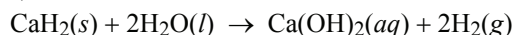


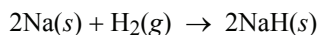
CHAPTER 21

NONMETALLIC ELEMENTS AND THEIR COMPOUNDS

- 21.11** Element number 17 is the halogen, chlorine. Since it is a nonmetal, chlorine will form the molecular compound HCl. Element 20 is the alkaline earth metal calcium which will form an ionic hydride, CaH₂. A water solution of HCl is called hydrochloric acid. Calcium hydride will react according to the equation (see Section 21.2 of the text).

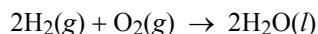


- 21.12 (a)** Hydrogen reacts with alkali metals to form ionic hydrides:



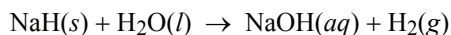
The oxidation number of hydrogen drops from 0 to -1 in this reaction.

- (b)** Hydrogen reacts with oxygen (combustion) to form water:

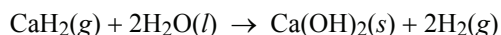


The oxidation number of hydrogen increases from 0 to +1 in this reaction.

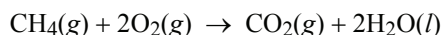
- 21.13** NaH: Ionic compound. It reacts with water as follows:



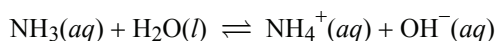
CaH₂: Ionic compound: It reacts with water as follows:



CH₄: Covalent compound. Unreactive. It burns in air or oxygen:

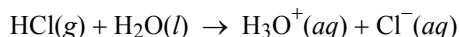


NH₃: Covalent compound. It is a weak base in water:



H₂O: Covalent compound. It forms strong intermolecular hydrogen bonds. It is a good solvent for both ionic compounds and substances capable of forming hydrogen bonds.

HCl: Covalent compound (polar). It acts as a strong acid in water:



- 21.14** Hydrogen forms an interstitial hydride with palladium, which behaves almost like a solution of hydrogen atoms in the metal. At elevated temperatures hydrogen atoms can pass through solid palladium; other substances cannot.

21.15 The equation is: $\text{CaH}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(aq) + 2\text{H}_2(g)$

First, let's calculate the moles of H_2 using the ideal gas law.

$$\text{mol H}_2 = \frac{\left(746 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)(26.4 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(293 \text{ K})} = 1.08 \text{ mol H}_2$$

Now, we can calculate the mass of CaH_2 using the correct mole ratio from the balanced equation.

$$\text{Mass CaH}_2 = 1.08 \text{ mol H}_2 \times \frac{1 \text{ mol CaH}_2}{2 \text{ mol H}_2} \times \frac{42.10 \text{ g}}{1 \text{ mol CaH}_2} = \mathbf{22.7 \text{ g CaH}_2}$$

21.16 The number of moles of deuterium gas is:

$$n = \frac{PV}{RT} = \frac{(0.90 \text{ atm})(2.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.074 \text{ mol}$$

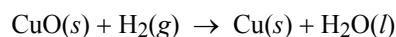
If the abundance of deuterium is 0.015 percent, the number of moles of water must be:

$$0.074 \text{ mol D}_2 \times \frac{100\% \text{ H}_2\text{O}}{0.015\% \text{ D}_2} = 4.9 \times 10^2 \text{ mol H}_2\text{O}$$

At a recovery of 80 percent the amount of water needed is:

$$\frac{4.9 \times 10^2 \text{ mol H}_2\text{O}}{0.80} \times \frac{0.01802 \text{ kg H}_2\text{O}}{1.0 \text{ mol H}_2\text{O}} = \mathbf{11 \text{ kg H}_2\text{O}}$$

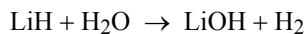
21.17 According to Table 19.1 of the text, H_2 can reduce Cu^{2+} , but not Na^+ . (How can you tell?) The reaction is:



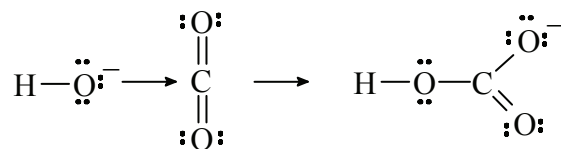
21.18 (a) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$

(b) $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$

(c) $2\text{Li} + \text{H}_2 \rightarrow 2\text{LiH}$

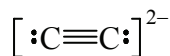


21.25 The reaction can be represented:

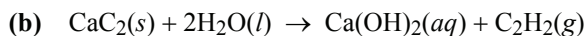
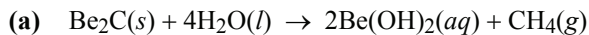


The lone pair on the hydroxide oxygen becomes a new carbon-oxygen bond. The octet rule requires that one of the electron pairs in the double bond be changed to a lone pair. What is the other resonance form of the product ion?

