, are also used for phase transfer of permanganate ion into the organic phase (149). Complexing the permanganate's cation, or replacing it with a quaternary ammonium or phosphonium ion, allows the permanganate to be dissolved in nonpolar solvents such as benzene or methylene chloride (150). This results in a mild, but effective oxidizing agent, where olefins can be converted by $KMnO_4$ in good yields into either 1,2-diols or aldehydes.

The use of solid supports in conjunction with permanganate reactions leads to modification of the reactivity and selectivity of the oxidant. The use of an inert support, such as bentonite (see CLAYS, SURVELY), copper sulfate pentahydrate, molecular Molecular Sieves (qv) (151), or silica, results in an oxidant that does not react with alkenes, but can be used, for example, to convert alcohols to ketones (152). A solid supported permanganate reagent, composed of copper sulfate pentahydrate and potassium permanganate (153), has been shown to readily convert secondary alcohols into ketones under mild conditions, and in contrast to traditional permanganate reactivity, the reagent does not react with double bonds (154).

Heterogeneous permanganate oxidation of alkenes employing moist alumina as the solid support and methylene chloride as the solvent also results in cleavage of carbon–carbon double bonds. Aldehydes are the products (155). In addition to mild reaction conditions, heterogeneous permanganate oxidation reactions result in easy work-up and product isolation. The spent oxidant is adsorbed onto the solid support and is easily removed through filtration. The product is recovered through evaporation of the solvent.

Solid sodium permanganate monohydrate has been shown to be a selective synthetic reagent (156). It is typically used in hexane for the heterogeneous oxidation of aldehydes, alcohols, and sulfides. Synthetic methodology based on crystal surfaces exhibited greater selectivity, higher yield, and easier work-up as compared to aqueous permanganate reactions.

9. Economic Aspects

U.S. exports of manganese ore, manganese ferroalloys, and manganese dioxide increased during 2003, while exports of manganese metal decreased. The biggest year-to-year changes were for manganese dioxide and manganese ore, which increased by 23% and 22%, respectively, compared with 2002. Table 17 is a list of the U.S. producers of manganese products in 2003 (11).

Among U.S. imports of manganese chemicals on a gross weight basis, those of manganese dioxide increased by 35% from those in 2002. Australia continues to be the leading supplier of manganese dioxide, supplying 59% of the imports. The leading sources of potassium permanganate continued to be the Czech Republic and India, with 61% and 39%, respectively in 2003. U.S. Bureau of the Census data for 2003 for imports under the classification of sulfates, alums, peroxosulfates, and other suggested that imports of manganese sulfate, on a gross weight basis, increased by 18% as the imports of these materials increased by 65% for China. Imports from Mexico decreased by 3%.

Primary or nonrechargeable alkaline batteries, in which electrolytic manganese dioxide is used, continued to expand their share of the market. Primary batteries continue to find growing application, particularly in digital cameras. Sanyo Energy (USA) introduced a new primary lithium-manganese dioxide cell which can replace two alkaline AA batteries (157). In the secondary or rechargeable market, lithium-based technologies, including lithium batteries comprising lithium manganese oxides are gaining ground. Lithium batteries recharge faster than nickel ones and are very light weight. They are currently used in consumer electronics (cell phones, laptop computers, and PDAs) and in military electronics such as radios, mine detectors, and thermal weapons sights (158).

10. Analytical Chemistry

The general analytical chemistry of manganese is discussed elsewhere (159–164). A review covering more modern techniques, specifically for manganese dioxide, has also been published (165). A series of analytical techniques and procedures have been developed to study the metabolic fate of manganese (166,167).

The presence of manganese can be detected by formation of the purple MnO_4^- upon oxidation using bismuth or periodate in acidic solution. A very sensitive test is the reaction of Mn^{2+} and formaldoxime hydrochloride in aqueous alkaline solution, which also leads to the production of a purple MnO_4^- color. Modern quantitative methods for manganese determination rely heavily on instrumentation. For the analysis of high (>0.1% Mn) concentrations of manganese, potentiometric titration involving the titration of manganese(II) ion with permanganate ion in a neutral pyrophosphate solution is the most appropriate analytical method. This titration results in formation of a pyrophosphate complex of trivalent manganese (168).

$$4\,Mn^{2+} + MnO_4^- + 8\,H^+ + 15\,H_2P_2O_7^{2-} \longrightarrow 5\,Mn(H_2P_2O_7)_3^{3-} + 4\,H_2O$$

For low to medium (<0.0.1% Mn) concentration, atomic absorption/emission spectroscopy is widely used (169–170). Manganese can be determined by atomic absorption spectroscopy in an air–acetylene flame without significant interferences and a Mn concentration of 0.03 mg/L results in approximately 1% absorption at the 279.5 nm resonance line (171). The detection limit for manganese by flame atomic absorption is around 0.01 ppm, the detection limit by furnace atomic absorption is 0.002 ppm, and the detection limit via inductively coupled plasma emission spectroscopy is about 0.005 ppm. Spectrophotometry is also frequently used for the analysis of manganese using colorimetric methods. A comprehensive review has been published (172). There are a wide range of direct color-forming reactions of manganese and organic ligands.

The classical spectrophotometric method involves the oxidation of manganese to permanganate. Characteristic ultraviolet and visible spectra of the various oxymanganate ions are shown in Figure 12 (173). Convenient wavelengths for measurements of permanganate and manganate(VI) are 525 and 603 nm, respectively. Because manganese dioxide interferes, this material must first be removed by filtration or centrifugation.

Solid potassium permanganate is usually assayed volumetrically using sodium oxalate.

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

Even though the mechanism of the reaction between oxalate and permanganate is extremely complicated, titration under acidic conditions is extremely accurate. This is the recommended method for standardization of permanganate solutions.

An alternative method for the analysis of permanganate is the use of conventional iodometric methods (174) where excess potassium iodide is added to a solution of permanganate under acidic conditions. The liberated iodide is then titrated with standard thiosulfate solution using starch as an indicator.

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O$$
$$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$$

The iodide method can also be applied to the analysis of other manganese species, but mixtures of permanganate, manganate, and MnO_2 interfere with one another in the iodometric method.

The proportion of manganese dioxide in ores and synthetic products is commonly measured by determining the samples active oxygen. This is a measurement of the amount of manganese having a valence greater than two. The weighed material is digested with a measured excess of reducing agent (potassium iodide, sodium oxalate, ferrous sulfate, arsenious oxide, or vanadyl sulfate) and the unconsumed reducing agent determined by titration (162,164). Using differential thermal analysis (DTA), it is possible to determine the presence of specific MnO_2 phases in the mixture (175).

A detailed review of the methods for determination of low manganese concentration in water and waste is available (176). A review on the speciation of Mn in fresh waters has been reported (177). Reviews for the chemical analysis of Mn in seawater, soil and plants, and air are presented in References (178,179), and (180), respectively.

11. Health and Safety Factors

Manganese appears to be an essential trace element for all living organisms (see MINERAL NUTRIENTS). Its concentration in organisms primarily depends on the species. Plants contain between 1–700 mg/kg, ocean fish between 0.3–4.6 mg/kg, and muscles of mammals 0.2–3 mg/kg (181). Manganese appears to be particularly stored and concentrated in tissues rich in mitochondria. Manganese, a cofactor for the enzyme pyruvate carboxylase (182), is also thought to act as a nonspecific activator for the enzymes succinate dehydrogenase, prolidase, arginase, alkaline phosphatase, farnesyl pyrophatase, superoxide dismutase, glycosyl transferases, and adenosine triphosphatases (183).

Manganese is considered an essential micronutrient for plants, which are thought to assimilate the element in the divalent state from soil. Deficiency of manganese can be a significant factor in reducing crop yields, which has been shown to occur in soils of high organic matter and pH values above 6.5 (184). Plant species vary widely in manganese requirements, as well as tolerance for excess manganese concentrations within their tissues. Data from a variety of species suggest the manganese deficiency occurs when plant tops contain less than about 20 ppm manganese on a dry weight basis. A concentration of up to about 500 ppm manganese is considered adequate. Manganese concentrations typically greater than about 500–1000 ppm have been reported to be toxic (185).

Studies have shown manganese to be required for good health in animals (186). Manganese deficiency in animals includes impaired growth, skeletal abnormalities (187), and altered metabolism of (qv) (188) and lipids. Manganese is considered an essential trace element for humans, although there is no direct evidence for this. The National Academy of Sciences recommended dietary allowance for adults is 2.5–5.0 mg/d of manganese (189). The usual daily intake of manganese for humans is in the range of 2–9 mg/d of Mn and comes primarily from food (190).

Food	Manganese content, mg/kg
nut products	18.21–46.83
grain products	0.42–40.70
legumes	2.24–7.73
fruits	0.20–10.38
vegetables	0.42–6.64
meat, fish, and eggs	0.10–3.99
beverages	0.0–2.09
milk	0.02–0.49

Groundwater concentrations of manganese are generally <100 μg/L, although values ≥ 1000 μg/L are not uncommon. Surface water sources contain an average of 58 μg/L (191) and U.S. rivers have a median value of 24 μg/L (192,193).

Environmentally, manganese-bearing particulate matter is usually removed from air using dust collecting devices such as electrostatic precipitators, filter systems, cyclones, or wet scrubbers (see AIR POLLUTION CONTROL METHODS). In the case of liquids, soluble manganese can be removed from liquid effluents through precipitation as a hydrous oxide by adjustment of the pH to >8.3 using $Ca(OH)_2$, plus the application of an oxidizing agent such as O_2, Cl_2, ClO_2, NaClO, or $KMnO_4$. Aeration is also effective, provided the pH is raised to above 9.4. The final disposal of the resulting manganese dioxide-containing sludges depends on local conditions and regulations. These sludges are usually deposited in landfills.

Inhalation of particulate manganese compounds, such as manganese dioxide, can lead to an inflammatory response in the lungs of both humans and animals. This response is characteristic of all inhalable particulate matter, however, suggesting that the manganese compound is not specifically responsible. Inhalation of soluble manganese compounds does not cause an inflammatory response in the lungs of test rabbits (194). There are reports of increased susceptibility to lung infections reported for both humans and animals where there is a chronic exposure to manganese dusts. This is considered secondary to the irritation caused by the inhaled particulate matter. General population exposure to manganese compounds in the air in nonurban areas is about 5 ng/m^3; in urban areas, 33 ng/m^3; and in source dominated areas, 135 ng/m^3 (195). In the soil, manganese is estimated to be in the 40–900 mg/kg range. The maximum reported is 7000 mg/kg (196). The lowest observed adverse effect level (LOAEL) (197) reported for Mn by inhalation is 0.14 mg/m^3. This results in a chronic exposure by inhalation minimal risk level (MRL) of 0.3 μg/m^3. The dermal absorption of inorganic manganese compounds is not considered toxicologically significant. The primary exposure of the general population to manganese compounds is from diet. Very few poisoning have occurred from ingestion (198).

There is conclusive evidence from human studies that inhalation exposure to high levels of manganese compounds can lead to a disabling syndrome of neurological effects termed manganism (198,199). Clinically, many similarities exist between the syndrome of manganism and Parkinson's disease, a progressive disease resulting from destruction of cells of the basal ganglia; however, manganism is considered a distinct and much more complex disease (200) effecting multiple systems. The onset of the illness may be expressed by slow speech without tone or inflection, dull and emotionless facial expressions, and slow and clumsy limb movements. In the later stages of the disease, walking becomes difficult and a characteristic staggering gait develops. Voluntary movements are accompanied by tremors, and a variety of behavioral changes have also been reported. The incapacitations caused by chronic manganese poisoning result in permanent disability, but the disease is not fatal (201). It has only been documented in workers exposed to high levels of manganese dust or fumes in mines or foundries, typically following several years of exposure. The lowest average concentration of manganese at which a case of chronic manganese poisoning has occurred was 30 mg/m^3, found in a manganese mill (202). The neurological damage produced by prolonged excessive exposure to manganese is mainly irreversible, but some anti-Parkinsonian drugs such as L-dopa, have been reported to reverse some of the neuromuscular symptoms (see NEUROREGULATORS) (203).

Human and animal studies indicate that inorganic manganese compounds have a very low acute toxicity by any route of exposure. The toxicity values for a given Mn compound are shown in Table 18 to depend on the species of test animal as well as the route of exposure. Manganese concentrations as high as 2000 ppm were found to be tolerated by test animals over a six-month period without any ill effects (205).

Only a small (ca 3%) fraction of ingested or inhaled manganese is absorbed, which occurs primarily by the intestines (206). Once absorbed, manganese is regulated by the liver, where it is excreted into the bile and passes back into the intestine, where some reabsorption may occur (207). Manganese is eliminated almost exclusively (>95%) by the bile in the gastrointestinal tract.

Limited laboratory studies have shown manganese to have mutagenic effects in bacteria, bacteriophage T4, and yeast (208). Tests on mice and rats have shown that neither Mn powder nor MnO_2 have any tumorigenic effects. However, manganese(II) acetylacetonate tested in the same series produced malignant neoplasms (209). No evidence of carcinogenic activity of manganese(II) sulfate monohydrate to male or female rats has been found, but male and female mice exposed to this compound had marginally increased incidence of thyroid gland follicular cell adenomas and significantly increased incidence of follicular cell hyperplasia (210). The carcinogenicity of manganese in humans is probably small (211).

Regulations and guidelines have been established in many countries for manganese and its compounds (Tables 19 and 20).

Potassium permanganate under RCRA definition meets the criteria of an ignitable waste, and if discarded is considered a hazardous waste. The reportable quantity (RQ) (218) for potassium permanganate is 45.4 kg (100 lbs) and releases into the environment greater than this value must be reported to the U.S. Coast Guard National Response Center.

12. Uses

The most significant nonferrous use of manganese compounds is for primary batteries, where manganese dioxide is the principal constituent of the cathode mix. In the standard Leclanché cell, zinc and ammonium chloride are mixed to form the electrolyte, a mixture of carbon and MnO_2 forms the cathode, and zinc acts as the anode (219). The principal cell reaction is as follows:

$$Zn^{2+} + 2\,NH_4Cl + MnO_2 + e^- \longrightarrow Zn(NH_3)_2Cl_2 + MnOOH + H^+$$

A secondary reaction forming hetaerolite is also known:

$$Zn^{2+} + 2\,MnO_2 + 2\,e^- \longrightarrow ZnO{\cdot}Mn_2O_3$$

The cathode mix for a Leclanché primary battery consists of 50–60% manganese dioxide ore, 5–10% acetylene black, 10–20% ammonium chloride, and 3–12% zinc chloride. The remainder is water (see BATTERIES, PRIMARY CELLS).

Battery-active manganese dioxides include the naturally occurring manganese ores, chemical manganese dioxides, or electrolytic manganese dioxides. The highest activity for battery use has been attributed to γ-phase manganese dioxide, which exhibits poor crystallinity. Generally, the energy intensity of dry cells increases as the proportion of synthetic manganese dioxide added to the cathode mixture increases (220,221). Thus naturally occurring manganese dioxide ores have the highest use in low cost general-purpose batteries. Heavy-duty cells utilize mixtures of native ore, EMD, and zinc chloride as the electrolyte.

Primary battery system	Volume energy density, kJ/dm^3
carbon	440
heavy-duty	660
alkaline–MnO_2	470–840
Li–MnO_2	ca 1450

In the case of the alkaline manganese dioxide cell, only high quality synthetic manganese dioxide, typically an EMD (222), is used and graphite is the cathode. The anode is an amalgamated zinc. Potassium hydroxide serves as the electrolyte and the reaction can be summarized as follows:

$$Zn^0 + 2\,MnO_2 + H_2O \longrightarrow ZnO + 2\,MnOOH$$

For the alkaline manganese cell, cell voltage corresponds to the reduction (223) of the γ-MnO_2 from $MnO_{1.95}$ to $MnO_{1.5}$. Reduction in oxidation state from

$MnO_{1.95}$ to $MnO_{1.75}$ corresponds to a transformation of the initial gamma phase to the δ-MnO_2 phase. Further reduction leads to the formation of MnOOH. The alkaline manganese cells are characterized by improved high load discharge characteristics, improved storage characteristics, and low temperature performance.

Manganese dioxides prepared from Li_2MnO_3 show promise for use in lithium battery applications. Capacities are reported to be in excess of 200 mA·h/g at a cut-off voltage of 2.0 V, and the electrochemical reaction is reversible. Rechargeable batteries containing a $LiMn_2O_4$ electrode and an aqueous electrolyte have been demonstrated to be a safe and cost-effective alternative to nickel–cadmium and lead–acid batteries (224). Manganese dioxide is a mild oxidizing agent. It is used for the production of various organic compounds, for the curing of polysulfide rubber sealants, and for numerous other industrial applications (Table 21).

Uses of manganese compounds (Table 22) range from a number of agricultural applications to polyester applications. The carbonate and sulfate salts act as the starting material for a variety of other manganese salts. Manganese(II) salts also act as oxidation catalysts. Manganese, in the form of oxides, is 10–30% of the composition of soft ferrite (see FERRITES).

The first known report on the use of potassium permanganate for taste and odor control were given (233) to the London Water Board where the chemical was used at the turn of the century to remove tastes attributed to the growth of *Tabelleria* at the West Middlesex Works (see ODOR MODIFICATION). Potassium permanganate has been readily applied to the treatment of potable water (234). It removes, through oxidation, objectionable tastes and odors present in raw water sources (235); oxidizes soluble iron and manganese into insoluble form (236-238); lessens or eliminates the need for activated carbon treatment, eg, oxidizes As(III) to As(V) which is then efficiently absorbed by alum (239); allows for the reduction in the formation of chlorinated organics (235); and inhibits infestation by the zebra mussel .

Potassium permanganate is also used for wastewater treatment. It oxidizes organic compounds that are toxic or inhibitory to biological systems (242,243). Vinyl chloride [75-01-4] in water can be oxidized by permanganate at a molar ratio of 3.15 parts $KMnO_4$:1 (244). Addition of potassium permanganate, prior to sludge dewatering at a pulp and paper mill wastewater treatment facility, results in the elimination of hydrogen sulfide odor and corrosivity from the dewatering belt presses and downstream areas (245). Potassium permanganate can be used to regenerate manganese greensand that has been used to remove iron and manganese from potable and industrial wastes (246).

Phenol can be oxidized and hence removed, ie, to levels <20 μg/L, from wastewater (247). Moreover, addition of potassium permanganate to the return activated sludge results in reduction of odors issued from the aeration tanks of conventional activated sludge wastewater treatment plants without any change occurring to the microbiology of the system (248).

Printed circuit boards manufacture is aided by the use of $KMnO_4$. Alkaline permanganate solution is used to remove resin smeared on the interior hole wall of multilayered printed circuit boards. Additionally the hole wall is etched, resulting in a surface with excellent adhesion characteristics, for electrodeless copper (249). The alkaline permanganate etchback system containing >60 g/L $KMnO_4$ and 40–80 g/L NaOH at 70–80°C, is effective for difunctional, tetrafunctional, and polyimide resin substrates, where the level of etchback is directly proportional to the immersion time (10–20 min) (250).

Alkaline solutions consisting of approximately 160 g/L $NaMnO_4$ and 60 g/L NaOH at 75°C and contact times in the range of 15 minutes, exhibit high etch rates for printed circuit boards (251,252). The resulting manganese residues can readily be removed by acid neutralization. Addition of K^+, Rb^+, and Cs^+ as co-ions to an alkaline $NaMnO_4$ solution maintains etch rates of resin substrates comparable to solutions of higher $NaMnO_4$ concentrations (253).

Potassium permanganate has been found to be an effective (>99%) detoxicant for decontamination by several carcinogenic compounds, among which are benzo[a]anthracene [56-55-3], benzo[a]pyrene [50-32-8], 7,12-dimethylbenzanthracene [57-97-6], and 3-methylcholanthrene [56-49-5] (254). Acidic permanganate has also been used to detoxify wastewater containing the carcinogen *N,N*-dimethyl-4-amino-4′-hydroxyazobenzene [2496-15-3] (255), whereas alkaline permanganate detoxifies melphalan in laboratory wastes (256). High levels (>99%) of decontamination of carcinogenic laboratory wastes have been obtained using 0.5 *N* H_2SO_4. Materials oxidized included 3,3′-dichlorobenzidine [91-94-1], 3,3′-diaminobenzidine [91-95-2], 1-naphthylamine [134-32-7], 2-naphthylamine [91-59-8], 2,4-diaminotoluene [95-80-7], benzidine [92-87-5], *o*-tolidine [119-937], 4-aminobiphenyl [92-67-1], 4-nitrobiphenyl [92-93-3], and 4,4′-methylenebis(*o*-chloroaniline) [101-14-4] (257,258).

Alkaline permanganate pretreatment of steel for the removal of heat scale and smut prior to acid pickling results in faster descaling and reduced metal attack (see METAL SURFACE TREATMENTS, CASE HARDENING; METAL TREATMENTS). Stainless steel alloys can also be cleaned by alkaline permanganate followed by pickling in nonoxidizing acids (259).

A report that hydrothermally treated potassium permanganate can be used to develop a new layered lithium-manganese oxide cathode material has been published (260).

Several studies on the use of manganese materials to produce different nanotechnologies, including nanotubes from rate-earth manganese oxide-based compounds manganites for possible use in spin-polarized injection and magnetic storage media (261); nanobelts converted from lithium manganese powders for possible nanoelectronic and optoelectronic applications (262); oriented nanobelts of manganese tetraoxide for potential use in nanocables and nanocomputers (263); and semiconductor nanocrystals from manganese-doped zinc sulfides for potential application in nonlinear optical devices (264).

BIBLIOGRAPHY

“Manganese Compounds” in *ECT* 2nd ed., Vol. 13, pp. 1–55, by J. O’Hay, The Harshaw Chemical Co.; in *ECT* 3rd ed., Vol. 14, pp. 844–895, by A. H. Reidies, Carus Chemical Co.; in *ECT* 4th ed., Vol. 15, pp. 991–1055, by Kenneth Pisarczyk, Carus Chemical Company; “Manganese Compounds” in *ECT* (online), posting date: December 4, 2000, by Kenneth Pisarczyk, Carus Chemical Company.

CITED PUBLICATIONS

1. J. Emsley, *The Elements*, Clarendon Press, Oxford, U.K., 1989.
2. R. L. Heath, *Table of the Isotopes, Handbook of Chemistry and Physics*, 57th ed., CRC Press, Boca Raton, Fla.
3. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd ed., John Wiley & Sons, Inc., New York, 1966.
4. T. A. Zordan and L. G. Hepler, *Chem. Rev.* **68**, 737 (1968).
5. C. C. Liang, *Encyclopedia of the Electrochemistry of the Elements*, Vol. 1, Marcel Dekker, New York, 1973, p. 349.
6. J. C. Hunter and A. Kozawa, in A. J. Bard, R. Parson, and J. Jordan, ed., *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, 1988, 429–439.
7. A. K. Covington, T. Cressey, B. G. Lever, and H. R. Thirsk, *Trans. Faraday Soc.* **58**, 1975 (1962).
8. A. Carrington, *M. C. R. Symons, J. Chem. Soc.*, 3373 (1956).
9. G. L. Dettuff, *Bureau of Mines Minerals Yearbook*, U.S. Dept. of the Interior, Washington, D.C., 1977, p. 255; G. Charlot, *Théorie et Méthods Nouvelles d' Analyse Qualitative*, 3rd ed., Masson, Paris.
10. D. B. Wellbeloved, P. M. Craven, and J. W. Waudby, *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A16, VCH, Weinheim, Germany, 1990, p. 80.
11. L. A. Carathers, "Manganese," *Minerals Yearbook*, U.S. Geological Survey, Reston, Va., 2003.
12. B. W. Haynes, *U.S. Bur. Mines Bull.* **679**, 2–32 (1980).
13. G. Hubred, *Miner. Sci. Eng.* **7**, 71 (1975).
14. D. S. Cronan, *Endeavour* **2**(2), 80 (1978).
15. R. G. Burns and V. Burns, *Philos. Trans. R. Soc. London Ser. A.* **286**, 283 (1977).
16. G. P. Glasby and G. L. Hubred, *Comprehensive Bibliography of Marine Manganese Nodules*, Memoir 71, New Zealand Oceanographic Institute, Wellington, 1976, p. 55.
17. M. A. Meylan, B. K. Dugolinski, and L. Fortin, *Bibliography and Index to Literature on Manganese Nodules, Key to Geophysical Records Documentation No. 6*, National Oceanic and Atmospheric Administration, Washington, D.C., 1874–1975, p. 365, p. 60 addendum.
18. National Oceanic and Atmospheric Administration, *Description of Manganese Nodule Processing Activities for Environmental Studies*, 3 Vols., NTIS, Springfield, Va., 1977, PB-274 913, PB-274 914, PB-274 915.
19. R. D. W. Kemmit, in J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, eds., *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press Ltd., Oxford, U.K., 1973, p. 816.
20. U.S. Pat. 4,110,082 (Aug. 29, 1978), V. Michaels-Christopher.
21. F. H. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley-Interscience, New York, 1980, 736–752.
22. J. E. Ellis and R. A. Faltynek, *J. Am. Chem. Soc.* **99**, 1801 (1977).
23. R. Taube, *Chem. Zvesti* **19**, 215 (1965).
24. F. Calderazzo, R. Ercoli, G. Natta, I. Wender, and P. Pino, eds., *Organic Synthesis via Metal Carbonyls*, Vol. 1, Wiley-Interscience, New York, 1968.
25. U.S. Pat. 2,868,697 (Jan. 13, 1959), J. B. Bingeman and A. F. Limper (to Ethyl Corp.).
26. Ger. Pat. 45,071 (Jan. 5, 1966), H. J. Koch and F. Henneberger.
27. H. Marcy, in F. Matthes and G. Wehner, eds., *Anorganisch-Technische Verfahren*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, Germany, 1964.

