





LIMITING REACTANT

11-50. Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. The number of moles of  $P_4(s)$  is

$$\text{moles of } P_4 = (20.0 \text{ g}) \left( \frac{1 \text{ mol } P_4}{123.90 \text{ g } P_4} \right) = 0.1614 \text{ mol}$$

and the number of moles of  $NaOH(s)$  is

$$\text{moles of } NaOH = (50.0 \text{ g}) \left( \frac{1 \text{ mol } NaOH}{40.00 \text{ g } NaOH} \right) = 1.250 \text{ mol}$$

Because one mole of  $P_4(s)$  reacts with three moles of  $NaOH(aq)$ , we see that 0.1614 moles of  $P_4(s)$  require 0.4842 moles of  $NaOH(aq)$ . Thus,  $NaOH(aq)$  is in excess and  $P_4(s)$  is the limiting reactant. The mass of  $PH_3(g)$  produced is

$$\text{mass of } PH_3 = (0.1614 \text{ mol } P_4) \left( \frac{1 \text{ mol } PH_3}{1 \text{ mol } P_4} \right) \left( \frac{33.99 \text{ g } PH_3}{1 \text{ mol } PH_3} \right) = 5.49 \text{ g}$$

11-52. Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. The number of moles of  $NaBr$  is

$$\text{moles of } NaBr = (25.0 \text{ g}) \left( \frac{1 \text{ mol } NaBr}{102.89 \text{ g } NaBr} \right) = 0.243 \text{ mol}$$

and the number of moles of  $Cl_2(g)$  is

$$\text{moles of } Cl_2 = (25.0 \text{ g}) \left( \frac{1 \text{ mol } Cl_2}{70.90 \text{ g } Cl_2} \right) = 0.353 \text{ mol}$$

Each mole of  $Cl_2$  requires two moles of  $NaBr$ , or 0.353 moles of  $Cl_2$  require 0.706 moles of  $NaBr$ . Thus,  $Cl_2$  is in excess and  $NaBr$  is the limiting reactant. The mass of  $Br_2(l)$  produced is

$$\begin{aligned} \text{mass of } Br_2 &= (0.243 \text{ mol } NaBr) \left( \frac{1 \text{ mol } Br_2}{2 \text{ mol } NaBr} \right) \left( \frac{159.8 \text{ g } Br_2}{1 \text{ mol } Br_2} \right) \\ &= 19.4 \text{ g} \end{aligned}$$

11-54. (a) The balanced equation is



(b) Because we are given the quantities of two reactants, we must check to see if one of them is a limiting reactant. We have the stoichiometric correspondences

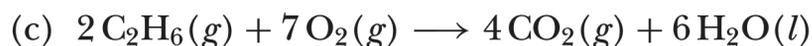
$$25.0 \text{ g } CaCO_3 \rightleftharpoons 0.250 \text{ mol } CaCO_3$$

$$15.0 \text{ g } HCl \rightleftharpoons 0.411 \text{ mol } HCl$$

Therefore,  $HCl$  is the limiting reactant because 0.411 moles of  $HCl$  require only 0.205 moles of  $CaCO_3$ . The mass of calcium chloride produced is

$$\text{mass of } CaCl_2 = (0.411 \text{ mol } HCl) \left( \frac{1 \text{ mol } CaCl_2}{2 \text{ mol } HCl} \right) \left( \frac{110.98 \text{ g } CaCl_2}{1 \text{ mol } CaCl_2} \right) = 22.8 \text{ g}$$

(c) Only 0.205 moles of  $CaCO_3$  will react, and so there is an excess of  $(0.250 - 0.205)$  moles = 0.045 moles of  $CaCO_3$ , or 4.50 grams remaining.



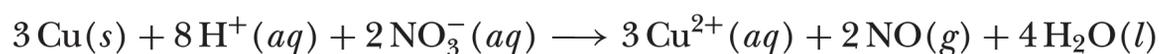
$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \{4 \Delta H_{\text{f}}^{\circ}[\text{CO}_2(g)] + 6 \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)]\} - \{2 \Delta H_{\text{f}}^{\circ}[\text{C}_2\text{H}_6(g)] + 7 \Delta H_{\text{f}}^{\circ}[\text{O}_2(g)]\} \\ &= (4)(-393.5 \text{ kJ}\cdot\text{mol}^{-1}) + (6)(-285.8 \text{ kJ}\cdot\text{mol}^{-1}) \\ &\quad - (2)(-84.0 \text{ kJ}\cdot\text{mol}^{-1}) - (7)(0 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -3120.8 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Two moles, or 60.14 grams, of  $\text{C}_2\text{H}_6(g)$  are burned, and so the enthalpy of combustion per gram is

$$\text{enthalpy of combustion per gram} = \frac{-3120.8 \text{ kJ}}{60.14 \text{ g}} = -51.89 \text{ kJ}\cdot\text{g}^{-1}$$

The enthalpy of combustion per gram increases as the number of hydrogen atoms increases.