21.26 The Lewis structure is:



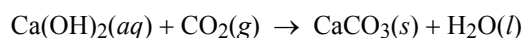
21.27 The reactions are:



21.28 (a) The reaction is: $2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g)$

Is this an endo- or an exothermic process?

(b) The hint is generous. The reaction is:

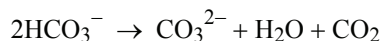


The visual proof is the formation of a white precipitate of CaCO_3 . Why would a water solution of NaOH be unsuitable to qualitatively test for carbon dioxide?

21.29 Magnesium and calcium carbonates are insoluble; the bicarbonates are soluble. Formation of a precipitate after addition of MgCl_2 solution would show the presence of Na_2CO_3 .

Assuming similar concentrations, which of the two sodium salt solutions would have a higher pH?

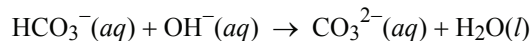
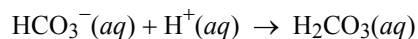
21.30 Heat causes bicarbonates to decompose according to the reaction:



Generation of carbonate ion causes precipitation of the insoluble MgCO_3 .

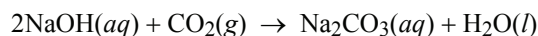
Do you think there is much chance of finding natural mineral deposits of calcium or magnesium bicarbonates?

21.31 Bicarbonate ion can react with either H^+ or OH^- .



Since ammonia is a base, carbonate ion is formed which causes precipitation of CaCO_3 .

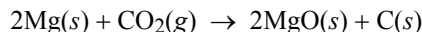
21.32 The wet sodium hydroxide is first converted to sodium carbonate:



and then to sodium hydrogen carbonate: $\text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow 2\text{NaHCO}_3(aq)$

Eventually, the sodium hydrogen carbonate precipitates (the water solvent evaporates since NaHCO_3 is not hygroscopic). Thus, most of the white solid is NaHCO_3 plus some Na_2CO_3 .

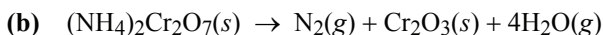
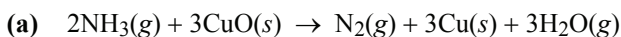
- 21.33** Table 19.1 of the text shows that magnesium metal has the potential to be an extremely powerful reducing agent. It appears inert at room temperature, but at high temperatures it can react with almost any source of oxygen atoms (including water!) to form MgO. In this case carbon dioxide is reduced to carbon.



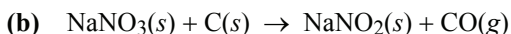
How does one extinguish a magnesium fire?

- 21.34** Carbon monoxide and molecular nitrogen are isoelectronic. Both have 14 electrons. What other diatomic molecules discussed in these problems are isoelectronic with CO?

- 21.39** The preparations are:



- 21.40** (a) $2\text{NaNO}_3(s) \rightarrow 2\text{NaNO}_2(s) + \text{O}_2(g)$



- 21.41** The balanced equation is: $\text{NH}_2^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_3(aq) + \text{OH}^-(aq)$

In this system the acid is H_2O (proton donor) and the base is NH_2^- (proton acceptor). What are the conjugate acid and the conjugate base?

- 21.42** The balanced equation is: $2\text{NH}_3(g) + \text{CO}_2(g) \rightarrow (\text{NH}_2)_2\text{CO}(s) + \text{H}_2\text{O}(l)$

If pressure increases, the position of equilibrium will shift in the direction with the smallest number of molecules in the gas phase, that is, to the right. Therefore, the reaction is best run at high pressure.

Write the expression for Q_p for this reaction. Does increasing pressure cause Q_p to increase or decrease? Is this consistent with the above prediction?

- 21.43** Lightning can cause N_2 and O_2 to react: $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$

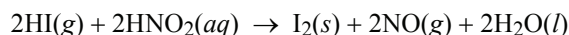
The NO formed naturally in this manner eventually suffers oxidation to nitric acid (see the Ostwald process in Section 21.4 of the text) which precipitates as rain. The nitrate ion is a natural source of nitrogen for growing plants.

- 21.44** The density of a gas depends on temperature, pressure, and the molar mass of the substance. When two gases are at the same pressure and temperature, the ratio of their densities should be the same as the ratio of their molar masses. The molar mass of ammonium chloride is 53.5 g/mol, and the ratio of this to the molar mass of molecular hydrogen (2.02 g/mol) is 26.8. The experimental value of 14.5 is roughly half this amount. Such results usually indicate breakup or dissociation into smaller molecules in the gas phase (note the temperature). The measured molar mass is the average of all the molecules in equilibrium.

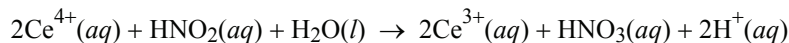


Knowing that ammonium chloride is a stable substance at 298 K, is the above reaction exo- or endothermic?

