

Work Session 21b: Electrochemistry and Balancing Redox Reactions

1. For the balanced chemical equation: $2 \text{KMnO}_4 + 10 \text{NaI} + 8 \text{H}_2\text{SO}_4 \rightarrow 5 \text{I}_2 + 2 \text{MnSO}_4 + 5 \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 8 \text{H}_2\text{O}$
What is the oxidizing agent? The reducing agent? Which atom is being oxidized? Which is being reduced?

2. Complete the chart

	Voltaic cell	Electrolytic cell
oxidation occurs at:		
reduction occurs at:		
value of ΔG :		
charge on anode:		
charge on cathode:		

3. Given the cell notation: $\text{Pt} | \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) || \text{Br}_2(\text{l}) | \text{Br}^-(\text{aq}) | \text{Pt}$
What are the two half reactions taking place? Which is the anode, which the cathode?

4. Write out the $\text{Fe}^{2+}|\text{Fe}$, the $\text{Cr}^{3+}|\text{Cr}$, and the $\text{Mn}^{2+}|\text{Mn}$ half-cells with voltages from the textbook. What is the reaction and the voltage when the iron cell is hooked up to each of the others?

5. Of the six substances in question 4, which is the strongest oxidizing agent? Which is the strongest reducing agent? Which is the weakest oxidizing agent? Which is the weakest reducing agent?

6. What is meant by the Q/K ratio? For E_{cell} to be positive, what must the Q/K ratio be? What happens to the current flow in a cell when $Q/K > 1$?

7. For the cell in question 3, what happens to the voltage if $[\text{Fe}^{2+}]$ increases? If $[\text{Fe}^{3+}]$ increases. If $[\text{Br}^-]$ increases?

8. Using the three half cells in question 4, what would a proper sacrificial anode material for chromium be? Explain.
9. In an electrolytic cell using molten KBr, what is formed at the anode? What is formed at the cathode? Would there be any differences if the KBr were dissolved in water rather than molten?
10. Nickel is electroplated from a NiSO₄ solution onto a copper sheet. How many grams of nickel will be deposited if a 2.5 A current runs for 30 minutes? How would your calculations differ if the substance deposited were silver from a AgNO₃ solution?

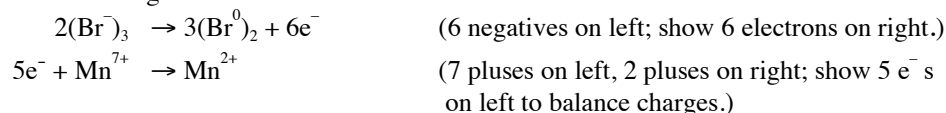
For the following two questions, see the following pages for steps to balance redox reactions using the half-cell method.

11. For the following unbalanced chemical equation, show the two half-cell reactions, and balance the equation:
$$\text{KMnO}_4(\text{aq}) + \text{KBr}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MnSO}_4(\text{aq}) + \text{Br}_2(\text{l}) + \text{K}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
12. For the following unbalanced net ionic reactions, add H⁺ ions and water, or OH⁻ ions and water as indicated and as needed. Show the two half-cell reactions for each.
- $$\text{Zn}(\text{s}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{Zn}^{+2}(\text{aq}) + \text{N}_2(\text{g}) \quad (\text{acidic solution})$$
- $$\text{Cl}_2(\text{aq}) + \text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad (\text{basic solution})$$

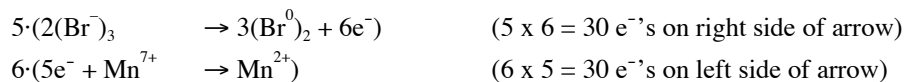
Steps to Balance Redox Chemical Equations Using the Half-Cell Method

Example: $\underline{\hspace{1cm}} \text{AlBr}_3 + \underline{\hspace{1cm}} \text{KMnO}_4 + \underline{\hspace{1cm}} \text{H}_2\text{SO}_4 \rightarrow \underline{\hspace{1cm}} \text{Al}_2(\text{SO}_4)_3 + \underline{\hspace{1cm}} \text{Br}_2 + \underline{\hspace{1cm}} \text{MnSO}_4 + \underline{\hspace{1cm}} \text{K}_2\text{SO}_4 + \underline{\hspace{1cm}} \text{H}_2\text{O}$

- Go through each element on each side and determine its oxidation number.** Use the oxidation number rules from the textbook. A few things to notice:
 - Elements like K or Al, in compounds, always have the fixed oxidation number of +1 for K and +3 for Al; The metals in columns 1, 2, and 13 have valences of +1, +2, and +3.
 - Oxygen, in compounds other than peroxides, is always -2;
 - Hydrogen, in compounds, is almost always +1.
 - Also note that what we are looking for is a change in oxidation number from left to right in a reaction. Sulfate groups, SO_4^{2-} , if shown on the left and right of the equation, have no change in oxidation number for either of the constituent elements.
- List each element that has a change of oxidation number.** In this reaction, Br is -1 on the left and 0 on the right. Mn is +7 on the left and +2 on the right. (In AlBr_3 , the Al is +3, and there are 3 Br's, so each Br must be -1). If you do not understand how these numbers are figured, stop right now and read pages 148 to 153 and 896 to 899 in your textbook.
- Show each of these changes in a "skeleton half-cell",** a reaction showing the element in one oxidation state changing to that element in the other oxidation state. If there are subscripts on the element, include them. Parentheses help to identify these cases. Balance each half-cell for numbers of atoms. Show the oxidation number per atom times the number of atoms in the unit as a superscript. Count the total charge on each side of the arrow. Add the proper number of electrons to balance for charges:



- Multiply each half-cell by the multiplier necessary to get the electrons in each half cell equal.** In this case, it will be a 5 and a 6:



- The heart of the balancing has been accomplished. 30 Br atoms with a -1 oxidation number are being transformed into 30 Br atoms with 0 oxidation number, while 6 Mn atoms with a 7+ oxidation number are being transformed into 6 Mn atoms with a +2 oxidation number. There must be the same number of electrons totally given off in one half-cell as there is the number of electrons totally taken in for the other half-cell.
- Transform this information to the reaction :** Multiply the 5 x the $2(\text{Br}^-)_3$'s to get 10 Br_3 's. The 10 goes before the AlBr_3 . Multiply the 6 x the 3Br_2 's to get 15 Br_2 's. Multiply the Mn half-cell by the 6.