28. D. F. DeCraene and A. Reidies, *personal communication*, Chemetals Corp., Baltimore, Md., 1979.
29. Brit. Pat. 680,710 (Oct. 8, 1952), A. L. Hock and J. A. Dukes (to Magnesium Elektron Ltd.).
30. T. E. Moore, M. Ellis, and P. W. Selwood, *J. Am. Chem. Soc.* **72**, 856–866 (1950).
31. P. R. Khangaonkar and V. N. Mista, *J. Inst. Eng. (India)* **55**(Part MM), 59 (1975).
32. G. W. Kor, *Metall. Trans.* **9B**, 307 (1978).
33. S. K. Singh, T. Deb Roy, and K. P. Abraham, *Trans. Indian Inst. Met.* **27**, 87 (1974).
34. U.S. Pat. 3,375,097 (Mar. 26, 1968), J. Y. Welsh (to Manganese Chemicals Corp.).
35. W. Dautzenberg, in W. Dautzenberg, *Ullmanns Encyklopädie der Technischen Chemie*, 3rd ed., Vol. 12, Urban und Schwarzenberg, München-Berlin, 1960 p. 217.
36. T. E. Moore, M. Ellis, and P. W. Selwood, *J. Am. Chem. Soc.* **72**, 856–866 (1950).
37. U.S. Pat. 2,504,404 (Apr. 18, 1950), A. L. Flenner (to E. I. du Pont de Nemours & Co., Inc.).
38. J. B. Goodenough and A. L. Loeb, *Phys. Rev.* **98**, 391 (1955).
39. H. A. Lehmann and K. Teske, *Z. Anorg. Allg. Chem.* **336**, 197 (1965).
40. J. A. Conner and E. A. V. Ebsworth, *Peroxy Compounds of Transition Metals, Advances in Inorganic Chemistry and Radiochemistry*, N.7, Vol. 6, Academic Press, Inc., New York, 1961.
41. H. Gehrke, *MnO_2 Deposition in Feedlot Water Lines in South Dakota*, Completion Report No. PB-278809 for projects A-048-SDAK and A-058-SDAK, U.S. Dept. of the Interior, Office of Water Research and Technology, Washington, D.C., Jan. 1978.
42. W. Stumm and J. J. Morgan, *Aquatic Chemistry*, Wiley-Interscience, New York, 1970.
43. H. S. Posselt, F. J. Anderson, and W. J. Weber, Jr., *Environ. Sci. Technol.* **2**, 1087 (1968).
44. H. S. Posselt, A. H. Reidies, and W. J. Weber, Jr., *J. Am. Water Works Assoc.* **60**, 48 (1968).
45. R. G. Burns and V. M. Burns, *Structural Relationships Between Manganese(IV) Oxides in The Manganese Dioxide Symposium*, Vol. 1, I. C. Sample Office, 1975.
46. A. Byström and A. M. Byström, *Acta Cryst.* **3**, 146–151 (1950).
47. K. J. Euler, *J. Power Sources* **8**, 133–144 (1982).
48. M. M. Thackeray, *Prog. Batt. Batt. Mater.* **11**, 150–157 (1992).
49. R. Giovanoli, *Thermochimica Acta* **234**, 303–313 (1994).
50. M. A. Malati, *Chem. Ind.*, 446–452 (Apr. 24, 1971).
51. P. Ruetschi, *J. Electrochem. Soc., Electrochem. Sci. Tech.*, 2737–2744 (Dec. 1984).
52. H. S. Posselt, F. J. Anderson, and W. J. Weber, Jr., *ES&T* **2**(12), 1087–1093 (1968).
53. M. J. Gray and M. A. Malati, *J. Chem. Tech. Biotechnol.* **29**, 127–134 (1979).
54. J. W. Murray, *Geochim. Cosmochim. Acta* **39**, 505–519 (1975).
55. J. J. Morgan and W. Stumm, *J. Colloid Sci.* **19**, 347–359 (1964).
56. M. J. Gray, M. A. Malati, and W. M. Rophael, *J. Electroanal. Chem.* **89**, 135–140 (1978).
57. T. W. Healy, A. P. Herring, and D. W. Fuerstenau, *J. Coll. Interface Sci.* **21**, 435–444 (1966).
58. M. A. Malati, A. A. Yousef, and M. A. Arafa, *Chem. Ind.*, 459–460 (1969).
59. A. J. Fatiadi, *Organic Chem., Part 1, Synth.* (2), 65–104 (1976).
60. U.S. Pat. 4,299,735 (Nov. 10, 1981), P. G. Mein and A. H. Reidies (to Carus Corp.).
61. U.S. Pat. 5,260,248 (Nov. 9, 1993), N. Singh and K. S. Pisarczyk (to Carus Corp.).
62. U.S. Pat. 4,290,923 (Sept. 22, 1981), P. G. Mein and A. H. Reidies (to Carus Corp.).
63. H. A. Lehmann and K. Teske, *Z. Anorg. Allg. Chem.* **336**, 197 (1965).
64. U.S. Pat. 3,780,158 (Dec. 18, 1973), J. Y. Welsh (to Diamond Shamrock Corp.).
65. U.S. Pat. 3,780,159 (Dec. 18, 1973), J. Y. Welsh (to Diamond Shamrock Corp.).

66. U.S. Pat. 2,956,860 (Oct. 18, 1960), J. Y. Welsh (to Manganese Chemicals Corp.).
67. K. J. Euler and H. Mueller-Helsa, *J. Power Sources* **4**, 77 (1979).
68. Y. F. Shen and co-workers, *Science* **260**, 511–515 (Apr. 1993).
69. G. D. Van Arsdale and C. G. Maier, *Trans. Electrochem. Soc.* **33**, 109 (1918).
70. Rus. Pat. 82344 (Mar. 27, 1929), H. Inoue and S. Haga.
71. P. M. DeWolff, J. W. Visser, R. Giovanoli, and R. Brütsch, *Chimia (Buenos Aires)* **32**, 257 (1978).
72. D. A. J. Swinkels and K. N. Hall, *Prog. Batt. Batt. Mater.* **11**, 16–24 (1992).
73. J. Y. Welsh, *Electrochem. Technol.* **5**, 504 (1967).
74. T. Matsumura, *personal communication*, Toyo Soda Manufacturing Co., Ltd., Tokyo, Japan, 1979.
75. G. Kano, *Mem. Faculty Eng. (FUKUI University)* **34**(2), (1986).
76. G. Strauss and A. G. Hoechst, *personal communication*, Werk Knapsack, Germany, 1978.
77. U.S. Pat. 3,375,097 (Mar. 26, 1968), J. Y. Welsh (to Manganese Chemicals Corp.).
78. C. B. Ward, A. I. Walker, and A. R. Taylor, *Prog. Batt. Batt. Mater.* **11**, 40–46 (1992).
79. Brit. Pat. 1,124,317 (Aug. 21, 1968), (to Knapsack Aktiengesellschaft).
80. T. Naguoki, in A. Kozawa and R. J. Brodd eds., *Manganese Dioxide Symposium*, Vol. 1, I. C. Sample Office c/o Union Carbide Corp., Parma Technical Center, Cleveland, Ohio, 1975.
81. Brit. Pat. 1,423,503 (Feb. 4, 1976), H. Kojima (to Mitsui Mining and Smelting Co., Ltd.).
82. E. Preisler, *Prog. Batt. Batt. Mater.* **10** (1991).
83. R. Huber, in K. V. Kordesch, ed., *Batteries*, Vol. 1, Marcel Dekker, Inc., New York, 1974, 28–29.
84. W. C. Gardiner, *J. Electrochem. Soc.* **125**, 22C (1978).
85. Brit. Pat. 1,423,503 (Feb. 4, 1976), H. Kojima (to Mitsui Mining and Smelting Co., Ltd.).
86. U.S. Pat. 3,065,155 (Nov. 20, 1962), J. Y. Welsh (to Manganese Chemicals Corp.).
87. U.S. Pat. 3,702,287 (Nov. 7, 1972), H. Yamagishi and M. Tanaka (to Nippon Kokan Kabushiki Kaisha).
88. Belg. Pat. 871,683 (Feb. 15, 1979), (to Diamond Shamrock Technologies, SA).
89. E. Preisler, personal communication; E. Preisler and A. H. Reidies, *Winnacker-Küchler, Chemische Technologie*, Vol. 2, 4th ed., Carl Hanser Verlag, München, Germany, 1981.
90. E. Preisler, *J. Appl. Electrochem.* **19**(4), 540–546 (1989).
91. H. Lux, *Z. Naturforsch* **1**, 281 (1946).
92. K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.* **79**, 2822 (1957).
93. T. Chen, *The Oxidation of Alkenes, Alcohols and Sulfides by Manganates*, MS dissertation, University of Regina, Saskatchewan, Canada, 1991, p. 262.
94. D. G. Lee, C. R. Moylan, T. Hayashi, and J. I. Brauman, *J. Am. Chem. Soc.* **109**, 3003–3010 (1987).
95. R. S. Nyholm and P. R. Woolliams, in W. L. Jolly, ed., *Inorganic Synthesis*, Vol. XI, McGraw Hill, New York, 1968, 56–61.
96. G. J. Palenik, *Inorg. Chem.* **6**(3), 507–511 (Mar. 1967).
97. F. R. Duke, *J. Phys. Chem.* **56**, 882 (1952).
98. H. I. Schlesinger and H. B. Siems, *J. Am. Chem. Soc.* **46**(9), 1965–1978 (1924).
99. R. Landsberg, *P. Orgel, Chem. Technol.* **13**, 665 (1961).
100. D. Arndt, *Manganese Compounds as Oxidizing Agents in Organic Chemistry*, Open Court Publishing Co., LaSalle, Ill., 1981, 169–177.
101. H. Firouzabadi and E. Ghaderi, *Tetrahedron Lett.* (9), 839–840 (1978).
102. N. A. Frigerio, *J. Am. Chem. Soc.* **91**, 6200 (1969).

103. G. Lauf, *personal communication*, Carus Chemical Co., LaSalle, Ill., 1994.
104. R. Colton and J. H. Canterford, *Halides of The Transition Elements*, Wiley-Interscience, New York, 1969, 212–213.
105. F. H. Herbstein, M. Kapon, and A. Weissman, *J. Therm. Anal.* **41**, 303–322 (1991).
106. J. P. Suttle, in M. C. Sneed and R. C. Brasted, eds., *Comprehensive Inorganic Chemistry*, Vol. 6, Van Nostrand Co., New York, 1957, p. 141.
107. *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Manganese Part C 2, System Nymber 56, Springer-Verlag, New York, 1975, p. 177.
108. O. Sackur and W. Taegener, *Z. Elektrochem.* **18**, 718–724 (1912).
109. G. J. Palenik, *Inorg. Chem.* **6**(3), 503–507 (Mar. 1967).
110. A. H. Reidies, *personal communication*, Carus Chemical Co., LaSalle, Ill., 1994.
111. A. H. Reidies, *personal communication*, Spolek Pro Chemickov a Hutni Vyrobu n.p., Usti n. Labem, 1977.
112. BE 905 130 (1986), M. O. Gonzalez Garcia (to Industrial Quimica del Nalón S. A.).
113. H. Marcy in F. Matthes and G. Wehner, eds., *Anorganisch-Technisache Verfahren*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, DDR, (1964).
114. A. K. Kohli and K. T. Cherian, *personal communication*, The Swadeshi Chemicals Private Ltd., Bombay, India, 1977.
115. V. M. Markavoa, A. P. Popova, I. M. Vulfovich, and V. M. Pisnyi, *Khim. Tekhnol. Soedin. Margantsa* (1), 78 (1975).
116. A. P. Popova, I. M. Vulfovich, and V. M. Markova, *Khim. Tekhnol. Soedin. Margantsa* (1), 66 (1975).
117. USSR Pat. 145,894 (Apr. 6, 1962), M. N. Machulkin and co-workers.
118. V. M. Markova, A. P. Popova, I. M. Vulfovich, and V. M. Pisnyi, *Khim. Tekhnol. Soedin. Margantsa* (1), 78 (1975).
119. K. Teske and H. A. Lehmann, *Chem. Technol.* **17**, 493 (1965).
120. USSR Pat. 150,828 (Oct. 25, 1962), M. N. Machulkin and co-workers.
121. U.S. Pat. 2,940,821 (June 14, 1960), M. B. Carus and A. H. Reidies (to Carus Chemical Co.).
122. U.S. Pat. 2,940,822 (June 14, 1960), M. B. Carus and A. H. Reidies (to Carus Chemical Co.).
123. U.S. Pat. 2,940,823 (June 14, 1960), M. B. Carus and A. H. Reidies (to Carus Chemical Co.).
124. W. Baronius and J. Marcy, *Chem. Technol.* **18**, 723 (1966).
125. Ref. 27, 744–750.
126. D. K. Taraphdar, S. K. Ghosal, and R. N. Mukherja, *Indian J. Technol.* **12**, 260 (1974).
127. U.S. Pat. 2,843,537 (July 15, 1958), M. B. Carus (to Carus Chemical Co.).
128. U.S. Pat. 2,908,620 (Oct. 13, 1959), M. B. Carus (to Carus Chemical Co.).
129. U.S. Pat. 3,062,734 (Nov. 6, 1962), M. B. Carus (to Carus Chemical Co.).
130. U.S. Pat. 3,172,830 (Mar. 9, 1965), M. B. Carus (to Carus Chemical Co.).
131. Ref. 29, p. 753.
132. T. Kaczmarek, J. Chwalczyk, and B. Kolomyjek, *Chemik* **25**, 2, 58 (1972).
133. E. Müller, ed., *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. IV/1b, Georg Thieme Verlag, Stuttgart, Germany, 1975.
134. A. J. Fatiadi, *J. Synth. Org. Chem.* (2), 85–127 (1987).
135. W. A. Waters, *Q. Rev. Chem. Soc.* **12**, 277 (1958).
136. J. W. Ladbury and C. F. Cullis, *Chem. Rev.* **58**, 403 (1958).
137. R. Stewart, *Oxidation Mechanisms*, W. A. Benjamin, Inc., Amsterdam, the Netherlands, 1964, 58–76.
138. R. Stewart, in K. B. Wiberg, ed., *Oxidation in Organic Chemistry*, Part A, Academic Press, Inc., New York, 1965.