- 21.45** The oxidation number of nitrogen in nitrous acid is +3. Since this value is between the extremes of a +5 and -3 for nitrogen, nitrous acid can be either oxidized or reduced. Nitrous acid can oxidize HI to I₂ (in other words HI acts as a reducing agent).



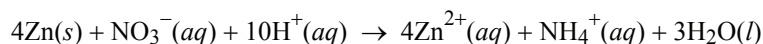
A strong oxidizing agent can oxidize nitrous acid to nitric acid (oxidation number of nitrogen +5).



- 21.46** The highest oxidation state possible for a Group 5A element is +5. This is the oxidation state of nitrogen in nitric acid (HNO₃).



- 21.48** Nitric acid is a strong oxidizing agent in addition to being a strong acid (see Table 19.1 of the text, $E_{\text{red}}^\circ = +0.96\text{V}$). The primary action of a good reducing agent like zinc is reduction of nitrate ion to ammonium ion.

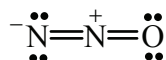


- 21.49** The balanced equation is: $2\text{KNO}_3(s) + \text{C}(s) \rightarrow 2\text{KNO}_2(s) + \text{CO}_2(g)$

The maximum amount of potassium nitrite (theoretical yield) is:

$$57.0 \text{ g KNO}_3 \times \frac{1 \text{ mol KNO}_3}{101.1 \text{ g KNO}_3} \times \frac{1 \text{ mol KNO}_2}{1 \text{ mol KNO}_3} \times \frac{85.11 \text{ g KNO}_2}{1 \text{ mol KNO}_2} = \mathbf{48.0 \text{ g KNO}_2}$$

- 21.50** One of the best Lewis structures for nitrous oxide is:



There are no lone pairs on the central nitrogen, making this an AB₂ VSEPR case. All such molecules are linear. Other resonance forms are:



Are all the resonance forms consistent with a linear geometry?

- 21.51** (a) $\Delta G_{\text{rxn}}^\circ = 2\Delta G_{\text{f}}^\circ(\text{NO}) - [0 + 0]$

$$173.4 \text{ kJ/mol} = 2\Delta G_{\text{f}}^\circ(\text{NO})$$

$$\Delta G_{\text{f}}^\circ(\text{NO}) = \mathbf{86.7 \text{ kJ/mol}}$$

- (b) From Equation (18.14) of the text:

$$\Delta G^\circ = -RT \ln K_{\text{p}}$$

$$173.4 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K}) \ln K_{\text{p}}$$

$$\mathbf{K_{\text{p}} = 4 \times 10^{-31}}$$

(c) Using Equation (14.5) of the text [$K_p = K_c(0.0821 T)^{\Delta n}$], $\Delta n = 0$, then $K_p = K_c = 4 \times 10^{-31}$

$$21.52 \quad \Delta H^\circ = 4\Delta H_f^\circ[\text{NO}(g)] + 6\Delta H_f^\circ[\text{H}_2\text{O}(l)] - \{4\Delta H_f^\circ[\text{NH}_3(g)] + 5\Delta H_f^\circ[\text{O}_2(g)]\}$$

$$\Delta H^\circ = (4)(90.4 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - [(4)(-46.3 \text{ kJ/mol}) + (5)(0)] = -1168 \text{ kJ/mol}$$

21.53 The atomic radius of P (128 pm) is considerably larger than that of N (92 pm); consequently, the $3p$ orbital on a P atom cannot overlap effectively with a $3p$ orbital on a neighboring P atom to form a pi bond. Simply stated, the phosphorus is too large to allow effective overlap of the $3p$ orbitals to form π bonds.

$$21.54 \quad \Delta T_b = K_b m = 0.409^\circ\text{C}$$

$$\text{molality} = \frac{0.409^\circ\text{C}}{2.34^\circ\text{C}/m} = 0.175 \text{ m}$$

The number of grams of white phosphorus in 1 kg of solvent is:

$$\frac{1.645 \text{ g phosphorus}}{75.5 \text{ g CS}_2} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 21.8 \text{ g phosphorus/kg CS}_2$$

The molar mass of white phosphorus is:

$$\frac{21.8 \text{ g phosphorus/kg CS}_2}{0.175 \text{ mol phosphorus/kg CS}_2} = 125 \text{ g/mol}$$

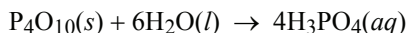
Let the molecular formula of white phosphorus be P_n so that:

$$n \times 30.97 \text{ g/mol} = 125 \text{ g/mol}$$

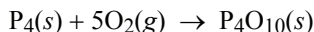
$$n = 4$$

The molecular formula of white phosphorus is **P₄**.

21.55 You won't find a reaction that starts with elemental phosphorus and ends with phosphoric acid. However there is more than one reaction having phosphoric acid as a product. One possibility is the reaction of P_4O_{10} with water.