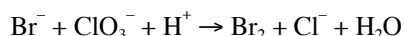


- The rest of the balancing is done "by inspection"** There are 6 K's on the left, so there must be 3 K_2SO_4 's shown on the right. There are 10 Al's on the left, so there must be 5 $\text{Al}_2(\text{SO}_4)_3$'s on the right. 24 oxygens from the KMnO_4 will turn up as 24 H_2O molecules on the right. This will require 24 H_2SO_4 molecules on the left. Fill in the numbers and count all atoms to see if everything balances.



The oxidation/reduction participants are shown with underlined factors in this reaction. Mn atoms in permanganate ions are oxidizing Br atoms in bromide ions. This is the information that is most important to know in oxidation/reduction (redox) reactions.

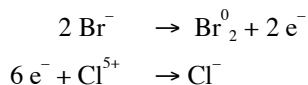
Example Using a Net Ionic Equation



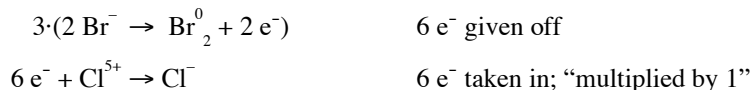
- Go through each element on each side and determine its oxidation number.**

2. List each element that has a change of oxidation number. Br and Cl

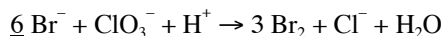
3. Show each of these changes in a "skeleton half-cell":



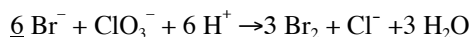
4. Multiply each half-cell by the multiplier necessary to get the electrons in each half cell equal.



6. Transform this information to the reaction :



7. The rest of the balancing is done "by inspection"



It's the 3 oxygens on the ClO_3^- that end up as water, requiring 6 H^+ 's to do so.

Taking Care of Oxygen atoms

Many redox reactions involve reagents like MnO_4^- ions or $\text{Cr}_2\text{O}_7^{2-}$ ions turning into Mn^{2+} ions or Cr^{3+} ions. The oxygen atoms attached to the Mn or Cr have to end up somewhere. When you finish balancing a reaction "by inspection", the oxygen atom numbers may not balance. If so, the process used to balance their numbers is different in acid and in basic solutions.

In acid solutions, H^+ 's will react with the oxygens to form water. So for each MnO_4^- changing to a Mn^{2+} , 8 H_2O 's will be required. These 8 H^+ 's could come from 4 H_2SO_4 molecules or 8 HCl molecules or 8 H_3O^+ ions or simply from the 8 H^+ 's which are often shown in really stripped-down net ionic reactions. (If H_3O^+ is used as the source of the H^+ 's, remember that it is H_2O with an H^+ attached, so 8 H_3O^+ will take care of 4 O's, to produce a total of 12 H_2O 's.)

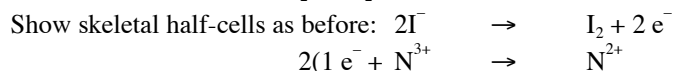
On the side with too much oxygen, per oxygen, add 2 $\text{H}^+ \rightarrow$ On the side with too little oxygen, per oxygen, add 1 H_2O

In basic solutions, H_2O molecules react with the oxygens to form 2 OH^- ions, so for each MnO_4^- ion, 4 H_2O 's would turn into 8 OH^- ions. The OH^- could come from NaOH , or any of the strong bases.

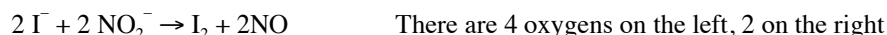
On the side with too much oxygen, per oxygen, add 1 $\text{H}_2\text{O} \rightarrow$ On the side with too little oxygen, per oxygen, add 2 OH^-

In redox reactions, to emphasize the actual participating species, a form of net ionic equation is often shown where just the reacting materials are noted, with information as to whether the solution is acidic or basic.

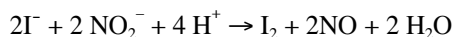
Example 1: Acidic solution $2\text{I}^- + \text{NO}_2^- \rightarrow \text{I}_2 + \text{NO}$



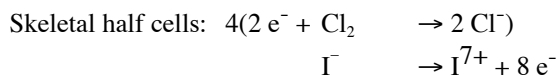
and transfer numbers to equation:



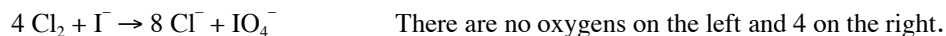
So, to take care of the oxygen imbalance in this acid solution, add 4 H^+ 's to the left and 2 H_2O 's to the right:



Example 2: Basic solution $\text{Cl}_2 + \text{I}^- \rightarrow \text{Cl}^- + \text{IO}_4^-$



and transfer numbers to equation:



To take care of the oxygen imbalance in this basic solution, add 8 OH^- 's to the left and 4 H_2O 's to the right:

