

(b) When one mole of FeCl_3 dissolves, it produces 3 moles of Cl^- ions and 4 total moles of ions. The concentration of Cl^- is: $\frac{3}{4}(1.2 \text{ mM}) = 0.90 \text{ mM Cl}^-(\text{aq})$.

4.11 *Analyze/Plan.* The plot shows indicator color versus volume of standard solution added. Consider how the indicator changes color in a titration like the one in Figure 4.18, and relate this behavior to the shapes shown in the graph.

Solve. The “green” data set is expected from a titration like the one in Figure 4.18. The indicator color remains constant until the reaction is very near the equivalence point. Within a very small volume of standard solution added, the indicator color changes rapidly. This behavior is shown in green. The red graph shows a constantly changing indicator color.

4.12 *Analyze/Plan.* The purpose of every titration is to determine the equivalence point. Based on the indicator behavior described in the exercise, decide how the amount of reactants and products in the titration beaker relate to the equivalence point. Given this reaction mixture, design an experiment to reach the equivalence point.

Solve. This indicator is colorless in acid and blue in base. When it is added to the beaker, the solution is dark blue, so the solution is quite basic. This means that the amount of base added is already greater than the amount of acid initially present. To reach the equivalence point, more acid must be added to the titration beaker.

First, record the volume of base added. Then, find a standard acid solution (an acid of very well-known concentration) or standardize an acid solution (probably HCl). Rinse and fill a clean buret with the standard acid. Carefully titrate the mixture in the beaker until the blue color fades and finally disappears. Record the volume of standard acid added. Subtract the amount of added acid from the total amount of base added. The remaining amount of base is the volume required to reach equivalence with the original acid sample. This procedure is called “back titration.”

General Properties of Aqueous Solutions (Section 4.1)

4.13 (a) False. Electrolyte solutions conduct electricity because *ions* are moving through the solution.

(b) True. The conductivity is unchanged as long as the concentration of electrolytes is unchanged. Because ions are mobile in solution, the added presence of uncharged molecules does not inhibit conductivity.

4.14 (a) False. Methanol is an organic alcohol, and the $-\text{OH}$ group is not ionizable. The neutral methanol molecules in solution do not support the movement of charge. The solution does not conduct electricity.

(b) True. CH_3COOH is a weak electrolyte. When it dissolves in water, a small percentage of the molecules ionize to form H^+ and CH_3COO^- ions. The presence of a small concentration of ions produces a weakly conducting solution, and the specific presence of H^+ makes the solution acidic.

4.15 Statement (b) is most correct. Statements (a) and (c) are incorrect because water is not a strong acid and the hydrogen and oxygen bonds of water are not broken by ionic solids.

- 4.16 Anions are negatively charged. They will be attracted to and thus physically closer to the partially positive portion of the water molecule, which is the hydrogens.
- 4.17 *Analyze/Plan.* Given the solute formula, determine the separate ions formed upon dissociation. *Solve.*
- (a) $\text{FeCl}_2(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$
 - (b) $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^{+}(\text{aq}) + \text{NO}_3^{-}(\text{aq})$
 - (c) $(\text{NH}_4)_2\text{SO}_4(\text{aq}) \rightarrow 2 \text{NH}_4^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 - (d) $\text{Ca}(\text{OH})_2(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$
- 4.18
- (a) $\text{MgI}_2(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$
 - (b) $\text{K}_2\text{CO}_3(\text{aq}) \rightarrow 2 \text{K}^{+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$
 - (c) $\text{HClO}_4(\text{aq}) \rightarrow \text{H}^{+}(\text{aq}) + \text{ClO}_4^{-}(\text{aq})$
 - (d) $\text{NaCH}_3\text{COO}(\text{aq}) \rightarrow \text{Na}^{+}(\text{aq}) + \text{CH}_3\text{COO}^{-}(\text{aq})$
- 4.19 *Analyze/Plan.* Apply the definition of a weak electrolyte to HCOOH.
- Solve.* When HCOOH dissolves in water, neutral HCOOH molecules, H^{+} ions and HCOO^{-} ions are all present in the solution. $\text{HCOOH}(\text{aq}) \rightleftharpoons \text{H}^{+}(\text{aq}) + \text{HCOO}^{-}(\text{aq})$
- 4.20
- (a) acetone (nonelectrolyte): $\text{CH}_3\text{COCH}_3(\text{aq})$ molecules only; hypochlorous acid (weak electrolyte): $\text{HClO}(\text{aq})$ molecules, $\text{H}^{+}(\text{aq})$, $\text{ClO}^{-}(\text{aq})$; ammonium chloride (strong electrolyte): $\text{NH}_4^{+}(\text{aq})$, $\text{Cl}^{-}(\text{aq})$
 - (b) NH_4Cl , 0.2 mol solute particles; HClO , between 0.1 and 0.2 mol particles; CH_3COCH_3 , 0.1 mol of solute particles

Precipitation Reactions (Section 4.2)

- 4.21 *Analyze.* Given: formula of compound. Find: solubility.
- Plan.* Follow the guidelines in Table 4.1, in light of the anion present in the compound and notable exceptions to the "rules." *Solve.*
- (a) MgBr_2 : soluble
 - (b) PbI_2 : insoluble, Pb^{2+} is an exception to soluble iodides
 - (c) $(\text{NH}_4)_2\text{CO}_3$: soluble, NH_4^{+} is an exception to insoluble carbonates
 - (d) $\text{Sr}(\text{OH})_2$: soluble, Sr^{2+} is an exception to insoluble hydroxides
 - (e) ZnSO_4 : soluble
- 4.22 According to Table 4.1:
- (a) AgI : insoluble (an exception to the generally soluble iodides)
 - (b) Na_2CO_3 : soluble, Na^{+} is an exception to insoluble carbonates
 - (c) BaCl_2 : soluble
 - (d) $\text{Al}(\text{OH})_3$: insoluble
 - (e) $\text{Zn}(\text{CH}_3\text{COO})_2$: soluble

- 4.23 *Analyze.* Given: formulas of reactants. Find: balanced equation including precipitates.
Plan. Follow the logic in Sample Exercise 4.3.
Solve. In each reaction, the precipitate is in bold type.
- (a) $\text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{AgNO}_3(\text{aq}) \rightarrow \mathbf{\text{Ag}_2\text{CO}_3(\text{s})} + 2 \text{NaNO}_3(\text{aq})$
- (b) No precipitate (all nitrates and most sulfates are soluble).
- (c) $\text{FeSO}_4(\text{aq}) + \text{Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow \mathbf{\text{PbSO}_4(\text{s})} + \text{Fe}(\text{NO}_3)_2(\text{aq})$
- 4.24 In each reaction, the precipitate is in bold type.
- (a) No precipitate. [CH_3COO^- gains H^+ to form $\text{CH}_3\text{COOH}(\text{aq})$, which is soluble.]
- (b) $\text{Cu}(\text{NO}_3)_2(\text{aq}) + 2 \text{KOH}(\text{aq}) \rightarrow \mathbf{\text{Cu}(\text{OH})_2(\text{s})} + 2 \text{KNO}_3(\text{aq})$
- (c) $\text{Na}_2\text{S}(\text{aq}) + \text{CdSO}_4(\text{aq}) \rightarrow \mathbf{\text{CdS}(\text{s})} + \text{Na}_2\text{SO}_4(\text{aq})$
- 4.25 *Analyze/Plan.* Follow the logic in Sample Exercise 4.4. From the complete ionic equation, identify the ions that don't change during the reaction; these are the spectator ions. *Solve.*
- (a) $2 \text{K}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) + \text{Mg}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{MgCO}_3(\text{s}) + 2 \text{K}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
Spectators: K^+ , SO_4^{2-}
- (b) $\text{Pb}^{2+}(\text{aq}) + 2 \text{NO}_3^-(\text{aq}) + 2 \text{Li}^+(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{PbS}(\text{s}) + 2 \text{Li}^+(\text{aq}) + 2 \text{NO}_3^-(\text{aq})$
Spectators: Li^+ , NO_3^-
- (c) $6 \text{NH}_4^+(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq}) + 3 \text{Ca}^{2+}(\text{aq}) + 6 \text{Cl}^-(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6 \text{NH}_4^+(\text{aq}) + 6 \text{Cl}^-(\text{aq})$
Spectators: NH_4^+ , Cl^-
- 4.26 Spectator ions are those that do not change during reaction.
- (a) $2 \text{Cr}^{3+}(\text{aq}) + 3 \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Cr}_2(\text{CO}_3)_3(\text{s})$; spectators: NH_4^+ , SO_4^{2-}
- (b) $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; spectators: K^+ , NO_3^-
- (c) $\text{Fe}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s})$; spectators: K^+ , NO_3^-
- 4.27 *Analyze.* Given: reactions of unknown salt with HBr , H_2SO_4 , NaOH . Find: Does the unknown salt contain K^+ or Pb^{2+} or Ba^{2+} ?
- Plan.* Analyze solubility guidelines for Br^- , SO_4^{2-} , and OH^- and select the cation that produces a precipitate with each of the anions.
- Solve.* K^+ forms no precipitates with any of the anions. BaSO_4 is insoluble, but BaCl_2 and $\text{Ba}(\text{OH})_2$ are soluble. Because the unknown salt forms precipitates with all three anions, it must contain Pb^{2+} .
- Check.* PbBr_2 , PbSO_4 , and $\text{Pb}(\text{OH})_2$ are all insoluble according to Table 4.1, so our process of elimination is confirmed by the insolubility of the Pb^{2+} compounds.
- 4.28 Br^- and NO_3^- can be ruled out because the BaBr_2 is soluble and all NO_3^- salts are soluble. CO_3^{2-} forms insoluble salts with the three cations given; it must be the anion in question.