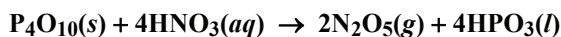
Can P_4O_{10} be formed from elemental phosphorus? Study of Section 21.4 of the text shows that P_4 combines with oxygen to form P_4O_{10} .



The synthesis of phosphoric acid is the result of these two steps in sequence.

Can you come up with an alternative synthesis starting with elemental phosphorus and chlorine gas?

21.56 The balanced equation is:



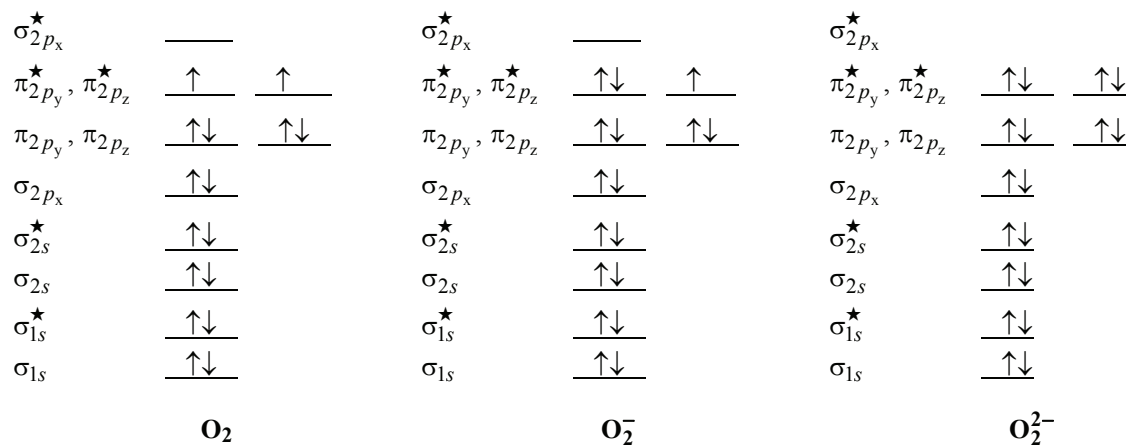
The theoretical yield of N_2O_5 is :

$$79.4 \text{ g P}_4\text{O}_{10} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{283.9 \text{ g P}_4\text{O}_{10}} \times \frac{2 \text{ mol N}_2\text{O}_5}{1 \text{ mol P}_4\text{O}_{10}} \times \frac{108.0 \text{ g N}_2\text{O}_5}{1 \text{ mol N}_2\text{O}_5} = \mathbf{60.4 \text{ g N}_2\text{O}_5}$$

- 21.57 (a) Because the P–H bond is weaker, there is a greater tendency for PH_4^+ to ionize compared to NH_4^+ . Therefore, PH_3 is a weaker base than NH_3 .
- (b) The electronegativity of nitrogen is greater than that of phosphorus. The N–H bond is much more polar than the P–H bond and can participate in hydrogen bonding. This increases intermolecular attractions and results in a higher boiling point.
- (c) Elements in the second period never expand their octets. A common explanation is the absence of $2d$ atomic orbitals.
- (d) The triple bond between two nitrogen atoms is one of the strongest atomic linkages known. The bonds in P_4 are highly strained because of the acute P–P–P angles and are more easily broken.

21.58 PH_4^+ is similar to NH_4^+ . The hybridization of phosphorus in PH_4^+ is sp^3 .

21.65 The molecular orbital energy level diagrams are:



Which of the three has the strongest bonding?

21.66 $\Delta G^\circ = \Delta G_f^\circ(\text{NO}_2) + \Delta G_f^\circ(\text{O}_2) - [\Delta G_f^\circ(\text{NO}) + \Delta G_f^\circ(\text{O}_3)]$

$$\Delta G^\circ = (1)(51.8 \text{ kJ/mol}) + (0) - [(1)(86.7 \text{ kJ/mol}) + (1)(163.4 \text{ kJ/mol})] = \mathbf{-198.3 \text{ kJ/mol}}$$

$$\Delta G^\circ = -RT \ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{198.3 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}$$

$$K_p = \mathbf{6 \times 10^{34}}$$

Since there is no change in the number of moles of gases, K_c is equal to K_p .

21.67 (a) As stated in the problem, the decomposition of hydrogen peroxide is accelerated by light. Storing solutions of the substance in dark-colored bottles helps to prevent this form of decomposition.

(b) The STP volume of oxygen gas formed is:

$$15.0 \text{ g soln} \times \frac{7.50\% \text{ H}_2\text{O}_2}{100\% \text{ soln}} \times \frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \times \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2\text{O}_2} \times \frac{22.41 \text{ L O}_2}{1 \text{ mol O}_2} = \mathbf{0.371 \text{ L O}_2}$$

21.68 Following the rules given in Section 4.4 of the text, we assign hydrogen an oxidation number of +1 and **fluorine** an oxidation number of **-1**. Since HFO is a neutral molecule, the oxidation number of **oxygen** is **zero**. Can you think of other compounds in which oxygen has this oxidation number?

