Spontaneity of Redox Reactions

- Compare the reaction when zinc metal is placed in copper(II) solution and the reaction when copper metal is placed in a zinc solution

*****Demo: Comparing two Similar Redox Reactions*****

reduced

net ionic equation : $Zn_{(s)} + Cu^{2+}_{(aq)} \xrightarrow[\text{spontaneous}]{} Zn^{2+}_{(aq)} + Cu_{(s)}$

oxidized

vs.

net ionic equation : $Cu_{(s)} + Zn^{2+}_{(aq)} \longrightarrow$ no rxn!

- Different atoms and ions have different abilities/strength to reduce or oxidize other atoms or ions
  - Atoms and ions are listed in tables, ranked according to their ability/tendency to oxidize or reduce other atoms or ions
  - A complete table is found on pg.7 of data booklet. Below is just a section of the table found in the data booklet.

Table of Selected Standard Electrode Potentials*

stronger ie. more reactive ↓ weaker ie. less reactive

weaker ie. less reactive ↑ stronger ie. more reactive

Reduction Half-Reaction	Electrical Potential $E°$ (V)
O.A. R.A.	
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.14
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-(aq)$	−0.15
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.26

in geneal $O.A. + ne^- \underset{\text{oxidized (reverse)}}{\overset{\text{(forward) reduced}}{\rightleftharpoons}} R.A.$

- We can use this table to predict if redox reactions will be spontaneous or not
- **<u>Redox Spontaneity Rule:</u>** a spontaneous redox reaction will occur only if the oxidizing agent (OA) is *<u>above</u>* the reducing agent (RA) in a redox table

<u>Spontaneous Redox Reaction</u>

$Br_2(l) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$
$Hg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Hg(l)$
$OCl^-(aq) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$Cl^-(aq) + 2OH^-(aq)$
$NO_3^-(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$N_2O_4(g) + 2H_2O(l)$
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$
$O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O_2(l)$
$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$
$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$

Example:

$Br_{2(l)}$ reacting with $H_2O_{2(l)}$ is spontaneous b/c O. A. is higher than R. A.

net redox rxn : $Br_{2(l)} + H_2O_{2(l)} \rightarrow 2Br^-_{(aq)} + O_{2(g)} + 2H^+_{(aq)}$

<u>Non - Spontaneous Redox Reaction</u>

$Br_2(l) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$
$Hg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Hg(l)$
$OCl^-(aq) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$Cl^-(aq) + 2OH^-(aq)$
$NO_3^-(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$N_2O_4(g) + 2H_2O(l)$
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$
$O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O_2(l)$
$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$
$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$

Example:

$Cu^{2+}_{(aq)}$ do <u>NOT</u> react spontaneously with $Hg_{(l)}$ b/c O. A. is lower than R. A.

- When applying the spontaneity rule, there are two general steps that we need to follow

✳ **Step 1:** Identify which reactant is the oxidizing agent and which one is the reducing agent.

different ways to complete step 1 depending on type of question

  - Can use the table on page 7 of data book to see if the atom/ion is listed as a oxidizing agent or reducing agent
  - Can use a net ionic equation to see which reactants are the reducing and oxidizing agents
  - Can use oxidation numbers
  - Can use the general rule that the more positive reactant will be the oxidizing agent and the more negative reactant will be the reducing agent

> Need to be able to predict what the products are if the reaction did occur. Remember, *<u>metals</u>* form <u>*positive ions*</u> (and vise versa) and *<u>non-metals</u>* form *<u>negative ions</u>* (and vise-versa).

Step 2: Located the oxidizing agent and the reducing agent on the table to determine the spontaneity of the reaction using the spontaneity rule.

EXAMPLES:

$Ag^{+}_{(aq)}$ $Zn_{(s)}$

1. Would the reaction between silver ions and zinc metal be spontaneous? If so, write out the net ionic reaction that occurs.

- could simply look at table on pg. 7

$Ag^{+}_{(aq)}$ (O.A.) is higher than $Zn_{(s)}$ (R.A.) on the table ∴ rxn is spontaneous

oxidized

net ionic equation: $2Ag^{+}_{(aq)} + Zn_{(s)} \longrightarrow 2Ag_{(s)} + Zn^{2+}_{(aq)}$

reduced

2. Write out the redox reaction that would occur first and most vigorously when tin (II) bromide solution is poured into acidified sodium dichromate solution?