139. D. G. Lee, in R. L. Augustine, ed., *Oxidation—Techniques and Applications in Organic Synthesis*, Vol. 1, Marcel Dekker, Inc., New York, 1969, 1–111.
140. D. G. Lee, *The Oxidation of Organic Compounds by Permanganate Ion and Hexavalent Chromium*, Open Court Publishing Co., La Salle, Ill., 1980.
141. L. F. Fieser and M. Fieser, *Reag. Org. Synth.* **1**, 942–952; **2**, 348; **4**, 30–31, 143; **5**, 562–563, John Wiley & Sons, Inc., New York, 1967, 1969, 1975, 1976.
142. Ref. 138, Table VII, p. 67.
143. V. N. Bobkov and Tr. VNII Vodosnabzh, *Kanaliz. Gidrotekhn. Sooruhz. i Inzh. Gidrogeol* (50), 48–50 (1975).
144. Ref. 138, 60–61.
145. S. S. Rawalay and H. Shechter, *J. Org. Chem.* **32**, 3129–3131 (1967).
146. Y. Sayato, K. Nakamuro, K. Tsuji, and M. Tonomura, *Nat. Inst. Hyg. Sci., Eisei Shikenjo Hokoku (Japan)* **93**, 54–57 (1975).
147. H. Yanagibashi, *Tokyo Ika Daigaku Zasshi* **20**(1), 1–50 (1962).
148. J. Dockx, *Synthesis*, 441–456 (Aug. 1973).
149. G. W. Gokel and H. D. Durst, *ALDRICHIMICA Acta* **9**(1), (1976).
150. D. G. Lee, in W. S. Trahanowski, ed., *Oxidation in Organic Chemistry*, Academic Press, Inc., New York, 1980.
151. S. L. Regen and C. Koteel, *J. Am. Chem. Soc.* **99**, 3837–3838 (1977).
152. N. A. Noureldin and D. G. Lee, *Tetrahedron Lett.* **22**, 4889 (1981).
153. F. M. Menger and C. Lee, *J. Org. Chem.* **44**, 3446–3448 (1979).
154. A. J. Fatiadi, *J. Synth. Org. Chem.* (2), 102 (1987).
155. D. G. Lee, T. Chen, and Z. Wang, *J. Org. Chem.* **58**(10), 2918–2919 (1993).
156. F. M. Menger and C. Lee, *Tetrahedron Lett.* **22**(18), 1655–1656 (1981).
157. D. M. MacArthur and G. E. Blomgren, *The Powers Review-Year 2002 Battery and Fuel Cell Industry Developments*, Chemac International Corp., Macomb, Mich., 2003, p. 13.
158. G. M. Ehrlich in D. Linden and T. B. Reddy, eds., *Handbook of Batteries*, The McGraw-Hill Companies, New York, 2002, pp. 35.1–35.93
159. R. Deblois, *Personal Communication*, Carus Chemical Co., La Salle, Ill., 1994.
160. N. H. Furman, ed., *Scott's Standard Methods of Chemical Analysis*, 6th ed., Vol. 1, D. Van Nostrand Co., Inc., Princeton, N.J., 1962, 638–655.
161. F. D. Snell and L. S. Ettre, eds., *Encyclopedia of Industrial Chemical Analysis*, Vol. 15, Wiley-Interscience, New York, 1972, 447–496.
162. A. J. Vogel, *A Text-Book of Quantitive Inorganic Analysis*, 3rd ed., Longman Group Ltd., London, U.K., 1961.
163. C. L. Wilson and D. W. Wilson, eds., *Comprehensive Analytical Chemistry*, Vol. IC, Elsevier Publishing Co., Amsterdam, the Netherlands, 1960, 617–621.
164. I. M. Kolthoff, E. B. Sandell, E. S. Mechan, and S. Bruckenstein, eds., *Quantitative Chemical Analysis*, 4th ed., The Macmillan Co., London, 1969.
165. D. Glover, B. Schumm, Jr., and A. Kozawa, eds., *Handbook of Manganese Dioxides–Battery Grade*, International Battery Material Association (IBBA, Inc.), Brunswick, Ohio, 1989.
166. U. L. Schramm and F. C. Wedler, *Manganese in Metabolism and Enzyme Function*, Academic Press, Inc., Orlando, Fla., and references therein, 1986, “Chapt. 18”.
167. F. Baruthio and co-workers, *Clin. Chem.* **34**(2), 227–234 (1988).
168. J. J. Lingane and R. Karplus, *Ind. Eng. Chem.* **18**(3), 191–194 (1946).
169. W. Slavin, *Atomic Absorption Spectroscopy*, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1968.
170. A. Montaser and D. W. Golightly, eds., *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd ed., VCH Publishers, Inc., New York, 1992.
171. B. Welz, *Atomic Absorption Spectrometry*, VCH, Weinheim, Germany, 1985.

172. B. Chiswell, G. Rauchle, and M. Pascoe, *Talanta* **37**(2), 237–259 (1990).
173. Ref. 138, Vol. 5, p. 14.
174. K. B. Wiberg, ed., *Oxidation in Organic Chemistry*, Vol. 5-A, Academic Press, Inc., New York, 1965, 13–20.
175. H. W. Fishburn, Jr., and W. E. Dill, Jr., "A Method for the Semiquantitative Analysis and Identification of Mixed Phases of Manganese Dioxide," paper presented at the *Power Sources Conference*, Atlantic City, N.J., May 10, 1961.
176. *Standard Methods for Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, D.C., 1992.
177. B. Chriswell and M. B. Mokhtar, *Talanta* **33**(8), 669–677 (1986).
178. E. Nakayamachal, *Anal. Sci.* **5**(2), 129–139 (1986).
179. N. C. Uren, C. J. Asher, and N. E. Longnecker, *Dev. Plant Soil Sci.* **33**, 309–328 (1988).
180. R. M. Riggin, E. J. Mezey, and W. M. Henry, *Gov. Rep. Announcement Index (U.S.)* **84**(12), 75 (1984).
181. H. J. M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, Inc., New York, 1979.
182. M. C. Scrutton, M. F. Utter, and A. S. Mildvan, *J. Biol. Chem.* **241**(15), 3480–3487 (1966).
183. R. Schiele, *Manganese in Metals and their Compounds in the Environment*, VCH, Weinheim, Germany.
184. M. Alexander, *Introduction to Soil Microbiology*, John Wiley and Sons, Inc., New York, 1967.
185. National Research Council, *Manganese: Medical and Biological Effects of Environmental Pollutants*, National Academy of Sciences, Washington, D.C., 1973.
186. G. Matrone and co-workers, *Manganese Geochem. Environ.* **2**, 29–39 (1977).
187. M. O. Admur, L. C. Norris, and G. F. Heuser, *Rat. Proc. Soc. Exptl. Biol. Med.* **59**, 254–255 (1945).
188. D. L. Baly, I. Lee, and R. Doshi, *FEBS Lett.* **239**(1), 55–58 (1988).
189. *Manganese in Recommended Dietary Allowances*, 9th ed., National Academy of Sciences, Washington, D.C., 1980, 154–157.
190. J. A. T. Pennington and co-workers, *J. Am. Diet Assoc.* **86**, 876–891 (1986).
191. J. F. Kopp and R. C. Kroner, *Trace Metals in Waters of The United States*, PB215680, U.S. Department of the Interior, Washington, D.C., 1967, p. 13.
192. R. A. Smith, R. B. Alexander, and M. G. Wolman, *Science* **235**, 1607–1615 (1987).
193. J. F. Kopp and R. C. Kroner, *Trace Metals in Waters of the United States*, PB215680, U.S. Department of the Interior, Washington, D.C., 1967.
194. P. Camner and co-workers, *Environ. Res.* **38**(2), 301–309 (1985).
195. *Toxicological Profile for Manganese and Compounds*, PB93-110781, Agency for Toxic Substances and Disease Registry, U.S. Public Health Service, Washington, D.C., 1992, p. 79.
196. Ref. 195, p. 80.
197. A. Iregren, *Neurotoxicol. Teratol.* **12**, 673–675 (1990).
198. R. J. Lewis, *Sr., Sax's Dangerous Properties of Industrial Materials*, 11th ed., Wiley, Hoboken, N.J., 2004.
199. Ref. 195, 15–16.
200. A. Barbeau, *NeuroToxicology* **1**, 13–36 (1984).
201. H. E. Stokinger, in G. D Clayton and F. E. Clayton eds., *Patty's Industrial Hygiene and Toxicology*, Vol. 2A, John Wiley & Sons, Inc., New York, 1978, 1749–1767.
202. *Scientific and Technical Assessment Report on Manganese*, PB-242-291, Environmental Protection Agency, Washington, D.C., 1975, 6–7.

203. H. A. Rosenstock, D. G. Simons, and J. S. Meyer, *J. Am. Med. Assoc.* **217**, 1354–1358 (1971).
204. *Registry of Toxic Effects of Chemical Substances*, National Institute of Occupational Safety and Health, Washington, D.C., Aug. 1994
205. R. J. Bull and G. F. Craun, *J. Am. Water Works Assoc.* **69**, 662 (1977).
206. I. Mena K. Horiuchi, K. Burke, and G. C. Cotzias, *Neurology* **17**, 128 (1969).
207. P. S. Papavasiliou, S. T. Miller, and G. C. Cotazias, *Am. J. Physiol.* **211**, 211–216 (1966).
208. A. Putrament, H. Baranowska, A. Ejchart, and W. Prazmo, *Methods Cell Biol.* **20**, 25 (1978).
209. A. Furst, *J. Nat. Cancer. Inst.* **60**(5), 1171 (1978).
210. *Chem. Reg. Rep.* **16**(13) (1992).
211. Ref. 198, p. 42.
212. J. Michael Davis, “Manganese and Rhenium,” in E. Bingham, B. Cohrssen, and C. H. Powell, eds., *Patty’s Toxicology*, 5th ed., John Wiley & Sons, Inc., New York, 2001.
213. *Permanganic Acid, Potassium Salt*, Registry of Toxic Effects of Chemical Substances, RTECS Number SD6475000, May 1993.
214. Ref. 195, pp. 97–98.
215. *American Conference of Governmental Industrial Hygienists*, 1986, 1988.
216. *Integrated Risk Information System*, U.S. Environmental Protection Agency, Washington, D.C., 1991.
217. Code of Federal Regulations, Title 40, Part 143.3, Washington, D.C., 1994.
218. “Superfund Ammendment Reauthorization Act,” Code of Federal Regulations, Title 40, Section 313, Part 302, Table 302.4, 1994.
219. D. Glover, B. Schumm, Jr., and A. Kozawa, eds., *Handbook of Manganese Dioxide Battery Grades*, International Battery Material Assoc., 1989.
220. G. Blomgren, B. Schumm, Jr., and L. F. Urry, in W. Gerhartz, ed., *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. A3, VCH Verlagsgesellschaft, Weinheim, Germany, 1985, 352–361.
221. M. Kronenberg, in Ref. 222, p. 393.
222. S. Toon, *Indust. Miner.*, 19–35 (July 1985).
223. D. M. Holton, W. C. Maskell, and F. L. Tye, in L. Pearce, ed., *Power Sources*, Vol. 10, The Paul Press, Ltd., London, 1985, 247–270.
224. L. Wu, J. R. Dahn, and D. S. Wainwright, *Science* **264**, 1115–1117 (1994).
225. J. R. Panek, in M. Morton, ed., *Polysulfide Rubbers in Rubber Technology*, 2nd ed., Van Nostrand Reinhold Co., New York.
226. R. Patel and D. Clifford, *Radium Removal from Water by Manganese Dioxide Adsorption and Diatomaceous Earth Filtration*, NTIS PB92-115260/AS, Springfield, Va., 1992.
227. B. McMichael, *Indust. Miner.*, 42 (May 1989).
228. N. Singh, “VOC Destruction at Low Temperatures Using a Novel Thermally Stable Transition-Metal Oxide-Based Catalyst,” presented at the *First North American Conference on Emerging Clean Air Technologies and Business Opportunities*, Toronto, Canada, Sept. 1994.
229. U.S. Pat. 4,208,527 (June 17, 1980), G. Horlbeck, K. Burzin, and R. Feinauer (to Chem. Werke Hüls Ag).
230. J. Bieleman, *Eur. Poly. Paint Colour J.* **182**(4311), 412–416 (1992).
231. J. D. Bailie and A. H. Zeitz, Jr., in D. M. Considine, ed., *Methylcyclopentadienylmanganese Tricarbonyl Combustion Improver in Energy Technology Handbook*, McGraw-Hill Book Co., Inc., New York, 1977.

