Procedure: (*a*) Mix in culture tube by shaking 0.5 g pyrolusite + 1 g NaOH + 1 g KNO_3. Project in H-3 and heat until molten. Cool. Shake with 30 ml water, filter equal amounts into the two cells of C-2. Project. (*b*) Gently add a dropperful of dil. HNO_3 to the liquid in cell *1*. (*c*) Drop a small lump of dry ice into cell *2*.

Observations: (*a*) KNO_3 oxidizes MnO_2 to green manganate, K_2MnO_4. (*b*) HNO_3 oxidizes the upper portion of the liquid in cell *1* to purple permanganate, MnO_4^-. (*c*) Dry ice converts green $MnO_4^=$ into purple permanganate, MnO_4^- (this is an industrial method).

Reactions: $3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2$.

Reference: HARPIN, R. E., J. CHEM. EDUC., **36**, A685, 1959.

Dem. 645—Oxygen from $KMnO_4$

To show: The preparation of oxygen from heating permanganate.

Materials: H-1, $KMnO_4$, splint.

Procedure: Project H-1 with the test tube quarter-full of $KMnO_4$. Heat with the small alcohol burner. Collect the evolved gas and test it for oxygen with a glowing splint.

Observations: Oxygen gas is evolved, the splint bursts into flame.

$$4KMnO_4 \rightarrow 2K_2O + 4MnO_2 + 3O_2$$

Dem. 646—MnO_2 as a Catalyst for H_2O_2 Decomposition

To show: Catalytic action of MnO_2 on hydrogen peroxide.

Materials: C-3, two splints, 3% H_2O_2, detergent, MnO_2.

Procedure: Project C-3 half-filled with H_2O_2. (*a*) Wet two sticks, dip into MnO_2 to collect some particles, drop the sticks into cells 2 and 3. (*b*) Drop some granules of detergent into cell 3.

Observations: (*a*) Vigorous decomposition of the H_2O_2 occurs on the surface of the MnO_2 particles. (*b*) As the O_2 gas evolves, it rises with the detergent as a foam.

Dem. 647—Permanganate + Fe(II)

To show: Titration of ferrous salt with standard permanganate solution.

Materials: 0.5 *N* $FeSO_4$, $(NH_4)_2SO_4 \cdot 6H_2O$ [98.04 g per 1000 ml solution], dil H_2SO_4, C-1, stirrer, 0.1 *N* $KMnO_4$ (3.16 g $KMnO_4$ per 1000 ml solution).

Procedure: Project C-1 half-full of water. Add a dropperful of dil. H_2SO_4. Drop in (class counting) 20 drops of 0.1 *N* $KMnO_4$. Now drop in (class counting) the $FeSO_4$ solution until the pink color vanishes.

Reactions: $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$

Note: Mohr's salt, $(NH_4)2FeSO_4 \cdot 6H_2O$ can be used in place of $FeSO_4$.

Dem. 648—Permanganate + SO_2 or H_2S

To show: The reduction of MnO_4^- by SO_2 or H_2S.

Materials: C-3, $KMnO_4$, $NaHSO_3$-aq, Na_2S-aq, H_2SO_4-dil.

Procedure: Project C-3 with cells quarter-full of dilute H_2SO_4. Add varying amounts of dil. $KMnO_4$ to each cell. Now titrate with $NaHSO_3$-aq or Na_2S-aq.

Observations: The violet $KMnO_4$ is reduced to colorless (pink) Mn^{+2}, according to reaction as

$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

Dem. 649—Permanganate + H_2O_2

To show: Titration of hydrogen peroxide with standard permanganate solution.

Materials: 0.1 *N* $KMnO_4$, dil. H_2SO_4, 3% H_2O_2, C-1, stirrer.

Procedure: Project C-1 half-full of water. To it add a dropperful of dil. H_2SO_4 + exactly 10 drops of $KMnO_4$. Now add H_2O_2 dropwise until the pink color disappears.

Reaction: $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + H_2O + 5O_2 \uparrow$.

Calculations: 0.1 *N* $KMnO_4$ contains 3.16 g $KMnO_4$ per 1000 ml solution. From the volume of solution of H_2O_2 used, calculate the % H_2O_2 in the original solution.

E. Group VIII. (Fe, Co, Ni)

Dem. 650—Oxidation and Reduction of Iron

Experiment developed by Edwin H. Cooper.

To show: The oxidation of Fe(II) and reduction of Fe(III).

Materials: *Soln A:* 0.4 g Mohr's salt ($Fe(NH_4)_2SO_4$,-$6H_2O$) + 4 ml 6 *M* H_2SO_4 + 100 ml water. $KMnO_4$-aq, $K_2Cr_2O_7$-aq, KSCN-aq, iron picture-wire; H-3.

Procedure: Project culture tubes one-quarter full of *Soln A* + 1 ml KCNS-aq (mixture should be practically colorless.) (*a*) Now add dropwise to red color $K_2Cr_2O_7$-aq to tube *1*, $KMnO_4$-aq to tube *2*, and H_2O_2 to tube 3. (*b*) Put 1-in. lengths of iron picture-wire into each tube and boil 1 min.

Observations: (*a*) $KMnO_4$, $K_2Cr_2O_7$ and H_2O_2 all oxidize Fe^{++} to Fe^{+++}, which then forms deep red $FeCNS^{++}$. (*b*) The iron wire reduces the ferric to ferrous; the red $FeCNS^{++}$ disappears and the solutions turn colorless.

Reactions: (*a*) $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$

(*b*) $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3 + K_2SO_4$

(*c*) $Fe^{+3} + CNS^- \rightleftarrows FeCNS^{++}$ deep red