$Sn^{2+}_{(aq)}$ $Br^{-}_{(aq)}$ $H^{+}_{(aq)}$ $Na^{+}_{(aq)}$ $Cr_2O_7{}^{2-}_{(aq)}$

strongest R.A.

strongest O.A.

simply look at table on Pg. 7

$$Cr_2O_7{}^{2-}_{(aq)} + 14H^{+}_{(aq)} + \cancel{6e^-} \longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

$$3\,Sn^{2+}_{(aq)} \longrightarrow 3\,Sn^{4+}_{(aq)} + \cancel{\overset{6}{\cancel{2}}e^-} \quad (\times 3)$$

net ionic equation: $Cr_2O_7{}^{2-}_{(aq)} + 14H^{+}_{(aq)} + 3Sn^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Sn^{4+}_{(aq)} + 7H_2O_{(l)}$

*****Now try pg. 440 #5-8 Blue Box, #3,5, 6 Section Review & Practice Problems #1, 2*****

Answers to Textbook Questions Page 440

Q5. (a) spontaneous
(b) nonspontaneous
(c) spontaneous
(d) nonspontaneous

Q6. Use silver nitrate because the reaction between cobalt metal, $Co_{(s)}$ and silver ions, $Ag^{+}_{(aq)}$, will proceed spontaneously.

Q7. Any of the following metals will work: Fe, Zn, Cr, Al, Mg, Na, Ca, Ba, Li.

The reactions for Fe, Zn, Mg, Ca, and Ba, are similar:
$Fe(s) + Cd^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cd(s)$

The reactions for Al and Cr are similar
$2Al(s) + 3Cd^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cd(s)$

The reactions for Na and Li are also similar:
$2Na(s) + Cd^{2+}(aq) \rightarrow 2Na^{+}(aq) + Cd(s)$

Q8. Any ion that is an oxidizing agent higher than tin(reducing agent), will be spontaneous. This could include Pb^{2+}, Fe^{3+}, Cu^{2+}, Cu^{+}, Ag^{+}, Au^{3+}, Co^{3+}, etc. However to be a salt, the metal ions need to be in an ionic compound that is soluble in water. For example $Pb(NO_3)_2$, $FeCl_3$, $CuSO_4$, $AgNO_3$, and so forth. The net ionic equations would be very similar (the anions are spectator ions, so they will not appear in the net ionic equations).

$Pb^{2+}(aq) + Sn(s) \rightarrow Pb(s) + Sn^{2+}(aq)$

$2Fe^{3+}_{(aq)} + 3Sn_{(s)} \rightarrow 2Fe_{(s)} + 3Sn^{2+}_{(aq)}$

$Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$

Section 12.1 Review Answers

Student Textbook page 440

3. Calcium metal will spontaneously oxidize when reacted with Fe^{2+}, Ni^{2+}, or Ag^{+}.

$Ca(s) + Fe^{2+}(aq) \rightarrow Ca^{2+}(aq) + Fe(s)$

$Ca(s) + 2Ag^{+}(aq) \rightarrow Ca^{2+}(aq) + 2Ag(s)$

$Ca(s) + Ni^{2+}(aq) \rightarrow Ca^{2+}(aq) + Ni(s)$

5. (a) The reaction will occur.

The complete balanced equation is: $2AgNO_{3(aq)} + Cd_{(s)} \rightarrow 2Ag_{(s)} + Cd(NO_3)_{2(aq)}$

The net ionic equation is: $2Ag + (aq) + Cd(s) \rightarrow 2Ag(s) + Cd^2 + (aq)$

The ionic equation is: $2Ag^+(aq) + 2NO_3^-(aq) + Cd(s) \rightarrow 2Ag(s) + Cd^2(aq) + 2NO_3^-(aq)$

(b) A reaction will not occur.

(c) The reaction will occur.

