Ionic and distilled water was used throughout the experiments. The experimental runs were carried out in 250 ml Erlenmeyer flasks, water and sodium hydroxide were mixed together and then manganese (II) sulfate was introduced. Samples were collected during the course of the reaction for the determination of Mn²⁺ concentration.

The reaction runs in a 500 ml gas washing bottle with a side inlet and fitted disc at the bottom, with nitrogen or oxygen flowing through the solution continuously. The reactions start immediately as the nitrogen or oxygen purge were applied, and the experiment runs were conducted. The Mn²⁺ was measured by following a method used by other workers². Sodium gluconate was added to the sample, resulting in the formation of colored complexes, which were then monitored by UV-Vis spectrophotometer. The intensity of the color is correlated to the Mn²⁺ ion concentration.

A UV spectrophotometer (model Milton Roy 1001 plus), interfaced to µ-Quant software, which runs on IBM PC was used. The cuvette width was 1 cm. The Mn²⁺ ion complexes have maximum absorbance at 235 nm and 450 nm. A wavelength of 450 nm was chosen in this study. Runs under vacuum were performed with the vacuum pump connected to Erlenmeyer flask with side outlet. The system was kept under vacuum throughout the experimental runs. Samples were taken periodically from the system and the UV-Vis absorbance measured. All the glassware and other containers used in this experiment were soaked with a mixture of H₂O₂/H₂SO₄ and then rinsed three times with de-ionized distilled waters.

RESULTS AND DISCUSSION

When a solution of Mn²⁺ is added to an alkaline solution, the initially colorless solution turns brown. The formation of a brownish solution is a clear indication of the presence of Mn³⁺, either in the form MnO(OH) or Mn(OH)₂. In alkaline media, sodium gluconate (NaGH₄) stabilizes Mn²⁺, Mn³⁺ and Mn⁴⁺ oxidation states. Reaction of dinuclear Mn²⁺-gluconate with O₂ is first order with respect to each reactant, yielding the Mn³⁺ species and H₂O₂. Further oxidation of the dinuclear Mn³⁺ complex gives Mn⁴⁺ complex and peroxide ion. All these reactions can be summarized as follows²:

\[ \text{Mn}^{2+} + \frac{1}{2} \text{O}_2 \rightarrow \text{[Mn}^{2+} \text{(GH}_3\text{)}_2\text{]}^{2+} + \frac{1}{2} \text{H}_2\text{O} \]

\[ 2[\text{Mn}^{2+} \text{(GH}_3\text{)}_2\text{]}^{2+} + \frac{1}{2} \text{H}_2\text{O} \rightarrow [\text{Mn}^{2+} \text{(GH}_3\text{)}_2\text{]}^{3+} + \frac{1}{2} \text{O}_2 \]

On standing [Mn³⁺(GH₃)₂(HO)₂]³⁺ is very slowly oxidized to [Mn⁴⁺(GH₃)₂(O₂)(HO)₂]⁴⁺ by O₂:

\[ [\text{Mn}^{3+} \text{(GH}_3\text{)}_2\text{(HO)}_2]\text{]^{3+} + \text{O}_2 + \text{3OH}^{-} \rightarrow [\text{Mn}^{4+} \text{(GH}_3\text{)}_2\text{O}_2\text{(HO)}_2]\text{]^{4+} + \text{H}_2\text{O} \]
It is known that the complex ion \( \text{Mn}^{4+} \cdot (\text{GH}_3)^2 \cdot \text{O}_2 \cdot \text{HO}_2 \) gives a cherry-red color while \( \text{Mn}^{3+} \cdot (\text{GH}_3)^2 \cdot \text{HO}_2 \) gives a brown color. Figure 1 presents the development of \( \text{Mn}^{3+} \) concentration as a function of wavelength at constant sodium hydroxide concentration. The \( \text{Mn}^{2+} \) concentrations used were 3 ppm, 6 ppm, 9 ppm, and 12 ppm. As expected, there was an increase in absorbance with an increase in the \( \text{Mn}^{3+} \) concentration. This is because increasing the concentration of \( \text{Mn}^{2+} \) results in an increase in \( \text{Mn}^{3+} \) concentration as indicated by the following equations:

\[
2\text{Mn}^{2+} + 4\text{OH}^- \rightarrow 2\text{Mn(OH)}_4^{2-} \\
4\text{Mn(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Mn}^{3+} + 12\text{OH}^- 
\]

The last two equations explain why increasing \( \text{Mn}^{2+} \) concentration results in an increase in \( \text{Mn}^{3+} \) concentration. Also, it is possible that the manganese (II) hydroxide can give various oxo species of manganese as indicated by the following reactions:

\[
2\text{Mn(OH)}_2 \rightarrow 2\text{MnOOH} + \text{H}_2\text{O} \\
3\text{MnO}^{2+} + 9\text{OH}^- \rightarrow 3\text{Mn(OH)}_3^{2+} + \text{OH}^- 
\]