21.69 Analogous to phosphorus in Problem 21.53, the $3p$ orbital overlap is poor for the formation of π bonds because of the relatively large size of sulfur compared to oxygen.

21.70 First, let's calculate the moles of sulfur in 48 million tons of sulfuric acid.

$$(48 \times 10^6 \text{ tons H}_2\text{SO}_4) \times \frac{2000 \text{ lb}}{1 \text{ ton}} \times \frac{453.6 \text{ g}}{1 \text{ lb}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.09 \text{ g H}_2\text{SO}_4} \times \frac{1 \text{ mol S}}{1 \text{ mol H}_2\text{SO}_4} = \mathbf{4.4 \times 10^{11} \text{ mol S}}$$

Converting to grams of sulfur:

$$(4.4 \times 10^{11} \text{ mol S}) \times \frac{32.07 \text{ g S}}{1 \text{ mol S}} = \mathbf{1.4 \times 10^{13} \text{ g S}}$$

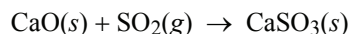
21.71 Each reaction uses $\text{H}_2\text{SO}_4(l)$ as a reagent.



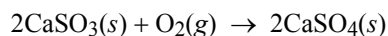
21.72 There are actually several steps involved in removing sulfur dioxide from industrial emissions with calcium carbonate. First calcium carbonate is heated to form carbon dioxide and calcium oxide.



The CaO combines with sulfur dioxide to form calcium sulfite.



Alternatively, calcium sulfate forms if enough oxygen is present.



The amount of calcium carbonate (limestone) needed in this problem is:

$$50.6 \text{ g SO}_2 \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g SO}_2} \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol SO}_2} \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = \mathbf{79.1 \text{ g CaCO}_3}$$

The calcium oxide–sulfur dioxide reaction is an example of a Lewis acid-base reaction (see Section 15.12 of the text) between oxide ion and sulfur dioxide. Can you draw Lewis structures showing this process? Which substance is the Lewis acid and which is the Lewis base?

- 21.73** To form OF_6 there would have to be six bonds (twelve electrons) around the oxygen atom. This would violate the octet rule.
- 21.74** The usual explanation for the fact that no chemist has yet succeeded in making SCl_6 , SBr_6 or SI_6 is based on the idea of excessive crowding of the six chlorine, bromine, or iodine atoms around the sulfur. Others suggest that sulfur in the +6 oxidation state would oxidize chlorine, bromine, or iodine in the -1 oxidation state to the free elements. In any case, none of these substances has been made as of the date of this writing.

It is of interest to point out that thirty years ago all textbooks confidently stated that compounds like ClF_5 could not be prepared.

Note that PCl_6^- is a known species. How different are the sizes of S and P?

- 21.75** The melting and boiling points of hydrogen sulfide are -85.5°C and -60.7°C , respectively. Those of water are, of course, 0°C and 100°C . Although hydrogen sulfide has more electrons and hence greater dispersion forces, water has the much higher melting and boiling points because of strong intermolecular hydrogen bonding. Water is a suitable solvent for many compounds, both ionic and molecular. Water has both acidic and basic properties. Hydrosulfuric acid, $\text{H}_2\text{S}(aq)$, is a weak diprotic acid. In its pure liquid form, hydrogen sulfide can dissolve a limited range of weakly polar substances. It is not amphoteric.
- 21.76** First we convert gallons of water to grams of water.

$$(2.0 \times 10^2 \text{ gal}) \times \frac{3.785 \text{ L}}{1 \text{ gal}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.00 \text{ g H}_2\text{O}}{1 \text{ mL}} = 7.6 \times 10^5 \text{ g H}_2\text{O}$$

An H_2S concentration of 22 ppm indicates that in 1 million grams of water, there will be 22 g of H_2S . First, let's calculate the number of moles of H_2S in $7.6 \times 10^5 \text{ g H}_2\text{O}$:

$$(7.6 \times 10^5 \text{ g H}_2\text{O}) \times \frac{22 \text{ g H}_2\text{S}}{1.0 \times 10^6 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{S}}{34.09 \text{ g H}_2\text{S}} = 0.49 \text{ mol H}_2\text{S}$$

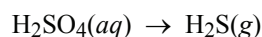
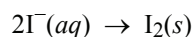
The mass of chlorine required to react with 0.49 mol of H_2S is:

$$0.49 \text{ mol H}_2\text{S} \times \frac{1 \text{ mol Cl}_2}{1 \text{ mol H}_2\text{S}} \times \frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = \mathbf{35 \text{ g Cl}_2}$$

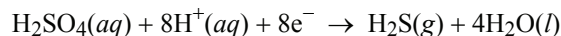
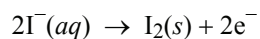
- 21.77** Copper reacts with hot concentrated sulfuric acid to yield copper(II) sulfate, water, and sulfur dioxide. Concentrated sulfuric acid also reacts with carbon to produce carbon dioxide, water, and sulfur dioxide.