- 4.29 *Analyze/Plan.* Using Table 4.1, determine the precipitates that could form when each of the unknowns is reacted with $\text{Ba}(\text{NO}_3)_2$ and NaCl . *Solve.*
- (a) True. If the unknown is $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 could precipitate.
 - (b) True. If the unknown is AgNO_3 , AgCl could precipitate.
 - (c) False (two ways). Ag_2SO_4 is a soluble ionic compound, and no combination of the possible unknowns and the two reagents could produce Ag_2SO_4 .
 - (d) True. This is the overall correct answer to the question.
 - (e) False, because (c) is false.
- 4.30 Consider all the possible combinations of $\text{Pb}^{2+}(\text{aq})$, $\text{Na}^+(\text{aq})$, $\text{Ca}^{2+}(\text{aq})$, $\text{CH}_3\text{COO}^-(\text{aq})$, $\text{S}^{2-}(\text{aq})$, and $\text{Cl}^-(\text{aq})$. Which of these compounds are insoluble ionic compounds that will precipitate when the solutions are combined?
- $\text{PbS}(\text{s})$ and $\text{PbCl}_2(\text{s})$ will precipitate.

Acids, Bases, and Neutralization Reactions (Section 4.3)

- 4.31 *Analyze.* Given: solute and concentration of three solutions. Find: the solution that is most acidic.
- Plan:* See Sample Exercise 4.6 and Table 4.2. Determine whether solutes are strong or weak acids or bases or nonelectrolytes. For solutions of equal concentration, strong acids will have greatest concentration of solvated protons. Take varying concentration into consideration when evaluating the same class of solutions.
- Solve.* (a) LiOH is a strong base, (b) HI is a strong acid, (c) CH_3OH is a molecular compound and nonelectrolyte. Solution (b), 0.2 M HI , is the most acidic solution.
- Check.* The solution concentrations weren't needed to answer the question.
- 4.32 $\text{NH}_3(\text{aq})$ is a weak base, whereas KOH and $\text{Ba}(\text{OH})_2$ are strong bases. $\text{NH}_3(\text{aq})$ is only slightly ionized, so even (a) 0.6 M NH_3 is less basic than (b) 0.150 M KOH . $\text{Ba}(\text{OH})_2$ has twice as many OH^- per mole as KOH , so (c) 0.100 M $\text{Ba}(\text{OH})_2$ is more basic than (b) 0.150 M KOH . The most basic solution is (c) 0.100 M $\text{Ba}(\text{OH})_2$.
- 4.33 (a) False. Sulfuric acid, H_2SO_4 , is a diprotic acid; it has two ionizable hydrogen atoms.
(b) False. According to Table 4.2, HCl is a strong acid.
(c) False. Methanol, CH_3OH , is a molecular nonelectrolyte.
- 4.34 (a) True. NH_3 produces OH^- in aqueous solution by reacting with H_2O (hydrolysis):
 $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$. The OH^- causes the solution to be basic. $\text{NH}_3(\text{aq})$ attracts an H^+ from water, leaving $\text{OH}^-(\text{aq})$ in the solution.
(b) False. According to Table 4.2, HF is not one of the strong acids.
(c) True. H_2SO_4 is a **diprotic** acid; it has two ionizable hydrogens. The first hydrogen completely ionizes to form H^+ and HSO_4^- , but HSO_4^- only **partially** ionizes into H^+ and SO_4^{2-} (HSO_4^- is a weak electrolyte). Thus, an aqueous solution of H_2SO_4 contains a mixture of H^+ , HSO_4^- , and SO_4^{2-} , with the concentration of HSO_4^- greater than the concentration of SO_4^{2-} .