232. R. Hage and co-workers, *Nature* **369**(6482), 637–639 (1994).
233. A. Houston, *15th, 19th, 20th, 25th Annual Reports to the Metropolitan Water Board*, London, 1920–1930.
234. K. J. Ficek, in Robert L. Sanks, ed., *Water Treatment Design for the Practicing Engineer*, Ann Arbor Science Publishers, Inc., Mich., 1978, Chapt. 21, 461–479.
235. K. J. Ficek and J. E. Boll, *Aqua* (7) (1980).
236. R. E. Hubel, E. W. Howe, A. Wilczak, T. A. Wolfe, and S. J. Tambini, *J. AWWA*, 43–51 (Aug. 1992).
237. W. R. Knocke, R. C. Hoehn, and R. L. Sinsabaugh, *J. AWWA*, 75–79 (Mar. 1987).
238. W. R. Knocke, J. E. Van Benschoten, M. J. Kearney, A. W. Soborski, and D. A. Reckhow, *J. AWWA*, 80–87 (June 1991).
239. G. F. Lauf and M. A. Waer, “Arsenic Removal Using Potassium Permanganate,” presented at the *1993 Water Quality Technology Conference*, Miami, Fla., Nov. 1993.
240. K. J. Ficek and M. A. Waer, *The Fifth National Conference on Drinking Water*, Winnipeg, Manitoba, Canada, 1992, 205–219.
241. P. L. Klerks and P. C. Fraleigh, *J. AWWA*, 92–100 (1991).
242. P. A. Vella, J. Munder, B. Patel, and B. Veronda, “Chemical Oxidation: A Tool for Toxicity Reduction,” *Proceedings of the 47th Industrial Waste Conference*, Purdue University, West Lafayette, Ind., 1992.
243. P. A. Vella, J. Munder, and B. Veronda, “Chemical Oxidation: A Tool for Toxicity Reduction and Bio-Enhancement,” presented at the *65th Water Environment Federation Conference and Exposition*, New Orleans, La., Sept. 1992.
244. U.S. Pat. 4,062,925 (1977), D. E. Witenhafer, C. A. Daniels, and R. F. Koebel (to B. F. Goodrich Co.).
245. J. H. Jackson, “Potassium Permanganate Solves Odor Problems at Consolided Mill,” Pulp Paper (1984).
246. W. Mangum, *Water Technol.* **26**(11), 44, 46–47 (2003).
247. P. A. Vella, G. Deshinsky, J. E. Boll, J. Munder, and W. M. Joyce, *Res. J. WPCF* **62**(7), 907–914 (Nov./Dec. 1990).
248. R. J. Pope and R. A. Weber, *Water Environment Federation Proceedings of the 66th Annual Conference and Exposition*, 1993, 447–456.
249. U.S. Pat. 4,425,380 (1984), F. J. Nuzzi and J. K. Duffy (to Kollmorgen Technologies.).
250. A. R. Del Gobbo and C. I. Courduvelis, *PC Fab.*, 54–59 (1987).
251. U.S. Pat. 4,601,783 (July 22, 1986), G. Krulik (to Morton Thiokol, Inc.).
252. N. V. Mandlich and G. A. Krulik, *Plat. Surf. Finish.*, 56–61 (Dec. 1992).
253. U.S. Pat. 4,601,784 (July 22, 1986), G. Krulik (to Morton Thiokol, Inc.).
254. M. Castegnaro, M. Coombs, M. A. Phillipson, M. C. Bourgade, and J. Michelon, *the 7th Polynuclear Aromatic Hydrocarbons, International Symposium*, Batelle Press, Columbus, Ohio, 1982, 257–268.
255. J. Barek and L. Kelnar, *Microchem. J.* **33**(2), 239–242 (1986).
256. J. Barek, M. Castegnaro, C. Malaveille, I. Brouet, and J. Zima, *Microchem. J.* **36**(2), 192–197 (1987).
257. J. Barek, *Microchem. J.* **33**, 97–101 (1986).
258. J. Barek, A. Berka, and M. Muller, *Microchem. J.* **33**(1), 102–105 (1986).
259. H. S. Posselt and F. J. Anderson, *Steel Wire Handbook*, Vol. 2, The Wire Association, Branford, Conn., 1969, 211–228.
260. H. Nakano, C. Okuda, and Y. Ukyo, *Key Engineering Materials* **248**, 143–146 (2003).
261. P. Levy and co-workers, *Appl. Physics Lett.* **83**(25), 5247–5249 (Dec. 2003).

262. L. Zhang and co-workers, *Chemical Communications (Royal Society of Chemistry)* **23**, 2910–2911 (Nov. 2003).
263. J. Wang and co-workers, *J. Mater. Sci. Technol.* **19**(5), 489–491 (May 2003).
264. H. J. Jeon, S. D. Moon, and C. Y. Park, *Molecular Crystals and Liquid Crystals* **407**, 49–56 (Dec. 2003).

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Table 1. **Isotopes of Manganese**

Isotope	Atomic mass	Half-life, $t_{1/2}$	Decay mode[a]
^{50}Mn		0.286 s	β^+
^{51}Mn		45 min	β^+, EC
^{52}Mn		5.7 d	β^+, EC
^{53}Mn	52.9413	2×10^6 yr	EC
^{54}Mn	53.9402	303 d	EC
^{55}Mn[b]	54.9381	stable	
^{56}Mn		2.576 h	β^-
^{57}Mn		1.7 min	β^-
^{58}Mn		1.1 min	β^-

[a] β^+ = positron emission, β^- = negative beta emission, and EC = orbital electron capture.

[b] The natural abundance of ^{55}Mn is 100%

Table 2. **Representative Manganese Compounds**[a]

Oxidation state	Geometry	Example
Mn^{3-}	tetrahedral	$Mn(NO)_3CO$
Mn^{2-}	square	$[Mn\ (phthalocyanine)]^{2-}$
Mn^{-}	trigonal bipyramid	$Mn\ (CO)_5^-$
Mn^{0}	octahedral	$Mn_2(CO)_{10}$
Mn^{+}	octahedral	$[Mn(CN)_6]^{5-}$
Mn^{2+}	tetrahedral	$MnCl_4^{2-}$
Mn^{3+}	octahedral	MnF_3
Mn^{4+}	octahedral	MnO_2
Mn^{5+}	tetrahedral	MnO_4^{3-}
Mn^{6+}	tetrahedral	MnO_4^{2-}
Mn^{7+}	tetrahedral	MnO_4^-

[a] Ref. 3.

Table 3. **Thermodynamic Data for Manganese Compounds at 25°C**

Substance[a]	Heat of formation, ΔH_f, kJ/mol[b]	Free energy of formation, ΔG_f, kJ/mol[b]	Entropy, S, J/(mol·K)[b]
Mn^+ (g)	1002.9		
Mn^{2+} (g)	2512.1		
Mn^{2+} (aq)	−222.6	−230.5	−71.1
$MnOH^+$ (aq)		−407.1	
$MnSO_3$ (aq)[c]	−1117.5	−987.8	37.7
Mn^{3+} (aq)		−87.9[d]	
MnO (aq)		−531.4[d]	
$MnO_4{}^{2-}$ (aq)	−656.9	−504.2	58.6[d]
$MnO_4{}^-$ (aq)	−543.5	−450.2	194.6
MnO	−384.9	−362.8	59.8
Mn_2O_3	−956.9	−879.1	110.5
Mn_3O_4	−1386.2	−1281.1	154.0
MnO_2	−520.5	−465.7	53.1
$Mn(OH)_2$	−698.7	619.2	96.2[d]
$Mn(OH)_3$	−924.7[d]	−795.0[d]	(100.4)
MnF_2	−795.0[d]	748.9[d]	93.1
$MnCl_2$	−483.7	−443.1	118.2
$MnBr_2$	−387.4	−372.4	(138.1)
MnI_2	−268.6	−272.0	(154.8)
$Mn(IO_3)_2$	−674.9	−522.6	255.2
MnS	−207.1	−211.3	78.2
MnS[e]	−213.4		
$MnSO_4$	−1066.5	958.6	112.1
$MnSO^4 \cdot H_2O$	−1377.4	1212.9	(154.8)
$Mn(NO_3)_2$	−698.7		
$Mn(NO_3)_2 \cdot 3H_2O$	−1485.3		
$Mn(NO_3)_2 \cdot H_2O$	−2371.9		
$Mn(NO_3)_2 \cdot 6H_2O$ (l)	−2331.7		
$MnCO_3$	−895.4	−820.0	85.8
$MnCO_3$[f]	−882.8	−811.7	113.00
K_2MnO_4	(−1179.9)		
$KMnO_4$	−839.3	−739.7	171.5
$BaMnO_4$	−1225.9	−1121.3	(154.8)
$Mn_2(CO)_{10}$	−1677.4		
$Mn_2(CO)_{10}$ (g)	−1614.6		

[a] Material is crystalline unless otherwise noted.

[d] To convert J to cal, divide by 4.184; items in parentheses are estimates.

[c] Ion pair.

[d] Approximate value.

[e] Alabandite.

[f] Solid precipitate.

Table 4. **Standard Reduction Potentials for Selected Manganese Compounds**

Reaction	Potential, E^0, V	Reference
Acid solution		
$Mn^{2+} + 2\,e^- \rightarrow Mn^0$	−1.18	5
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	ca 1.5	6
$MnO_2(c) + 4\,H^+ + 2\,e^- \rightarrow Mn^{2+} + 2\,H_2O$	1.23	7
$MnO_4{}^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	1.51	5
$MnO_4{}^- + 4\,H^+ + 3\,e^- \rightarrow MnO_2 + 2\,H_2O$	1.70	5
Basic solution		
$Mn(OH)_2(c) + 2\,e^- \rightarrow Mn^0 + 2\,OH^-$	−1.56	5
$MnO_2(c) + 2\,H_2O + 2\,e^- \rightarrow Mn(OH)_2 + 2\,OH^-$	−0.05	5
$MnO_4{}^- + 4\,H_2O + 5\,e^- \rightarrow Mn(OH)_2 + 6\,OH^-$	0.34	5
$MnO_4{}^- + 2\,H_2O + 3\,e^- \rightarrow MnO_2 + 4\,OH^-$	0.59	5
$MnO_4{}^- + e^- \rightarrow MnO_4{}^{2-}$	0.56	8
$MnO_2 + H_2O + 2\,e^- \rightarrow Mn(OH_2) + 2\,OH^-$	−0.05	5
$MnO_2 + H_2O + 2\,e^- \rightarrow \gamma\text{–}MnOOH + OH^-$	0.19	5
$MnO_4{}^{-2} + e^- \rightarrow MnO_4{}^{-3}$	0.27	5

Table 5. **Manganese Minerals of Economic Significance**

Mineral	CAS Registry number	Approximate composition	Crystal	Mn%
pyrolusite	[14854-26-3]	β-MnO_2	tetragonal	63.2
braunite		$Mn^{2+}Mn^{3+}{}_6SiO_{12}$	orthorhombic	66.6
nsutite		$(Mn^{2+}, Mn^{3+}, Mn^{4+})(O,OH)_2$	hexagonal	
manganite	[52019-58-6]	γ-MnOOH	monoclinic	62
psilomelane	[12322-95-1]	$(Ba,Mn^{2+})_3(O,OH)_6Mn_{18}O_{16}$	monoclinic	45–60
cryptomelane	[12260-01-4]	$K_{1-2}Mn_8O_{16}{\cdot}xH_2O$	tetragonal	62
hausmannite	[1309-55-3]	Mn_3O_4	tetragonal	73
jacobsite		Fe_2MnO_4		23.8
bixbyite		$(Mn,Fe)_2O_3$		30–40
rhodonite	[14567-57-8]	$(Mn,Fe,Ca)SiO_3$		42
rhodochrosite	[14476-12-1]	$MnCO_3$		47.6
bementite	[66733-93-5]	$Mn_3Si_2O_5(OH)_4$		43.2
todorokite		$(Ca,Na,K)(Mg,Mn^{2+})$-$Mn_5O_{12}{\cdot}xH_2O$	monoclinic	
ramsdellite	[12032-73-4]	MnO_2		63

Table 6. **Physical Properties of Manganese(II) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density[a], g/cm^3	Mp,°C	Bp, °C	Solubility
manganese acetate tetrahydrate	[15243-27-3]	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	pale red crystals	monoclinic	1.589			sl sol H_2O, sol ethanol, methanol
manganese borate	[12228-91-0]	$MnB_4O_7 \cdot 8H_2O$	white to pale red solid					insol H_2O, ethanol, sol dil acids
manganese carbonate[b]	[589-62-9]	$MnCO_3$	pink solid	trigonal $D^6{}_{3d}$	3.125	dec >200		sol prod H_2O: 8.8×10^{-11} sol in dil acids
manganese chloride	[7773-01-5]	$MnCl_2$	pink crystal solid	trigonal $D^5{}_{3d}$	2.977_{25}	650	1190	v sol H_2O, sol pyridine, ethanol, insol ether
manganese hydroxide[c]	[18933-05-6]	$Mn(OH)_2$	white to pink	hexagonal $D^3{}_{3d}$	3.26_{25}	dec 140		sol acid, sol base at higher temp
manganese nitrate hexahydrate	[17141-63-8]	$Mn(NO_3)_2 \cdot 6H_2O$	colorless to slightly pink crystals	rhombic $D^{16}{}_{2h}$	1.82	25.8	129.4	v sol, H_2O, sol ethanol
manganese(II) oxide[d]	[1344-43-0]	MnO	green	cubic Fm3m $o^5{}_h$	5.37_{23}	1945		insol H_2O
manganese sulfate	[7785-87-7]	$MnSO_4$	almost white crystal solid	orthorhombic $D^{17}{}_{2h}$	3.25	700	dec 850	sol 52 g/100 g H_2O, sl sol methanol, insol ether
manganese dihydrogen phosphate dihydrate	[18718-07-5]	$Mn(H_2PO_4)_2 \cdot 2H_2O$	almost colorless crystal solid four-sided prisms			$-H_2O$, 100		sol H_2O, insol ethanol, deliquescent

[a] Temperatures in °C of readings given as subscript.