The complete balanced reaction is: $2Al(s) + 3HgCl_2(aq) \rightarrow 2AlCl_3(aq) + 3Hg(s)$

The net ionic equation is: $2Al(s) + 3Hg^2(aq) \rightarrow 2Al^3(aq) + 3Hg(s)$

The ionic equation is: $2Al(s) + 3Hg^{2+}(aq) + 6Cl^-(aq) \rightarrow 2Al^{3+}(aq) + 3Hg(s) + 6Cl^-(aq)$

6. Possible answers for each part are shown below, although many answers exist. In general, equations must be balanced, oxidizing agents must gain electrons, and reducing agents must lose electrons. Spontaneous reactions will only occur if the oxidizing agent is higher than the reducing agent (or the reducing agent is lower than the oxidizing agent).

a) $2Al(s) + 3Fe^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Fe(s)$
b) $2Al(s) + 3Fe^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Fe(s)$
c) $Al(s) + Au^{3+}(aq) \rightarrow Al^{3+}(aq) + Al^{3+}(aq) + Au(s)$
d) $3Cu(s) + 2Au^{3+}(aq) \rightarrow 3Cu^{2+}(aq) + 2Au(s)$

EXAMPLE: Use the following information to rank the oxidizing agents from strongest to weakest.

R.A. / O.A.	$2X_{(s)} + Y^{2+}_{(aq)} \rightarrow 2X^{+} + Y_{(s)}$	$Y^{2+}_{(aq)}$ higher than $X_{(s)}$
O.A. / R.A.	$L_{(s)} + X_{(s)} \rightarrow L^{-}_{(aq)} + X^{+}_{(aq)}$	$L_{(s)}$ higher than $X_{(s)}$
R.A. / O.A.	$L^{-}_{(aq)} + Y^{2+}_{(aq)} \rightarrow$ no reaction	$Y^{2+}_{(aq)}$ lower then $L^{-}_{(aq)}$

Step 1: Look at one reaction at a time and identify the oxidizing agent and the reducing agent. Use the same four methods located on the previous page (table, oxidation numbers, net ionic equation, or general rule).

Step 2: Using the spontaneity rule, position the oxidizing agent relative to the reducing agent depending on whether the data indicated the reaction to be spontaneous or not. Remember a redox table always lists the oxidizing agents on the left side and the reducing agents on the right side.

Step 3: Repeat steps 1 & 2 for all other reactions given, but continue to position the oxidizing and reducing agents in *one* table

	O.A.	R.A.	
strongest O.A. ✓?	$L_{(s)}$	$L^{-}_{(aq)}$	weaker
	$Y^{2+}_{(aq)}$	$Y_{(s)}$	
not possible? b/c last rxn	~~$L_{(s)}$~~	~~$L^{-}_{(aq)}$~~	
weaker	$X^{+}_{(aq)}$	$X_{(s)}$	strongest R.A.

If the spontaneity of the reactions was arranged in a table format, what do you notice?

RA \ OA	$X^{+}_{(aq)}$	$L_{(s)}$	$Y^{2+}_{(aq)}$	
$X_{(s)}$		✓	✓	← strongest R.A. b/c causes the most rxns!
weakest R.A. → $L^{-}_{(aq)}$	X		X	
$Y_{(s)}$	X	✓		
	↑ weakest O.A.	↑ strongest O.A. b/c causes the most rxns!		

EXAMPLE: Using the following information, to develop a redox table and then answer the following questions.

O.A. R.A.

$B^+(aq) + D(s) \rightarrow D^+(aq) + B(s)$ $B^+_{(aq)}$ higher than $D_{(s)}$

O.A. R.A.

$D^+(aq) + C(s) \rightarrow$ No reaction $D^+_{(aq)}$ lower than $C_{(s)}$

O.A. R.A.

$C^+(aq) + B(s) \rightarrow B^+(aq) + C(s)$ $C^+_{(aq)}$ higher than $B_{(s)}$

a. What is the strongest reducing and oxidizing agent?

Strongest R.A. is $D_{(s)}$

strongest O.A. is $C^+_{(aq)}$

b. What metal is the most reactive?

metal $D_{(s)}$

	O.A.		R.A.		
strongest O.A.	$C^+_{(aq)} + e^- \rightleftharpoons$		$C_{(s)}$? ✓		weaker
	$B^+_{(aq)} + e^- \rightleftharpoons$		$B_{(s)}$		
			~~$C_{(s)}$~~ ?	not possible b/c of last rxn.	
weaker	$D^+_{(aq)} + e^- \rightleftharpoons$		$D_{(s)}$		strongest R.A.

Now try Practice Problems

Practice Problems

1. Would a spontaneous reaction occur if iron (II) chloride ($FeCl_{2(aq)}$) is poured into an aluminium can?

2. A student is required to store an aqueous solution of iron(III) nitrate. She has a choice of a copper, tin, iron, or silver container. Choose an appropriate container which would be most suitable for storing the solution.