Can you write balanced equations for these processes?

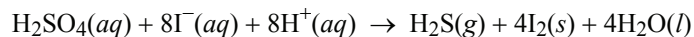
- 21.78** A check of Table 19.1 of the text shows that sodium ion cannot be reduced by any of the substances mentioned in this problem; it is a "spectator ion". We focus on the substances that are actually undergoing oxidation or reduction and write half-reactions for each.



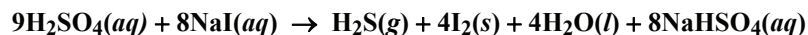
Balancing the oxygen, hydrogen, and charge gives:



Multiplying the iodine half-reaction by four and combining gives the balanced redox equation.



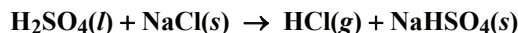
The hydrogen ions come from extra sulfuric acid. We add one sodium ion for each iodide ion to obtain the final equation.



21.81 A number of methods are available for the preparation of metal chlorides.

- (a) $\text{Na}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{s})$
- (b) $2\text{HCl}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g})$
- (c) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (d) $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- (e) $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$

21.82 Sulfuric acid is added to solid sodium chloride, not aqueous sodium chloride. Hydrogen chloride is a gas at room temperature and can escape from the reacting mixture.

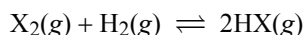


The reaction is driven to the right by the continuous loss of $\text{HCl}(\text{g})$ (Le Châtelier's principle).

What happens when sulfuric acid is added to a water solution of NaCl ? Could you tell the difference between this solution and the one formed by adding hydrochloric acid to aqueous sodium sulfate?

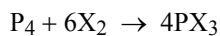
21.83 We use X_2 to represent molecular chlorine, bromine, and iodine.

- (a) These halogens combine directly with hydrogen gas as follows:

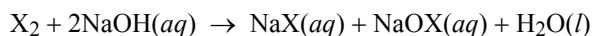


The reaction is most energetic for chlorine and least for iodine.

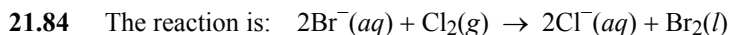
- (b) The silver salts, $\text{AgX}(\text{s})$, are all insoluble in water. Any of them can be prepared by precipitation using $\text{AgNO}_3(\text{aq})$ and $\text{NaX}(\text{aq})$ [see problem 21.81(e)].
- (c) Chlorine, bromine, and iodine are all good oxidizing agents. Their oxidizing power decreases from chlorine to iodine. For example, they oxidize many nonmetallic elements to the corresponding halides:



- (d) They react with $\text{NaOH}(\text{aq})$ to form a halide and a hypohalite:



(e) The differences between fluorine and the other halogens are discussed in Section 21.6 of the text.



The number of moles of chlorine needed is:

$$167 \text{ g Br}^- \times \frac{1 \text{ mol Br}^-}{79.90 \text{ g Br}^-} \times \frac{1 \text{ mol Cl}_2}{2 \text{ mol Br}^-} = 1.05 \text{ mol Cl}_2(g)$$

Use the ideal gas equation to calculate the volume of Cl_2 needed.

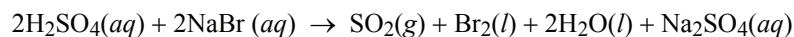
$$V_{\text{Cl}_2} = \frac{nRT}{P} = \frac{(1.05 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(293 \text{ K})}{(1 \text{ atm})} = \mathbf{25.3 \text{ L}}$$

21.85 The structures are:

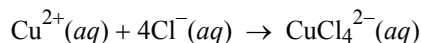


The HF_2^- ion has the strongest known hydrogen bond. More complex hydrogen bonded HF clusters are also known.

21.86 As with iodide salts, a redox reaction occurs between sulfuric acid and sodium bromide.

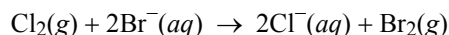


21.87 Fluoride, chloride, bromide, and iodide form complex ions (Sections 16.10 and 22.3 of the text) with many transition metals. With chloride the green CuCl_4^{2-} forms:



With fluoride, copper(II) forms an insoluble green salt, CuF_2 . Copper(II) cannot oxidize fluoride or chloride.

21.88 The balanced equation is:

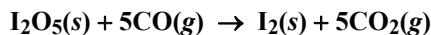


The number of moles of bromine is the same as the number of moles of chlorine, so this problem is essentially a gas law exercise in which P and T are changed for some given amount of gas.