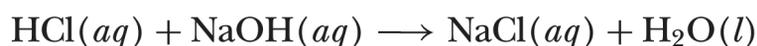
14-84. The equation for the net ionic reaction is



Thus, we have for  $\Delta H_{\text{rxn}}^{\circ}$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \{3 \Delta H_{\text{f}}^{\circ}[\text{Cu}^{2+}(aq)] + 2 \Delta H_{\text{f}}^{\circ}[\text{NO}(g)] + 4 \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)]\} \\ &\quad - \{3 \Delta H_{\text{f}}^{\circ}[\text{Cu}(s)] + 8 \Delta H_{\text{f}}^{\circ}[\text{H}^+(aq)] + 2 \Delta H_{\text{f}}^{\circ}[\text{NO}_3^-(aq)]\} \\ &= (3)(64.39 \text{ kJ}\cdot\text{mol}^{-1}) + (2)(91.3 \text{ kJ}\cdot\text{mol}^{-1}) + (4)(-285.8 \text{ kJ}\cdot\text{mol}^{-1}) \\ &\quad - (3)(0 \text{ kJ}\cdot\text{mol}^{-1}) - (8)(0 \text{ kJ}\cdot\text{mol}^{-1}) - (2)(-207.35 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -352.7 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

14-86. The equation for the reaction is



For 100 milliliters of 0.100 M  $\text{HCl}(aq)$  or  $\text{NaOH}(aq)$ , we have

$$n = (0.100 \text{ mol}\cdot\text{L}^{-1})(0.100 \text{ L}) = 0.0100 \text{ mol}$$

Therefore,

$$\Delta H = (0.0100 \text{ mol})(-55.7 \text{ kJ}\cdot\text{mol}^{-1}) = -0.557 \text{ kJ}$$

The temperature change of the resulting solution (0.200 L) is given by Equation 14.36 as

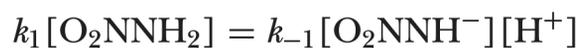
$$\begin{aligned} \Delta H &= -c_{\text{P,cal}} \Delta T \\ -557 \text{ J} &= -(200 \text{ mL}) \left( \frac{1.00 \text{ g}}{1.00 \text{ mL}} \right) \left( \frac{1 \text{ mol}}{18.02 \text{ g}} \right) (75.3 \text{ J}\cdot\text{mol}^{-1}) \Delta T \end{aligned}$$

or  $\Delta T = 0.666^{\circ}\text{C}$ .

14-88. The standard enthalpy is given by

$$\Delta H_{\text{rxn}} \approx \Delta U_{\text{rxn}} = -c_{\text{P}} \Delta T = -(38.70 \text{ kJ}\cdot\text{K}^{-1})(2.89 \text{ K}) = -112 \text{ kJ}$$

18-20. From step 1 of the reaction mechanism, the fast equilibrium allows us to write



and so the rate equation for the second step (rate determining) of the reaction mechanism becomes

$$\text{rate of reaction} = k_2[\text{O}_2\text{NNH}^-] = k_2 \left( \frac{k_1}{k_{-1}} \right) \frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]} = k \frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$$

This is consistent with the observed rate law with

$$k = \frac{k_2 k_1}{k_{-1}}$$

18-22. The observed rate law is (from Problem 18-19)

$$\text{rate of reaction} = k[\text{Cl}_2]^{3/2}[\text{CO}]$$

From step 3 of the reaction mechanism, we write

$$\text{rate of reaction} = k_3[\text{Cl}_3][\text{CO}] \quad (1)$$

Because steps 2 and 1 establish a fast equilibrium, we write

$$k_2[\text{Cl}][\text{Cl}_2] = k_{-2}[\text{Cl}_3] \quad (2)$$

Also,

$$k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2$$

and so

$$[\text{Cl}] = \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{1/2}$$

Substituting this expression for  $[\text{Cl}]$  into equation 2 gives

$$[\text{Cl}_3] = \frac{k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{Cl}_2]^{3/2}$$

and substituting this expression into equation 1 gives

$$\text{rate of reaction} = \frac{k_3 k_2 k_1^{1/2}}{k_{-2} k_{-1}^{1/2}} [\text{Cl}_2]^{3/2} [\text{CO}] = k [\text{Cl}_2]^{3/2} [\text{CO}]$$

which corresponds to the observed rate law. To determine whether this mechanism or the one given in Problem 18-19 occurs, we might determine whether a  $\text{Cl}_3$  intermediate is produced during the reaction.