4.35 *Analyze.* Given: chemical formulas. Find: classify as acid, base, salt; strong, weak, or nonelectrolyte.

Plan. See Tables 4.2 and 4.3. Ionic or molecular? Ionic, soluble: OH^- , strong base and strong electrolyte; otherwise, salt, strong electrolyte. Molecular: NH_3 , weak base and weak electrolyte; H-first, acid; strong acid (Table 4.2), strong electrolyte; otherwise weak acid and weak electrolyte. *Solve.*

- (a) HF: acid, mixture of ions and molecules (weak electrolyte)
- (b) CH_3CN : none of the above, entirely molecules (nonelectrolyte)
- (c) NaClO_4 : salt, entirely ions (strong electrolyte)
- (d) $\text{Ba}(\text{OH})_2$: base, entirely ions (strong electrolyte)

4.36 Because the solution does conduct some electricity, but less than an equimolar NaCl solution (a strong electrolyte), the unknown solute must be a weak electrolyte. The weak electrolytes in the list of choices are NH_3 and H_3PO_3 ; because the solution is acidic, the unknown must be H_3PO_3 .

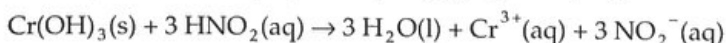
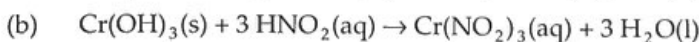
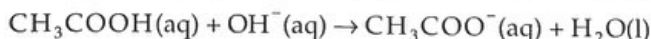
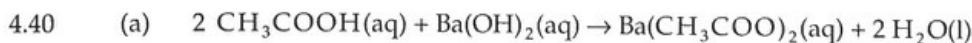
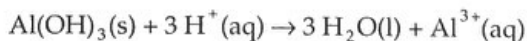
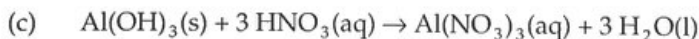
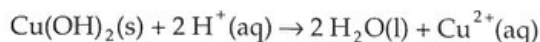
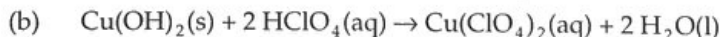
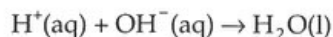
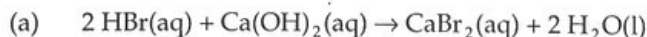
4.37 *Analyze.* Given: chemical formulas. Find: electrolyte properties.

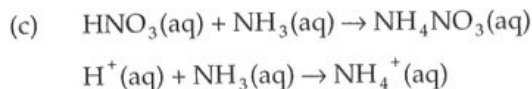
Plan. To classify as electrolytes, formulas must be identified as acids, bases, or salts as in Solution 4.35. *Solve.*

- (a) H_2SO_3 : H first, so acid; not in Table 4.2, so weak acid; therefore, weak electrolyte
- (b) $\text{CH}_3\text{CH}_2\text{OH}$: not acid, not ionic (no metal cation), contains OH group, but not as anion so not a base; therefore, nonelectrolyte
- (c) NH_3 : common weak base; therefore, weak electrolyte
- (d) KClO_3 : ionic compound, so strong electrolyte
- (e) $\text{Cu}(\text{NO}_3)_2$: ionic compound, so strong electrolyte

4.38 (a) LiClO_4 : strong (b) HClO : weak (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$: non
 (d) HClO_3 : strong (e) CuSO_4 : strong (f) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$: non