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{(760 \text{ mmHg})(2.00 \text{ L})}{288 \text{ K}} \times \frac{373 \text{ K}}{700 \text{ mmHg}} = \mathbf{2.81 \text{ L}}$$

- 21.89**
- | | | | |
|-----|-----------------|-------------------------|------------------------------|
| (a) | I_3^- | AB_2E_3 | linear |
| (b) | SiCl_4 | AB_4 | tetrahedral |
| (c) | PF_5 | AB_5 | trigonal bipyramidal |
| (d) | SF_4 | AB_4E | distorted tetrahedron |

21.90 The balanced equation is:



The oxidation number of iodine changes from +5 to 0 and the oxidation number of carbon changes from +2 to +4. **Iodine is reduced; carbon is oxidized.**

21.91 The balanced equations are:

- (a) $2\text{H}_3\text{PO}_3(aq) \rightarrow \text{H}_3\text{PO}_4(aq) + \text{PH}_3(g) + \text{O}_2(g)$
 (b) $\text{Li}_4\text{C}(s) + 4\text{HCl}(aq) \rightarrow 4\text{LiCl}(aq) + \text{CH}_4(g)$
 (c) $2\text{HI}(g) + 2\text{HNO}_2(aq) \rightarrow \text{I}_2(s) + 2\text{NO}(g) + 2\text{H}_2\text{O}(l)$
 (d) $\text{H}_2\text{S}(g) + 2\text{Cl}_2(g) \rightarrow 2\text{HCl}(g) + \text{SCl}_2(l)$

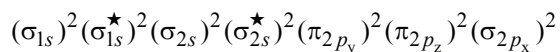
21.92 (a) SiCl_4 (b) F^- (c) F (d) CO_2

21.93 (a) Physical properties: the substances have different molar masses; a molar mass or gas density measurement will distinguish between them. Nitrous oxide is polar, while molecular oxygen is not; a measurement of dipole moment will distinguish between the two. Can you think of other differences? How about magnetic properties?

(b) Chemical properties: Oxygen reacts with NO to form the red-brown gas, NO_2 ; nitrous oxide doesn't react with NO. Can you think of other differences? What happens when you breathe nitrous oxide?

21.94 There is no change in oxidation number; it is zero for both compounds.

21.95 The acetylide ion has the electron configuration:



- 21.96 (a) $2\text{Na} + 2\text{D}_2\text{O} \rightarrow 2\text{NaOD} + \text{D}_2$ (d) $\text{CaC}_2 + 2\text{D}_2\text{O} \rightarrow \text{C}_2\text{D}_2 + \text{Ca}(\text{OD})_2$
 (b) $2\text{D}_2\text{O} \xrightarrow{\text{electrolysis}} 2\text{D}_2 + \text{O}_2$ (e) $\text{Be}_2\text{C} + 4\text{D}_2\text{O} \rightarrow 2\text{Be}(\text{OD})_2 + \text{CD}_4$
 $\text{D}_2 + \text{Cl}_2 \rightarrow 2\text{DCl}$
 (c) $\text{Mg}_3\text{N}_2 + 6\text{D}_2\text{O} \rightarrow 3\text{Mg}(\text{OD})_2 + 2\text{ND}_3$ (f) $\text{SO}_3 + \text{D}_2\text{O} \rightarrow \text{D}_2\text{SO}_4$

21.97 The Lewis structures are shown below. In PCl_4^+ , the phosphorus atom is sp^3 hybridized. In PCl_6^- , the phosphorus atom is sp^3d^2 .

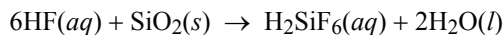


- 21.98 (a) At elevated pressures, water boils above 100°C .
 (b) Water is sent down the outermost pipe so that it is able to melt a larger area of sulfur.
 (c) Sulfur deposits are structurally weak. There will be a danger of the sulfur mine collapsing.

21.99 It is a solid, insoluble in water, has metalloid properties. Chemically it resembles F, Cl, Br, and I, but is less reactive.

21.100 The oxidation is probably initiated by breaking a C–H bond (the rate-determining step). The C–D bond breaks at a slower rate than the C–H bond; therefore, replacing H by D decreases the rate of oxidation.

21.101 Light bulbs are frosted with hydrofluoric acid. $\text{HF}(aq)$ is highly reactive towards silica and silicates.

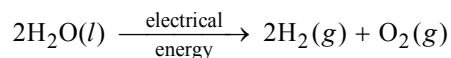


This reaction etches the glass, giving it a frosted appearance.

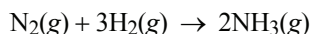
21.102 Organisms need a source of energy to sustain the processes of life. Respiration creates that energy. Molecular oxygen is a powerful oxidizing agent, reacting with substances such as glucose to release energy for growth and function. Molecular nitrogen (containing the nitrogen-to-nitrogen triple bond) is too unreactive at room temperature to be of any practical use.