## CATALYSIS

18-24. When  $[\text{H}_2\text{O}_2]_0$  is doubled with  $[\text{I}^-]_0$  and  $[\text{H}^+]_0$  constant, the initial rate doubles. Therefore, the reaction is first order in  $[\text{H}_2\text{O}_2]$ . When  $[\text{I}^-]_0$  is doubled with  $[\text{H}^+]_0$  and  $[\text{H}_2\text{O}_2]_0$  constant, the initial rate quadruples. The reaction is second order in  $[\text{I}^-]$ . When  $[\text{H}^+]_0$  is doubled with

The solubility due to the first equation is

$$s = [\text{Cr}^{3+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^3} = \frac{(6.3 \times 10^{-31} \text{ M}^4)[\text{H}_3\text{O}^+]^3}{(1.0 \times 10^{-14} \text{ M}^2)^3} = (6.3 \times 10^{11} \text{ M}^{-2})[\text{H}_3\text{O}^+]^3$$

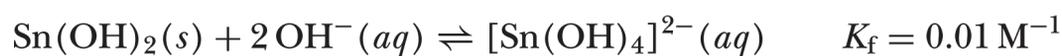
The solubility due to the second equation is

$$s = [\text{Cr}(\text{OH})_4^-] = K[\text{OH}^-] = \frac{(0.04)(1.0 \times 10^{-14} \text{ M}^2)}{[\text{H}_3\text{O}^+]} = \frac{4.0 \times 10^{-16} \text{ M}^2}{[\text{H}_3\text{O}^+]}$$

The total solubility is given by

$$s = [\text{Cr}^{3+}] + [\text{Cr}(\text{OH})_4^-] = (6.3 \times 10^{11} \text{ M}^{-2})[\text{H}_3\text{O}^+]^3 + \frac{4.0 \times 10^{-16} \text{ M}^2}{[\text{H}_3\text{O}^+]}$$

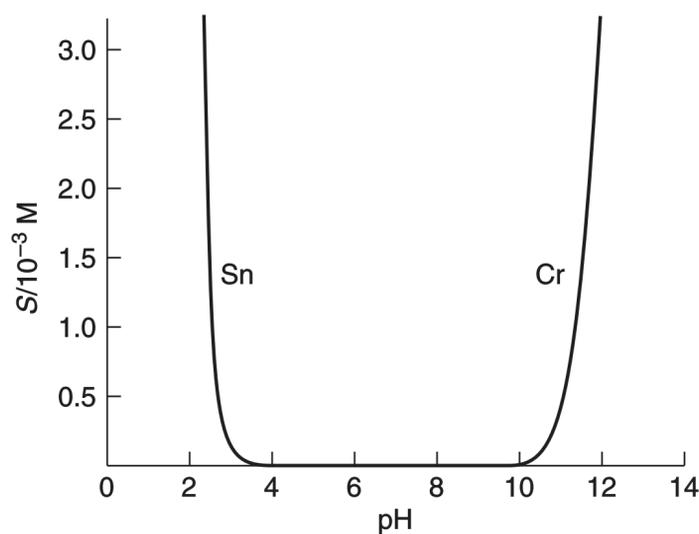
For  $\text{Sn}(\text{OH})_2(s)$ , the two relevant chemical equations are



The total solubility is given by

$$\begin{aligned} s &= [\text{Sn}^{2+}] + [\text{Sn}(\text{OH})_4^{2-}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} + K_{\text{f}}[\text{OH}^-]^2 \\ &= \frac{(5.5 \times 10^{-27} \text{ M}^3)[\text{H}_3\text{O}^+]^2}{(1.0 \times 10^{-14} \text{ M}^2)^2} + \frac{(0.01 \text{ M}^{-1})(1.0 \times 10^{-14} \text{ M}^2)^2}{[\text{H}_3\text{O}^+]} \\ &= (55 \text{ M}^{-1})[\text{H}_3\text{O}^+]^2 + \frac{1 \times 10^{-30} \text{ M}^3}{[\text{H}_3\text{O}^+]^2} \end{aligned}$$

The solubilities are plotted against pH in the following figure:



Thus, we see that the best separation is achieved between  $\text{pH} = 4$  and  $\text{pH} = 7$ .

22-96.\* Using the method and the results of the previous problem, we have

pH	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
$s/\text{M}$	3.3	1.0	0.33	0.11	0.055	0.045	0.044	0.044	0.044	0.044