[b] Also known as rhodochrosite [14476-12-1].

[c] Also known as pyrochroite [1310-97-0].

[d] Also known as manganosite [1313-12-8].

Table 7. **Solubility of Manganese Chloride in Water, g/100 g**

	Temperature, °C						
Compound	0	20	40	50	60	80	100
$MnCl_2{\cdot}4H_2O$	63.4	73.9	88.6	98.2			
$MnCl_2{\cdot}2H_2O$					108.6	112.7	115.3

Table 8. **Aqueous Solubility of Manganese Sulfate, g/g sat'd sol'n**

	Temperature, °C										
	0	20	26.1	31	40	50	60	70	80	90	100.7
$MnSO_4$	34.6	38.6	39.4	40.4	37.5	36.3	34.9	38.2	31.3	29	26.1

Table 9. **Physical Properties of Manganese(III) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/m^3	Mp, °C	Solubility
trimanganese tetraoxide[a]	[1317-35-7] α-phase[b]	Mn_3O_4	black crystals having metallic sheen	tetragonal D_{4h}^{19}	4.84	1560	insol H_2O
manganese(III) acetatedihydrate	[19513-05-4]	$Mn(C_2H_3O_2)_3\cdot 2H_2O$	cinnamon brown crystal solid				dec H_2O
manganese(III) acetylacetonate	[14284-89-0]	$Mn(C_5H_7O_2)_3$	brown to black crystal solid			172	insol H_2O, sol org solv
manganese(III) fluoride	[7783-53-1]	MnF_3	red crystals	monoclinic C_{2h}^6	3.54	dec (stable to 600)	dec H_2O
α-manganese(III) oxide	[1317-34-6]	Mn_2O_3	black to brown solid	rhombic(also cubic) D_{2h}^{15}	4.89_{25}	871–887 dec	insol H_2O
γ-manganese(III) oxide, hydrated	[1332-64-3]	$MnO(OH)$	black solid	monoclinic C_5^{2h}	4.2–4.4	250 dec to Mn_2O_3	insol H_2O, disproportionates in dilute acids

[a] Mixed Mn(II), Mn(III) valent compound.

[b] Also known as hausmannite [1309-55-3]

Table 10. **Physical Properties of Manganese(IV) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/cm^3	Mp, °C	Solubility
pentamanganese octaoxide[a]	[12163-64-3]	Mn_5O_8	black solid	monoclinic C^3_{2h}	4.85_{20}	550 dec to a Mn_2O_3	insol H_2O
β-manganese(IV) oxide	[14854-26-3]	MnO_2	black to gray crystal solid	tetragonal D^{14}_{4h}	5.026	535	insol H_2O
potassium manganate(IV)	[12142-27-7]	K_2MnO_3	black microscopic crystals		3.071_{25}	1100	dec H_2O, disproportionates

[a] Mixed valent Mn(II), Mn(IV) compound.

Table 11. **Manganese Dioxide Crystal Phases**[a]

Phase	Example mineral	Structure number	Description
α-MnO_2	hollandite group	(6) and (7)	tunnel structure of corner-shared double chains of (MnO_6) octahedra (2×2 channels)
β-MnO_2	pyrolusite	(8)	single chains of edge-shared (MnO_6) octahedra (1×1 channels)
γ-MnO_2	nsutite	(9)	regions of single and double chains of edge-shared (MnO_6) octahedra (both 2×1 and 1×1 channels)
			layers of edge-shared (MnO_6) octahedra
δ-MnO_2	ramsdellite	(10)	double chains of edge-shared (MnO_6) octahedra (2×1 channels)

[a] Structures are shown in Fig. 3; Ref. 45.

Table 12. **Langmuir Constants for the Absorption of Alkaline-Earth Cations on Manganese Dioxide**[a][b]

Ion	Ionic radius, pm	Colloidal hydrous manganese dioxide, X_m,[a] mol/mol	Hydrated radius, pm	δ-MnO_2, X_m[c] μmol/g
Mg^{2+}	65	0.100	297	58
Ca^{2+}	99	0.113	286	63
Sr^{2+}	113	0.135	277	65
Ba^{2+}	135	0.180	269	117

[a] Refs. 52 and 53.

[b] Absorption experiments conducted at pH 7.

[c] δ-MnO_2 powder exhibits a BET surface area of ca 4 m^2/g, and a zero point of charge at pH 3.33±0.5.

Table 13. **Properties of Electrolytic Manganese Dioxide**

Property	Typical ranges
density, g/cm^3	4.2–4.5
bulk density, g/cm^3	1.7–2.5
particle size, μm	<74
surface area, m^2/g	30–60
MnO_2, wt %	92

[a] Minimum value.

Table 14. **Physical Properties of Manganese(V) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/m^3	Mp, °C	Solubility
barium manganate(V)	[12231-83-3]	$Ba_3(MnO_4)_2$	emerald green crystals	rhombic ${D^5}_{3d}$	5.25	dec 960	insol H_2O
lithium manganate(V)	[12201-25-1]	Li_3MnO_4				dec >125	sol 3% LiOH at 0°C
potassium manganate(V)	[12142-41-5]	K_3MnO_4	turquoise blue microscopic crystals		2.78	dec 800–1100	v sol H_2O dec, hygroscopic, sol 40% KOH at −15°C
rubidium manganate(V)	[12438-62-9]	Rb_3MnO_4					
sodium manganate(V)	[12163-41-6]	Na_3MnO_4	bluish, dark green microscopic crystals	orthorhombic D^{15}_{2h}		dec 1250	v sol H_2O, dec, hygroscopic
strontium manganate(V)–strontium hydroxide		$Sr_3(MnO_4)_2 \cdot Sr(OH)_2$					insol H_2O

Table 15. **Physical Properties of Manganese(VI) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/m^3	Mp, °C	Solubility
barium manganate(VI)	[7787-35-1]	$BaMnO_4$	small green to black crystals	rhombic D_{2h}^{16}	4.85	dec 1150	insol H_2O sol product 2.46×10^{-10}
potassium manganate(VI)	[10294-64-1]	K_2MnO_4	dark green to black crystals	orthorhombic D_{2h}^{16}	2.80_{23}	dec 190	sol H_2O dec, sol KOH
sodium manganate(VI)	[15702-33-7]	Na_2MnO_4	small dark green needles	rhombic		dec 300	sol H_2O dec

Table 16. **Physical Properties of Manganese(VII) Compounds**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/m^3	Mp, °C	Solubility
potassium manganate(VI), manganate(VII) double salt	[12362-73-1]	$KMnO_4 \cdot K_2MnO_4$	dark, small hexagonal plates	monoclinic D^5_{3d}			sol H_2O dec
manganese heptoxide	[12057-92-0]	Mn_2O_7	dark red oil		2.396_{20}	5.9	v sol H_2O, hygroscopic
ammonium permanganate	[13446-10-1]	NH_4MnO_4	dark purple rhombic bipyramidal needles	rhombic D^{16}_{2h}	2.22_{25}	dec >70	8 g/100 g H_2O at 15°C
barium permanganate	[7787-36-2]	$Ba(MnO_4)_2$	dark purple crystals	rhombic D^{24}_{2h}	3.77	dec 95–100	72.4 g/100 g H_2O at 25°C
calcium permanganate tetrahydrate	[7789-81-3]	$Ca(MnO_4)_2 \cdot 4H_2O$	black crystals, solutions look purple		2.49	dec 130–140	388 g/100 g H_2O at 25°C, deliquescent
cesium permanganate	[13456-28-5]	$CsMnO_4$	dark purple rhombic bipyramidal prisms or needles	orthorhombic at RT and atmospheric pressure	3.579	dec 320	0.23 g/100 g H_2O at 20°C
lithium permanganate	[13452-79-7]	$LiMnO_4 \cdot 3H_2O$	long, dark purple needles	hexagonal	2.06_{25}	dec 190	71 g/100 g H_2O at 16°C
magnesium permanganate hexahydrate	[10377-62-5]	$Mg(MnO_4)_2 \cdot 6H_2O$	bluish gray crystals	rhombic C^7_{2v}	2.18	dec 130	v sol H_2O, sol CH_3OH, pyridine, glac acetic acid

Table 16. **(***Continued***)**

Compound	CAS Registry number	Formula	Appearance	Crystal system and space group	Density, g/m^3	Mp, °C	Solubility
potassium permanganate	[7722-64-7]	$KMnO_4$	dark purple bipyrimidal rhombic prisms	orthorhombic D^{16}_{2h}	2.703_{20}	dec 200–300	sol H_2O, acetic acid, trifluoroacetic acid, acetic anhydride, acetone, pyriding, benzonitrile, sulfolane
rubidium permanganate	[13465-49-1]	$RbMnO_4$	dark purple rhombic bipyramidal prisms	orthorhombic D^{16}_{2h}	3.23_{25}	dec 250	1.1 g/100 g H_2O at 19°C
silver permanganate	[7783-98-4]	$AgMnO_4$	dark purple	monoclinic C^{5}_{2h}	4.27	110 dec	0.92 g/100 g H_2O at 20°C
sodium permanganate	[10101-50-5]	$NaMnO_4 \cdot 3H_2O$	dark purple crystals		1.972	36.0	v sol H_2O, deliquescent
zinc permanganate hexahydrate	[23414-72-4]	$Zn(MnO_4)_2 \cdot 6H_2O$	black crystals, solutions look purple	rhombic C^{7}_{2v}	2.45	dec 90–105	v sol H_2O, deliquescent

Table 17. **U.S. Producers of Manganese Products in 2003**[a]

		Products[b]			
Company	Plant location	FeMn	SiMn	MnO_2	Type of process
Erachem Comilog	Baltimore, Md.			X	chemical
Do.	New Johnsonville, Tenn.			X	electrolytic
Highlanders Alloys LLC[c]	New Haven, W.Va	X	X		electric furnace
Eramet Marietta Inc.	Marietta, Ohio	X	X		electric furnace
Kerr-McGee Chemical LLC	Henderson, Nev.			X	electrolytic
Energizer Holdings, Inc., Eveready Battery Co.	Marietta, Ohio			X	electrolytic

[a] Ref. 11.

[b] FeMn, ferromanganese; SiMn, silicomanganese; MnO_2, synthetic manganese dioxide.

[c] Product information obtained from various industry trade publications. Company ceased production in January 2003.

Table 18. **Toxicity Data for Select Manganese Compounds**[a]

Compound	CAS Registry number	Test animal	Route of exposure	LD_{50} mg/kg
manganese(II) acetate	[638-38-0]	rat	oral	2940
cyclopentadienyl-manganese tricarbonyl	[12079-65-1]	mouse	iv	0.71
		rat	oral	22
manganese(II) chloride	[7773-01-5]	mouse	oral	1715
		mouse	ip	121
		mouse	intramuscular	255
		rat	oral	770
		rat	ip	700
		rat	intramuscular	700
		dog	iv	202
		rabbit	subcutaneous	180[b]
manganese(II) ethylenebis-(dithiocarbamate)	[12427-38-2]	rat	oral	3000
		mouse	oral	2600
		guinea pig	oral	6400[b]
manganese(II) oxide	[1344-43-0]	mouse	subcutaneous	1000
manganese(III) oxide	[1317-34-6]	mouse	subcutaneous	616
		rat	intratracheal	100[b]
manganese(IV) dioxide	[1313-13-9]	mouse	subcutaneous	422
		rat	intratracheal	50[b]
		rabbit	intravenous	45[b]
manganese(II) sulfate	[7785-87-7]	mouse	ip	332
manganese(II) sulfate tetrahydrate	[10101-68-5]	mouse	ip	534
manganese tricarbonyl methylcyclopenta-dienyl	[12108-13-3]	rat	oral	50
		rat	ip	23
		mouse	oral	230
		mouse	ip	152
calcium permanganate	[10118-76-0]	rabbit	iv	50[b]
potassium permanganate	[7722-64-7]	rat	oral	1090
		mouse	subcutaneous	500
		rabbit	oral	600[b]
		rabbit	iv	70[a]

[a] Refs. and 204.