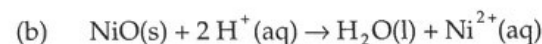
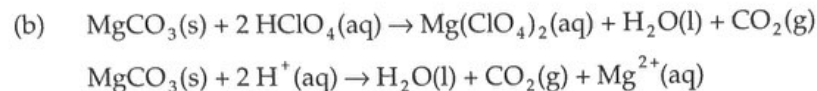
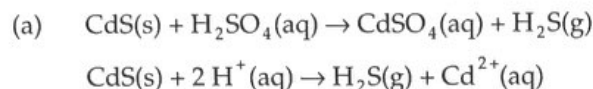
4.39 *Plan.* Follow Sample Exercise 4.7. *Solve.*





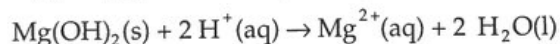
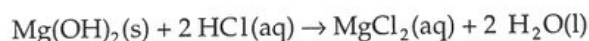
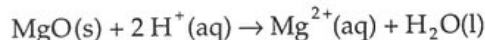
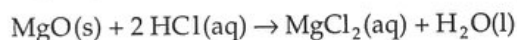
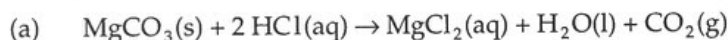
4.41 *Analyze.* Given: names of reactants. Find: gaseous products.

Plan. Write correct chemical formulas for the reactants, complete and balance the metathesis reaction, and identify either H_2S or CO_2 products as gases. *Solve.*

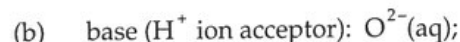
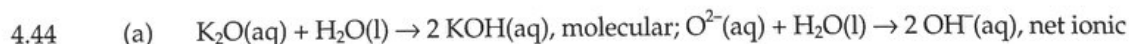


4.43 *Analyze.* Given the formulas or names of reactants, write balanced molecular and net ionic equations for the reactions.

Plan. Write correct chemical formulas for all reactants. Predict products of the neutralization reactions by exchanging ion partners. Balance the complete molecular equation, identify spectator ions by recognizing strong electrolytes, write the corresponding net ionic equation (omitting spectators). *Solve.*



(b) We can distinguish magnesium carbonate, $\text{MgCO}_3(\text{s})$, because its reaction with acid produces $\text{CO}_2(\text{g})$, which appears as bubbles. The other two compounds are indistinguishable because the products of the two reactions are exactly the same.



Oxidation–Reduction Reactions (Section 4.4)

4.45 (a) False. *Oxidation* is loss of electrons; *reduction* is gain of electrons. (LEO says GER.)

(b) True. When a substance is oxidized, its oxidation number increases. When a substance is reduced, its oxidation number decreases.

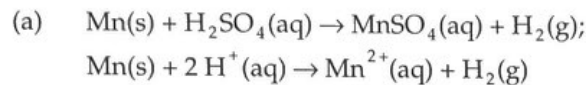
- 4.46 (a) True. Oxidation is loss of electrons; it can occur in the presence of any electron acceptor, not just oxygen.
- (b) False. Oxidation and reduction can only occur together, not separately. When a substance is oxidized, it loses electrons, but free electrons do not exist under normal conditions. If electrons are lost by one substance they must be gained by another, and vice versa.
- 4.47 *Analyze.* Given the labeled periodic chart, determine which regions are most and least easily oxidized.
- Plan.* Review the definition of oxidation and apply it to the properties of elements in the indicated regions of the chart. *Solve.*
- (a) Oxidation is loss of electrons. Elements easily oxidized form positive ions; these are metals. Elements in regions A and B are metals, and their ease of oxidation is shown in Table 4.5.
- (b) Elements not readily oxidized tend to gain electrons and form negative ions; these are nonmetals. Elements in region D are nonmetals and are least easily oxidized.
- 4.48 (a) BaSO_4 ; +6 (b) H_2SO_3 ; +4 (c) SrS ; -2 (d) H_2S ; -2
- (e) Sulfur is the third row of group 6A, the third column from the right on the periodic table. That is in region D on the designated chart.
- (f) Based on these compounds, the range of oxidation numbers for sulfur is +6 to -2. Sulfur and other nonmetals in region D can adopt both positive and negative oxidation numbers. This is also true for the metalloids in region C. These elements have properties of both metals and nonmetals and can thus adopt both positive and negative oxidation numbers.
- 4.49 *Analyze.* Given the chemical formula of a substance, determine the oxidation number of a particular element in the substance.
- Plan.* Follow the logic in Sample Exercise 4.8. *Solve.*
- (a) +4 (b) +4 (c) +7 (d) +1 (e) +3 (f) -1 (O_2^{2-} is peroxide ion)
- 4.50 (a) +3 (b) +3 (c) -2 (d) -3 (e) +3 (f) +6
- 4.51 *Analyze.* Given: chemical reaction. Find: element oxidized or reduced. *Plan.* Assign oxidation numbers to all species. The element whose oxidation number increases (becomes more positive) is oxidized; the one whose oxidation number decreases (becomes more negative) is reduced. *Solve.*
- (a) $\text{N}_2(\text{g})$ [N, 0] \rightarrow $2 \text{NH}_3(\text{g})$ [N, -3], N is reduced; $3 \text{H}_2(\text{g})$ [H, 0] \rightarrow $2 \text{NH}_3(\text{g})$ [H, +1], H is oxidized.
- (b) $\text{Fe}^{2+} \rightarrow \text{Fe}$, Fe is reduced; $\text{Al} \rightarrow \text{Al}^{3+}$, Al is oxidized
- (c) $\text{Cl}_2 \rightarrow 2 \text{Cl}^-$, Cl is reduced; $2 \text{I}^- \rightarrow \text{I}_2$, I is oxidized
- (d) $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$ (S, +6), S is oxidized; H_2O_2 (O, -1) \rightarrow H_2O (O, -2); O is reduced
- 4.52 (a) oxidation-reduction reaction; P is oxidized, Cl is reduced
- (b) oxidation-reduction reaction; K is oxidized, Br is reduced

