

# tested demonstrations



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## A Lecture Demonstration of the Various Oxidation States of Manganese

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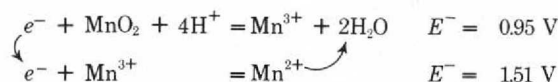
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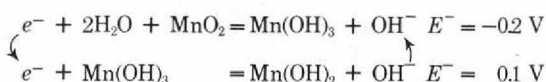
All the *d*-block elements can have more than one oxidation number (other than zero), the largest number being seven in the case of manganese. Compounds containing the various oxidation states of manganese have been prepared. The table shows the color and the various compounds<sup>1</sup> in which these states are present. Among these, Mn(II) in MnSO<sub>4</sub>, Mn(IV) in MnO<sub>2</sub>, and Mn(VII) in KMnO<sub>4</sub> are stable and are on our laboratory shelves. Mn(0) is available in the form of metal. The other states Mn(III), Mn(IV), and Mn(VI) are comparatively less stable, but can be prepared in the laboratory, in a very short time, by mixing the common available salts of the first three stabler states. Due to their characteristic color and their simple preparations, this can prove to be a very interesting class demonstration.

It is often found that a given oxidation number of an element can be obtained by reaction of compounds in which the element has higher and lower oxidation numbers. The redox potential can help to predict the direction of the reaction because if two electrode systems are linked to form a voltaic cell, the system which is higher in the series will become the negative pole (transferring electrons to the external system) and the system which is lower will become the positive pole. So in general for any pair of couples in the redox series, reaction will tend to go in such a way that taking the individual species in the couples in counter clockwise order, starting with the bottom left in the positions that they occupy in the series, gives the reactants and products of the possible reaction. A more convenient form for prediction is to write the half equations for the electrodes in a diagram as below

in acid conditions



in alkaline conditions

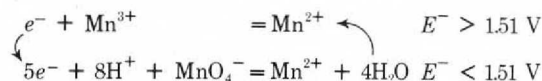


Here the redox potential values suggest that formation of Mn(II) from Mn(III) and Mn(IV) is not possible in acid or alkaline conditions. Predictions in this case refer only to stan-

Oxidation States of Manganese-

Oxidation State	Color	Compound in which present
(Zero)	Metallic Gray	Mn <sub>2</sub> (CO) <sub>10</sub>
(I)	...	Mn(CO) <sub>5</sub> Cl, K <sub>5</sub> [Mn(CN) <sub>6</sub> ]
(II)	Light Pink	MnSO <sub>4</sub> , MnCl <sub>2</sub>
(III)	Red	MnF <sub>3</sub> , Mn(acac) <sub>3</sub>
(IV)	Black	MnO <sub>2</sub> , Mn(SO <sub>4</sub> ) <sub>2</sub>
(V)	Blue	MnO <sub>4</sub> <sup>3-</sup>
(VI)	Green	MnO <sub>4</sub> <sup>2-</sup>
(VII)	Violet	MnO <sub>3</sub> <sup>+</sup> , MnO <sub>4</sub> <sup>-</sup> , MnO <sub>3</sub> F

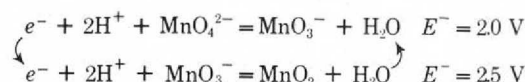
dard conditions—molar solutions of reactants and products present at the same time and a fixed temperature. In other conditions concentrations or temperature effects may alter the equilibrium position of the opposing electrode systems and lead to partial reversal of the change, provided the difference in *E*<sup>-</sup> values for the electrodes concerned is not greater than 0.4 V. When we mix Mn(II) and Mn(VII) in acid solutions



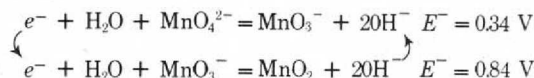
the reaction is just feasible, but the decrease of *pH* will favor the formation of Mn(III).

Mn(V) also cannot be prepared by mixing Mn(IV) and Mn(VI) in acid or alkaline conditions because the *E*<sup>-</sup> values differ by more than 0.4 V so reversal is not possible by change of conditions in acid or in alkaline conditions

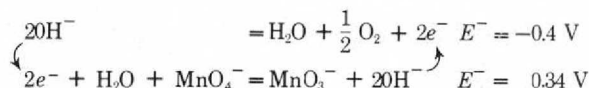
in acid



in alkaline conditions

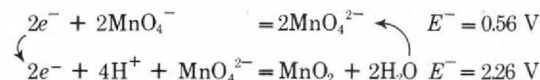


The reduction of Mn(VII) in a strongly basic solution

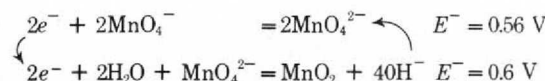


is possible at a very high *pH*.

Mn(VI) cannot be obtained by mixing Mn(VII) and Mn(IV) in acidic conditions, *E*<sup>-</sup> values being far apart.



In alkaline conditions *E*<sup>-</sup> values still do not favor the reaction, but as



<sup>1</sup> Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," Interscience Publishers, New York, 1972.

they are very close, change of conditions might reverse the reaction. Increase of alkalinity, therefore, tips the balance in favor of the reaction desired.

### Experimental

#### Preparation of Mn(II)

Dissolve about 12 g of hydrated Mn(II) sulfate in 100 ml of dilute sulfuric acid; a *light pink* colored solution containing Mn(II) is obtained.

#### Preparation of Mn(III)

Take about 50 ml of the solution of Mn(II) prepared above. Add to it 10 ml of concentrated sulfuric acid, cool the beaker under the tap, and then add 1 ml of 0.1 M  $\text{KMnO}_4$  solution. The resulting solution is *deep red* due to Mn(III). Dilution (rise of pH) returns Mn(II) and Mn(IV).

#### Preparation of Mn(IV)

A 10% suspension of  $\text{MnO}_2$  in acetone is stable for sufficient time to compare its *black color* due to Mn(IV) with the color of other states.

#### Preparation of Mn(V)

Add 150 g of potassium hydroxide (pellets) to 20 ml of water and add 4–5 crystals of  $\text{KMnO}_4$  to the paste and allow it to stand. A *blue color* will appear slowly on standing.

#### Preparation of Mn(VI)

To 50 ml of 0.01 M  $\text{KMnO}_4$  add 25 ml of 5% NaOH. Then add 10 g of solid  $\text{MnO}_2$ . Shake and filter and a *green colored* solution is produced showing the presence of Mn(VI). Add dilute sulfuric acid to the beaker containing the green solution, and the color changes to (violet) Mn(VII). This reversal can be done any number of times.

Another method is to place a layer (approximately 1 cm) of  $\text{MnO}_2$  solid on a filter and pour on it a  $\text{KMnO}_4$  solution (0.01 M), made alkaline by addition of NaOH. A green colored solution will appear in the filtrate below giving a beautiful contrast to the colors of Mn(VII) (violet) and Mn(VI) (*green*).

#### Preparation of Mn(VII)

A solution of 0.1 g of  $\text{KMnO}_4$  in 100 ml of water gives the beautiful *violet color* of Mn(VII).