We then held the concentration of \( \text{Mn}^{2+} \) constant and studied the development of \( \text{Mn}^{3+} \) at various concentrations of sodium hydroxide and the results are presented in Figure 2. There is an increase in \( \text{Mn}^{3+} \) absorbance with increase in sodium hydroxide concentration from 0.5 \( \mu \text{mol/µL} \) to 5 \( \mu \text{mol/µL} \). Further increase in the sodium hydroxide concentration results in decrease in \( \text{Mn}^{3+} \) concentration and results in the drop in absorbance. This observation is not unusual because addition of excess sodium hydroxide to \( \text{Mn(OH)}_3 \) results in the formation of soluble manganese complex:

\[
3\text{Mn}^{2+} + 9\text{OH}^- \rightarrow 3\text{Mn(OH)}_3^{2+} \\
\text{Mn(OH)}_3^{2+} + \text{OH}^- \rightarrow \text{Mn(OH)}_4^{-} 
\]

The formation of soluble \( \text{Mn(OH)}_4^- \) results in a decrease in the absorbance.

Previous workers had indicated that oxidation of \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \) can only take place in the presence of \( \text{O}_2 \). We then studied the effect of \( \text{N}_2 \) purge on the development of \( \text{Mn}^{3+} \) and the results are presented in Figure 3. The concentration of \( \text{Mn}^{2+} \) was 6 ppm and 12 ppm, and the concentration of sodium hydroxide was maintained at 1 \( \mu \text{mol/µL} \). The concentration of \( \text{Mn}^{3+} \) without \( \text{N}_2 \) purge was found to be higher than with \( \text{N}_2 \) purge at the two \( \text{Mn}^{2+} \) concentrations studied. This confirms that \( \text{O}_2 \) is involved in the oxidation of \( \text{Mn}^{2+} \) to \( \text{Mn}^{3+} \). Also, this observation proves that \( \text{Mn}^{2+} \) can be oxidized to \( \text{Mn}^{3+} \) in the absence of \( \text{O}_2 \).
We then studied the effect of O$_2$ purge instead of N$_2$ purge on the development of Mn$^{3+}$ and the results are presented in Figure 4. It is clear from the two concentrations of Mn$^{2+}$ used that with O$_2$ purge there is more development of Mn$^{3+}$ than without. This further supports the fact that oxidation of Mn$^{2+}$ to Mn$^{3+}$ can take place with O$_2$. Also, the more Mn$^{3+}$ formed results into faster disproportionation of Mn$^{3+}$ into Mn$^{2+}$ and Mn$^{4+}$.

Furthermore we studied the development of Mn$^{3+}$ at Mn$^{2+}$ concentrations 6 ppm and 9 ppm with and without O$_2$ purge as a function of time and the results are presented in Figure 5. It is clear that with O$_2$ purge the rate of development of Mn$^{3+}$ is enhanced and this is because O$_2$ rich environment results in the following equations being shifted further to the right:

- $4 \text{Mn(OH)}_2 + O_2 \rightarrow 4\text{MnOOH} + 2\text{H}_2\text{O}$
- $4 \text{Mn(OH)}_2 + O_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Mn}^{3+} + 12\text{OH}$

This observation confirms that the oxidation of Mn$^{2+}$ to Mn$^{3+}$ follows different kinetics when O$_2$ is present as opposed to when it is absent.
We then studied the development of Mn$^{3+}$ at normal conditions and under vacuum. It is clear that the development of Mn$^{3+}$ is slower and the amount of Mn$^{3+}$ formed is less. This was confirmed when the Mn$^{2+}$ concentration was increased to 9 ppm. All these observations lead to the conclusion that the oxidation of Mn$^{2+}$ to Mn$^{3+}$ can still take place in absence of O$_2$.

**CONCLUSION**

Manganese (II) is very unstable under alkaline medium. It is readily oxidized to Mn$^{3+}$ in the presence of oxygen or absence of oxygen. Manganese (III) species is also very unstable, once formed it readily disproportionate into Mn$^{3+}$ and Mn$^{4+}$. The Mn$^{4+}$, then undergoes hydrolysis to form MnO$_2$, which appears as a black precipitate. It has been demonstrated that removal of O$_2$ in Mn$^{2+}$ system under alkaline medium decreases the oxidation process of Mn$^{2+}$ to Mn$^{3+}$, well as the disproportionation of Mn$^{3+}$ to Mn$^{4+}$ and Mn$^{2+}$ species.

**REFERENCES**

12. BodinME, Sawyer DT. Electrochemical and Spectroscopic Studies of Mn(II), Mn(III) and Mn(IV) Gluconate Complexes. Inorganic Chemistry 1976; 15(7) 1538-1543.