- (c) oxidation–reduction reaction; C is oxidized, O is reduced
 (d) precipitation reaction

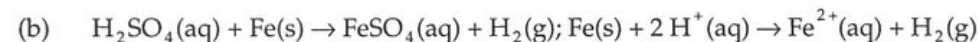
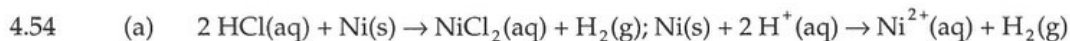
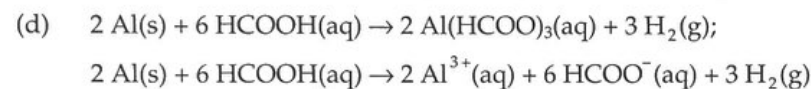
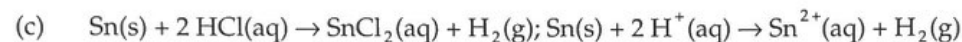
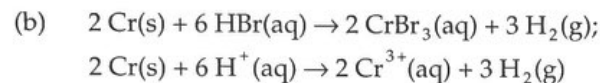
4.53 *Analyze.* Given: reactants. Find: balanced molecular and net ionic equations.

Plan. Metals oxidized by H^+ form cations. Predict products by exchanging cations and balance. The anions are the spectator ions and do not appear in the net ionic equations.

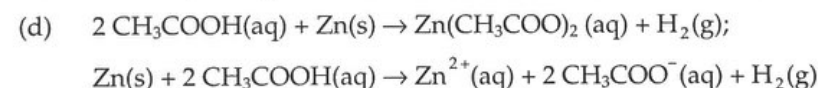
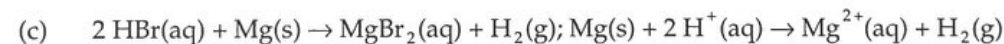
Solve.



Products with the metal in a higher oxidation state are possible, depending on reaction conditions and acid concentration.



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4.55 *Analyze.* Given: a metal and an aqueous solution. Find: balanced equation.

Plan. Use Table 4.5. If the metal is above the aqueous solution, reaction will occur; if the aqueous solution is higher, NR. If reaction occurs, predict products by exchanging cations (a metal ion or H^+), then balance the equation. *Solve.*

- (a) $Fe(s) + Cu(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Cu(s)$
 (b) $Zn(s) + MgSO_4(aq) \rightarrow NR$
 (c) $Sn(s) + 2 HBr(aq) \rightarrow SnBr_2(aq) + H_2(g)$
 (d) $H_2(g) + NiCl_2(aq) \rightarrow NR$
 (e) $2 Al(s) + 3 CoSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3 Co(s)$