21.103 Air contains O_2 and N_2 . Our aims are first to prepare NH_3 and HNO_3 . The reaction of NH_3 and HNO_3 produces NH_4NO_3 .

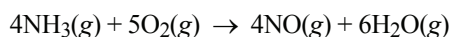
To prepare NH_3 , we isolate N_2 from air by fractional distillation. H_2 can be obtained by the electrolysis of water.



The synthesis of NH_3 from N_2 and H_2 is carried out at high pressure and temperature in the presence of a catalyst. The details are described in the Chemistry in Action essay in Chapter 14 of the text.



To prepare HNO_3 we employ the Ostwald process described in Section 13.6 of the text.



Next, $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

Then, $2\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{HNO}_2(aq) + \text{HNO}_3(aq)$

Finally, we react NH_3 with HNO_3 to obtain NH_4NO_3 .



21.104 We know that $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. We can first calculate ΔH° and ΔS° using data in Appendix 3 of the text. Then, we can calculate ΔG° and lastly K .

$$\Delta H^\circ = 2\Delta H_f^\circ[\text{CO}(g)] - \{\Delta H_f^\circ[\text{C}(s)] + \Delta H_f^\circ[\text{CO}_2(g)]\}$$

$$\Delta H^\circ = (2)(-110.5 \text{ kJ/mol}) - (0 + -393.5 \text{ kJ/mol}) = 172.5 \text{ kJ/mol}$$

$$\Delta S^\circ = 2S^\circ[\text{CO}(g)] - \{S^\circ[\text{C}(s)] + S^\circ[\text{CO}_2(g)]\}$$

$$\Delta S^\circ = (2)(197.9 \text{ J/K}\cdot\text{mol}) - (5.69 \text{ J/K}\cdot\text{mol} + 213.6 \text{ J/K}\cdot\text{mol}) = 176.5 \text{ J/K}\cdot\text{mol}$$

At 298 K (25°C),

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (172.5 \times 10^3 \text{ J/mol}) - (298 \text{ K})(176.5 \text{ J/K} \cdot \text{mol}) = 1.199 \times 10^5 \text{ J/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(1.199 \times 10^5 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}} = \mathbf{9.61 \times 10^{-22}}$$

At 1273 K (1000°C),

$$\Delta G^\circ = (172.5 \times 10^3 \text{ J/mol}) - (1273 \text{ K})(176.5 \text{ J/K} \cdot \text{mol}) = -5.218 \times 10^4 \text{ J/mol}$$

$$K = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-(-5.218 \times 10^4 \text{ J/mol})}{(8.314 \text{ J/K} \cdot \text{mol})(1273 \text{ K})}} = \mathbf{138}$$

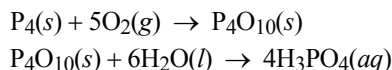
The much larger value of K at the higher temperature indicates the formation of CO is favored at higher temperatures (achieved by using a blast furnace).

- 21.105** At the normal boiling point, the pressure of HF is 1 atm. We use Equation (5.11) of the text to calculate the density of HF.

$$d = \frac{PM}{RT} = \frac{(1 \text{ atm})(20.01 \frac{\text{g}}{\text{mol}})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(273 + 19.5)\text{K}} = \mathbf{0.833 \text{ g/L}}$$

The fact that the measured density is larger suggests that HF molecules must be associated to some extent in the gas phase. This is not surprising considering that HF molecules form strong intermolecular hydrogen bonds.

- 21.106** The reactions are:



First, we calculate the moles of H_3PO_4 produced. Next, we can calculate the molarity of the phosphoric acid solution. Finally, we can determine the pH of the H_3PO_4 solution (a weak acid).

$$10.0 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{123.9 \text{ g P}_4} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{1 \text{ mol P}_4} \times \frac{4 \text{ mol H}_3\text{PO}_4}{1 \text{ mol P}_4\text{O}_{10}} = 0.323 \text{ mol H}_3\text{PO}_4$$

$$\text{Molarity} = \frac{0.323 \text{ mol}}{0.500 \text{ L}} = 0.646 \text{ M}$$

We set up the ionization of the weak acid, H_3PO_4 . The K_a value for H_3PO_4 can be found in Table 15.5 of the text.



Initial (M):	0.646	0	0
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.646 - x$	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.5 \times 10^{-3} = \frac{(x)(x)}{(0.646 - x)}$$

$$x^2 + 7.5 \times 10^{-3}x - 4.85 \times 10^{-3} = 0$$

Solving the quadratic equation,

$$x = 0.066 \text{ M} = [\text{H}_3\text{O}^+]$$

Following the procedure in Problem 15.118 and the discussion in Section 15.8 of the text, we can neglect the contribution to the hydronium ion concentration from the second and third ionization steps. Thus,

$$\text{pH} = -\log(0.066) = \mathbf{1.18}$$