3. Use the following spontaneous reactions to identify the strongest oxidizing agent and reducing agent.

$$Co_{(s)} + Pb^{2+}_{(aq)} \rightarrow Co^{2+}_{(aq)} + Pb_{(s)}$$

$$Pb_{(s)} + Pt^{2+}_{(aq)} \rightarrow Pb^{2+}_{(aq)} + Pt_{(s)}$$

$$Mg_{(s)} + Co^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Co_{(s)}$$

4. Use the following reactions to identify the most reactive metal and the most reactive ion.

$$Cd_{(s)} + 2H^{+}_{(aq)} \rightarrow Cd^{2+}_{(aq)} + H_{2(g)}$$

$$Hg_{(l)} + 2H^{+}_{(aq)} \rightarrow Hg^{+}_{(aq)} + H_{2(g)}$$

$$Be_{(s)} + Cd^{2+}_{(aq)} \rightarrow Be^{2+}_{(aq)} + Cd_{(s)}$$

$$Cd^{2+}_{(aq)} + Hg_{(l)} \rightarrow \text{no reaction}$$

5. Four metals were placed into test tubes containing various ion solutions. Their resulting behaviour is shown by the equations below. Create a reduction half-reaction table according to the chemicals tendency to react. Identify the strongest oxidizing agent and reducing agent.

$$Pt_{(s)} + 2\ H^{+}_{(aq)} \rightarrow \text{no reaction}$$

$$2\ Ce_{(s)} + 3\ Ni^{2+}_{(aq)} \rightarrow 2\ Ce^{2+}_{(aq)} + 3\ Ni_{(s)}$$

$$3\ Sr_{(s)} + 2\ Ce^{3+}_{(aq)} \rightarrow 3\ Sr^{3+}_{(aq)} + 2\ Ce_{(s)}$$

$$Ni_{(s)} + 2\ H^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + H_{2(g)}$$

6. An analytical chemist reacts an unknown metal X with a copper(II) sulfate solution, plating out copper metal. Metal X does not react with aqueous zinc nitrate.
   a. What is the order for these metal ions in decreasing tendency/ability to react?
   b. What group of metals are eliminated as a possible identity of the unknown metal?
   c. What other solutions might be chosen next to help identify the unknown metal?

Answers

1. A spontaneous reaction would occur because $Fe^{2+}_{(aq)}$ (O.A.) is higher than aluminum (R.A.).

2. $Fe^{3+}_{(aq)}$ would be the oxidizing agent because the metal ions convert back into metal atoms. Therefore, an appropriate container would be some metal that **will not** react spontaneously with the iron solution. A silver metal container would not react with the $Fe^{3+}_{(aq)}$ because the R.A. (silver metal) is higher than the $Fe^{3+}_{(aq)}$ (O.A.).

3. Strongest O.A. is $Pt^{2+}_{(aq)}$ and the strongest R.A. is $Mg_{(s)}$

4. Most reactive metal is $Be_{(s)}$ and the most reactive ion is $H^{+}_{(aq)}$

5.

$$Pt^{2+}_{(aq)} + 2e^{-}_{(aq)} \leftrightarrow Pt_{(s)}$$

$$2H^{+}_{(aq)} + 2e^{-}_{(aq)} \leftrightarrow H_{2(g)}$$

$$Ni^{2+}_{(aq)} + 2e^{-}_{(aq)} \leftrightarrow Ni_{(s)}$$

$$Ce^{3+}_{(aq)} + 3e^{-}_{(aq)} \leftrightarrow Ce_{(s)}$$

$$Sr^{3+}_{(aq)} + 3e^{-}_{(aq)} \leftrightarrow Sr_{(s)}$$

The strongest O.A. $Pt^{2+}_{(aq)}$ and the and the strongest R.A. is $Sr_{(s)}$

6.

a. Decreasing ability to react is $Cu^{2+}_{(aq)}$, $X^{n+}_{(aq)}$, and $Zn^{2+}_{(aq)}$
most reactive least reactive

b. $X_{(s)}$ can only be a metal found between $Cu_{(s)}$ and $Zn_{(s)}$ on the table of reduction half-reactions.

c. Could choose any solution between $Cu^{2+}_{(aq)}$ and $Zn^{2+}_{(aq)}$ such as $SnSO_{4(aq)}$, $CoSO_{4(aq)}$, $NiSO_{4(aq)}$, $PbSO_{4(aq)}$, etc.