[b] Value is LD_{LO} = lethal dose low, ie, lowest dose of a substance introduced by any route other than inhalation, administered over any given period of time in a single or divided dosage that has been reported to have caused death in the test organism.

Table 19. **Occupational Standards for Manganese Compounds**[a]

Country	Mn TWA, mg/m^3	Mn STEL[b], mg/m^3
United States	5[c]	
Australia	5	
Belgium	5	
Czechoslovakia	2	6
Denmark	2.5	
Finland	2.5	
Hungary	0.3	0.6
Japan	0.3	
the Netherlands	1	
Poland	0.3	
Sweden	5	2.5
United Kingdom	5	

[a] Refs. 212, 213.
[b] STEL = short – term exposure limit.
[c] Value is a PEL:C, ie, permissible exposure limit ceiling exposure limit.

Table 20. **U.S. Federal Guidelines for Manganese Compounds**[a]

Material	Mn concentration, mg/m^3	Reference
	TLV/TWA	
dust and compounds	5	
manganese tetroxide and manganese fume	1	
manganese cyclopentadienyltricarbonyl	0.1	
2-methylcyclopentadienyl manganese tricarbonyl	0.2	
	STEL	
manganese fume	3	215
chronic oral reference dose (RFD)[b]	0.1[c]	
chronic inhalation reference concentration (RFC)[b]	0.0004	
carcinogenic classification	group D: not classifiable as to human carcinogenicity	216
secondary maximum contaminant level (MCL) water	0.05[d]	217

[a] Ref. 214.

[b] RFD = average daily intake considered adequate and safe.

[c] Units are mg/(kg·d).

[d] Units are mg/L.

Table 21. **Uses of Manganese Dioxides**

Application	Use	Reference
curing agent	oxidation of mercaptan terminals of liquid polysulfide polymers into disulfide bonds by manganese dioxide results in polysulfide rubber	225
radium removal	absorption of radium onto precipitated manganese dioxide followed by diatomaceous earth filtration removes 80–97% of Ra present in groundwaters; removal not pH sensitive in the 6.5–9.5 range and surface loading of 370–740 Bq/mg (10–20 pCi/mg) MnO_2 results in equilibrium radium activities in the treated water of 37–185 Bq/L (1–5 pCi/L)	226
brick colorant	manganese ores are used as colorants in brick manufacture; color shades from brown to red and gray to black can be obtained	227
uranium refining	manganese dioxide as oxidizing agent in the refining of uranium ore into yellowcake	
oxidation catalyst	manganese dioxide in combination with transition-metal elements serve as highly active thermally stable catalysts for volatile organic compound (VOC) oxidation; catalysts operate at temperatures significantly lower than comparable noble metal-based catalysts	228
glassmaking	as decolorizer, manganese dioxide is a common compensating agent for the yellow-green color imparted to glass by iron; as colorant, Mn(III) imparts a violet color, and Mn(II) imparts a faint yellow color to the glass; as finning agent, eliminates gas bubbles in glass melt	

Table 22. **Uses of Manganese Compounds**

Compound	Use	Reference
manganese acetate	transesterification catalyst in the production of poly(ethylene terephthalate) (PETP) from dimethyl terephthalate to form polyester; catalyst for the oxidation alkanes to carboxylic acids	229
manganese oxide	source for fertilizer and animal nutrients; starting point for other Mn salts, preparation of ferrites	
manganese sesquioxide		
Mn_2O_3	production of ferrites, thermistors	
Mn_3O_4	production of soft ferrites, welding rod coatings	
manganese carbonate	production of ferrites, pigments	
manganese sulfate	micronutrient in fertilizer (ca 50% domestic consumption); trace mineral in animal feed (ca 35% domestic consumption)	
manganese soaps	manganese oleate [23250-73-9], manganese naphthenate [1336-93-2], manganese stearate [3353-05-7], and other manganese soaps are used as primary driers in oil or alkyd resin-based paints, printing inks, and varnishes and function as catalysts for the autooxidation of the resin; manganese octoates have been shown to act as superior driers exhibiting high gloss and extended storage performance in water-based alkyd resin systems	230
MMT	combustion improver, antiknock compound	231
manganese phosphates	phosphating primarily ferrous metals using manganese phosphate can provide a phosphate coating imparting the item corrosion protection and in other cases improving the retention of lubricant, thus improving the wear resistance of bearing surfaces	
manganese complexes from triazacyclonone ligands	effective catalysts for the low temperature bleaching of stains by hydrogen peroxide	232
manganese chloride	production of MMT	
Maneb, Mancozeb [8018-01-7]	leaf and soil fungicide	

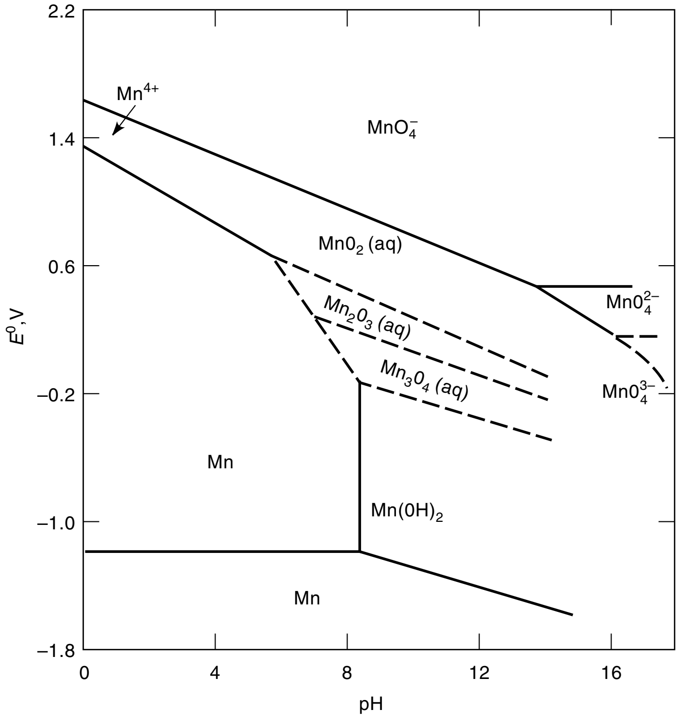


Fig. 1. pH potential diagram for manganese compounds at 25°C. (Courtesy of Springer-Verlag (9).)

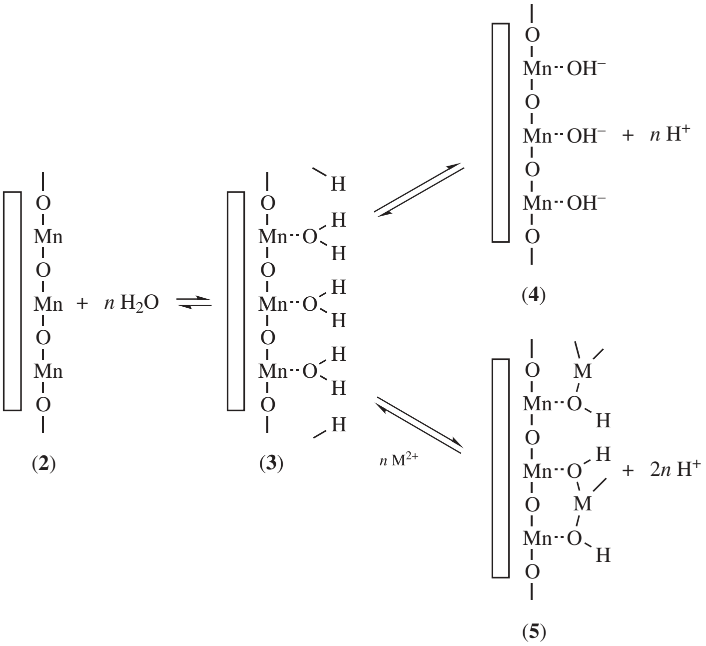
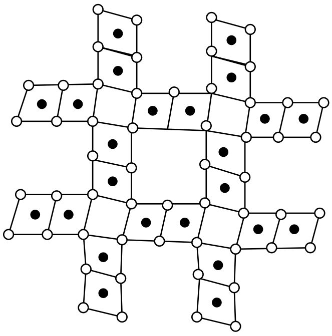


Fig. 2. Hydration of the surface structure of manganese dioxide (**2**) and subsequent reactions of hydrous manganese oxide (**3**) showing proton transfer (**4**) and ion exchange (**5**) where M^{2+} represents a divalent metal ion.



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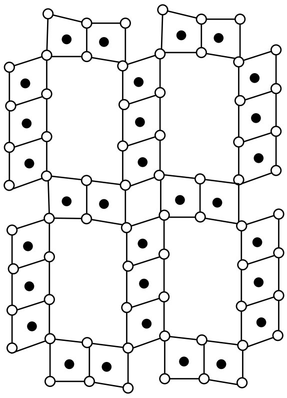

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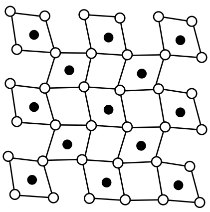

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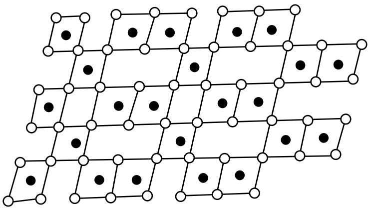
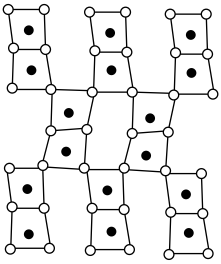


(9)



(10)

Fig. 3. Crystal structure of manganese dioxides where (●) represent Mn and (○), O^{2-}; and the lines define the octahedra; hollandite (**6**), psilomelane (**7**), pyrolusite (**8**), nsutite (**9**), and ramsdellite (**10**) (46).

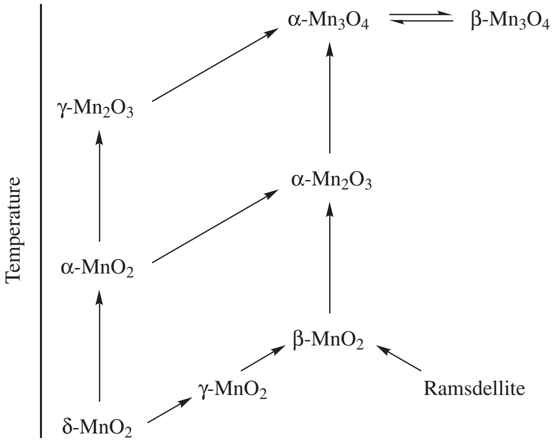


Fig. 4. Thermal transformation of manganese oxide phases.

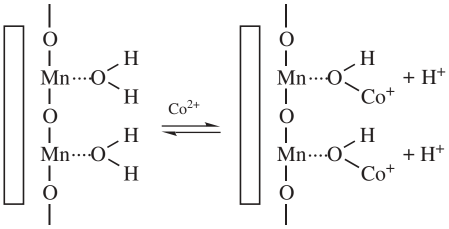


Fig. 5. Ion-exchange properties of hydrous manganese dioxide.

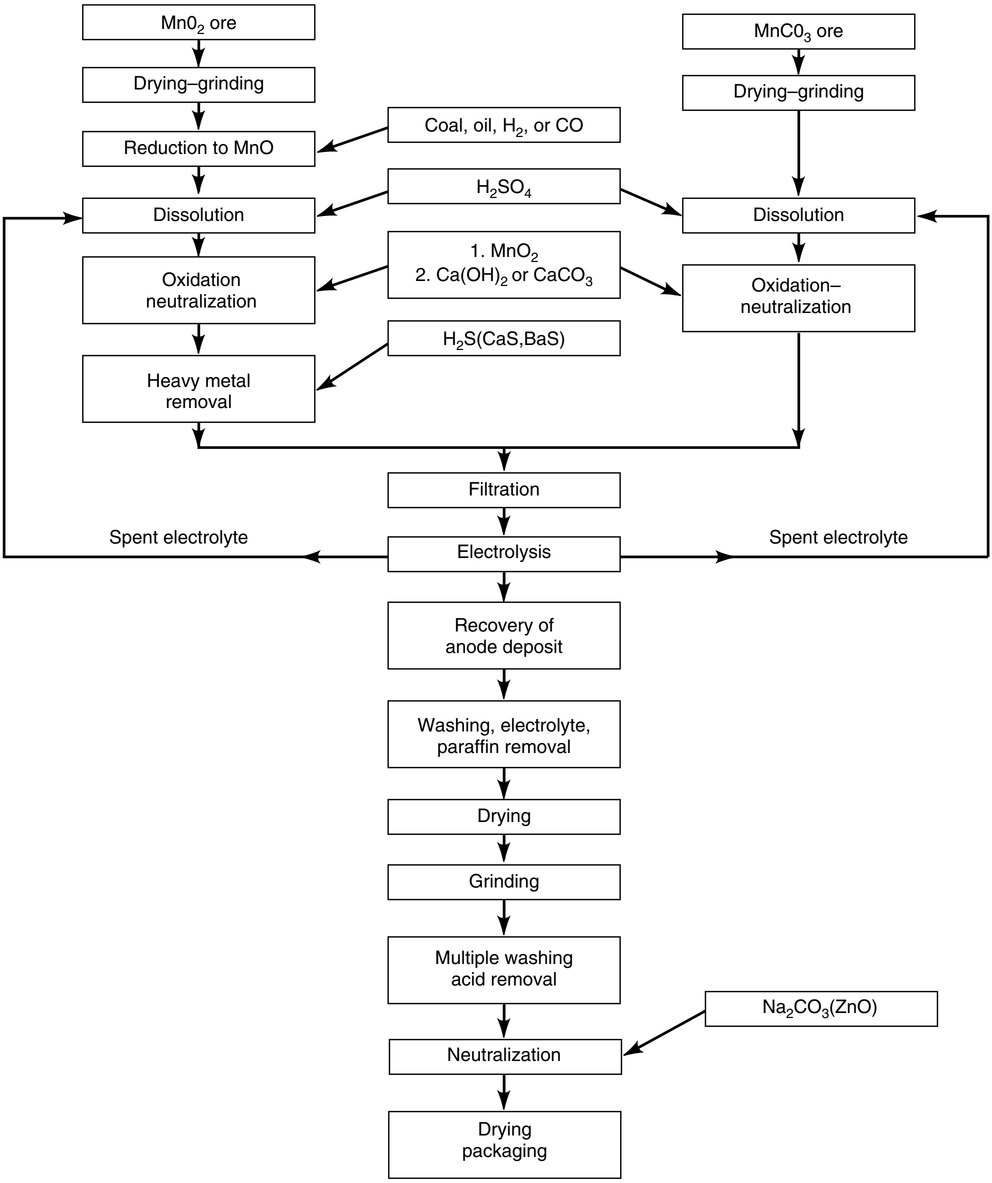


Fig. 6. EMD manufacture from manganese dioxide or rhodochrosite ore.

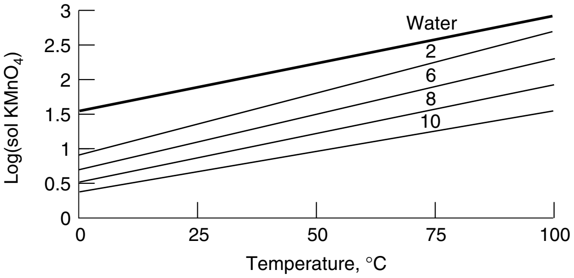


Fig. 7. Solubility of potassium permanganate, in g/L, in water and aqueous potassium hydroxide. Numbers represent KOH concentration in normality. Solubility can be approximated by the equation log(sol MnO_4, g/L)=1.288+0.016 T −0.103 N where T is temperature in °C and N is the KOH normality.

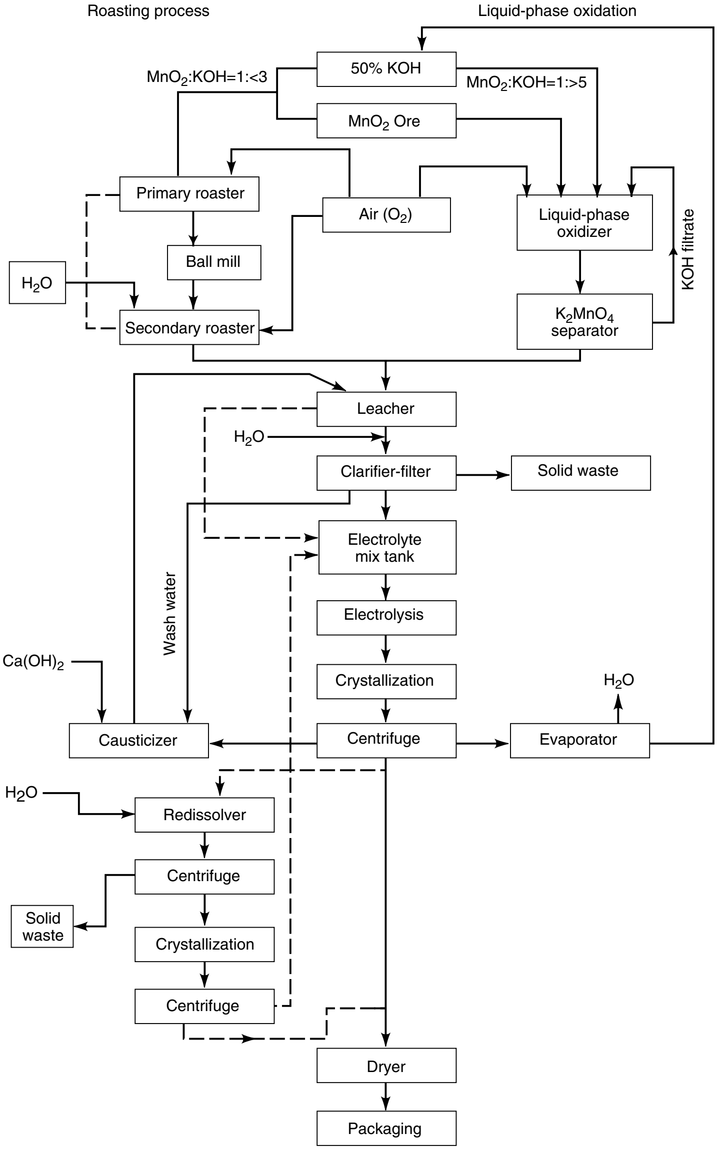


Fig. 8. Manufacture of potassium permanganate indicating both the roasting and the liquid-phase oxidation route; the latter is also known as the Carus process. The dashed line indicates an optional step.

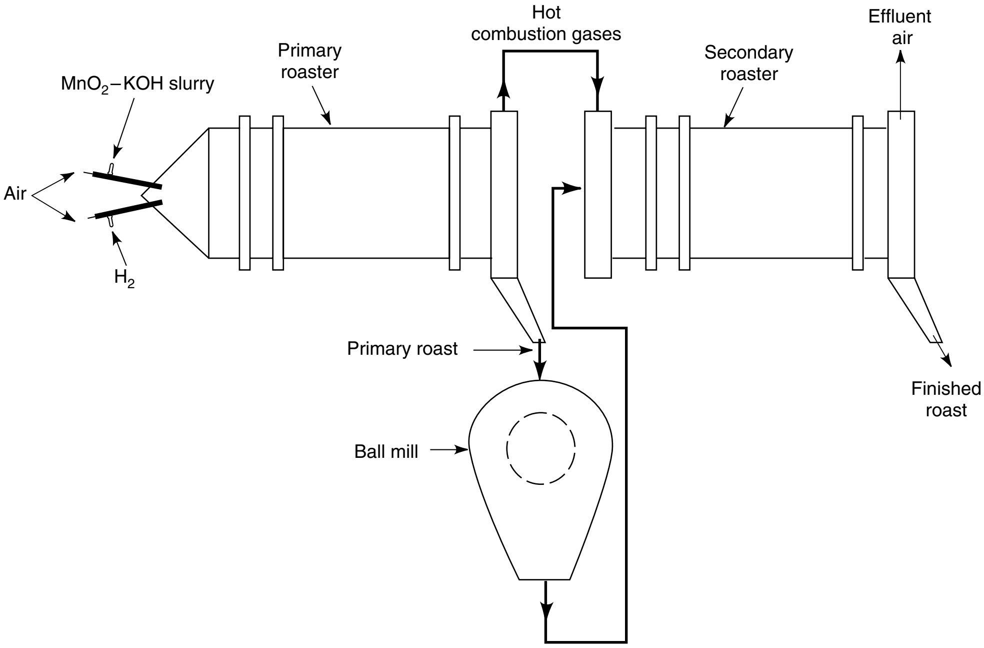


Fig. 9. Rotary kiln for the production of potassium manganate(VI).

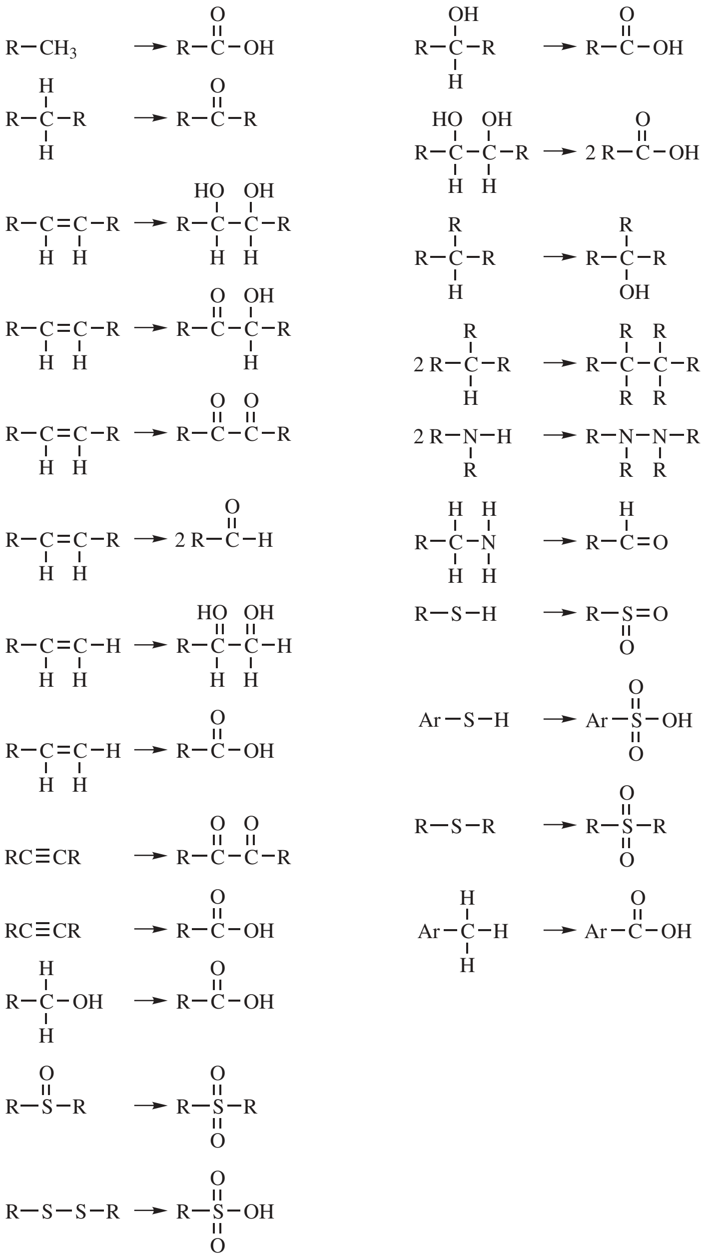


Fig. 10. Functional groups oxidized by potassium permanganate. Ar is an aryl group.

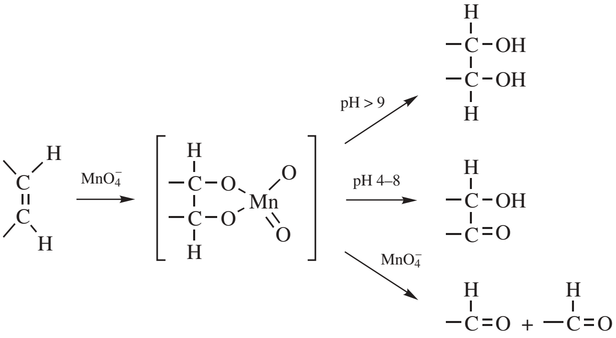


Fig. 11. Permanganate oxidation of alkenes.

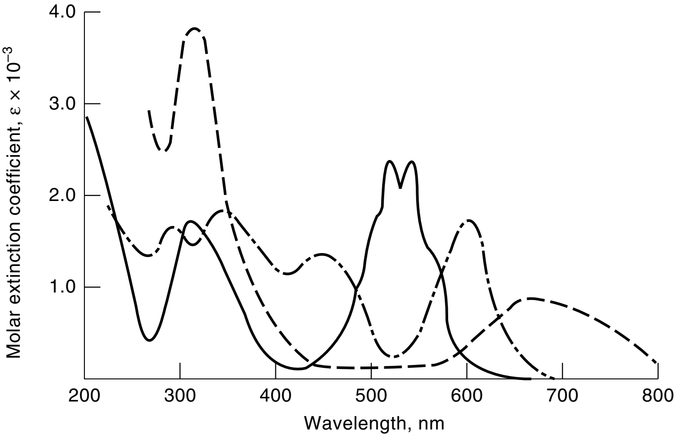


Fig. 12. Ultraviolet and visible spectrum of the oxyanions of manganese where (—) represents MnO_4^-, ([[art1]]) MnO_4^{2-}, and (— — —) MnO_4^{3-}. (Courtesy of Academic Press.)