31. This is an endothermic reaction so heat must be absorbed in order to convert reactants into products. The high temperature environment of internal combustion engines provides the heat.

33. a. Heat is absorbed from the water (it gets colder) as KBr dissolves, so this is an endothermic process.

b. Heat is released as CH_4 is burned, so this is an exothermic process.

c. Heat is released to the water (it gets hot) as H_2SO_4 is added, so this is an exothermic process.

d. Heat must be added (absorbed) to boil water, so this is an endothermic process.

35. $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$ $\Delta H = -1652$ kJ; Note that 1652 kJ of heat are released when

4 mol Fe react with 3 mol O_2 to produce 2 mol Fe_2O_3.

a. $4.00 \text{ mol Fe} \times \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} = -1650 \text{ kJ}$; 1650 kJ of heat released

b. $1.00 \text{ ml } Fe_2O_3 \times \frac{-1652 \text{ kJ}}{2 \text{ mol } Fe_2O_3} = -826 \text{ kJ}$; 826 kJ of heat released

c. $1.00 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} \times \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} = -7.39 \text{ kJ}$; 7.39 kJ of heat released

d. $10.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} = 0.179 \text{ mol Fe}$; $2.00 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g}} = 0.0625 \text{ mol } O_2$

0.179 mol Fe/0.0625 mol O_2 = 2.86; The balanced equation requires a 4 mol Fe/3 mol O_2 = 1.33 mol ratio. O_2 is limiting since the actual mol Fe/mol O_2 ratio is greater than the required mol ratio.

$0.0625 \text{ mol } O_2 \times \frac{-1652 \text{ kJ}}{3 \text{ mol } O_2} = -34.4 \text{ kJ}$; 34.4 kJ of heat released

41. Specific heat capacity is defined as the amount of heat necessary to raise the temperature of one gram of substance by one degree Celsius. Therefore, $H_2O(l)$ with the largest heat capacity value requires the largest amount of heat for this process. The amount of heat for $H_2O(l)$ is:

$$\text{energy} = s \times m \times \Delta T = \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times 25.0 \text{ g} \times (37.0^\circ\text{C} - 15.0^\circ\text{C}) = 2.30 \times 10^3 \text{ J}$$

The largest temperature change when a certain amount of energy is added to a certain mass of substance will occur for the substance with the smallest specific heat capacity. This is Hg(l), and the temperature change for this process is:

$$\Delta T = \frac{\text{energy}}{s \times m} = \frac{10.7\ \text{kJ} \times \frac{1000\ \text{J}}{\text{kJ}}}{\frac{0.14\ \text{J}}{\text{g}\ {}^{\circ}\text{C}} \times 550.\ \text{g}} = 140°\text{C}$$

43. s = specific heat capacity = $\frac{q}{m \times \Delta T} = \frac{133\ \text{J}}{5.00\ \text{g} \times (55.1 - 25.2)^{\circ}\text{C}}$ = 0.890 J/ECXg

From Table 6.1, the substance is aluminum.

45. | Heat loss by hot water | = | Heat gain by cooler water |

The magnitude of heat loss and heat gain are equal in calorimetry problems. The only difference is the sign (positive or negative). To avoid sign errors, keep all quantities positive and, if necessary, deduce the correct signs at the end of the problem. Water has a specific heat capacity = s = 4.18 J/°CXg = 4.18 J/KXg (ΔT in °C = ΔT in K).

Heat loss by hot water = $s \times m \times \Delta T = \frac{4.18\ \text{J}}{\text{g K}} \times 50.0\ \text{g} \times (330.\ \text{K} - T_f)$

Heat gain by cooler water = $\frac{4.18\ \text{J}}{\text{g K}} \times 30.0\ \text{g} \times (T_f - 280.\ \text{K})$; Heat loss = Heat gain, so:

$\frac{209\ \text{J}}{\text{K}} \times (330.\ \text{K} - T_f) = \frac{125\ \text{J}}{\text{K}} \times (T_f - 280.\ \text{K})$, $6.90 \times 10^4 - 209\ T_f = 125\ T_f - 3.50 \times 10^4$

$334\ T_f = 1.040 \times 10^5$, $T_f = 311\ \text{K}$

Note that the final temperature is closer to the temperature of the more massive hot water, which is as it should be.

47. Heat loss by Al + heat loss by Fe = heat gain by water; Keeping all quantities positive to avoid sign error:

$$\frac{0.89\ \text{J}}{\text{g}\ {}^{\circ}\text{C}} \times 5.00\ \text{g Al} \times (100.0°\text{C} - T_f) + \frac{0.45\ \text{J}}{\text{g}\ {}^{\circ}\text{C}} \times 10.00\ \text{g Fe} \times (100.0 - T_f)$$
$$= \frac{4.18\ \text{J}}{\text{g}\ {}^{\circ}\text{C}} \times 97.3\ \text{g}\ H_2O \times (T_f - 22.0°\text{C})$$

$4.5(100.0 - T_f) + 4.5(100.0 - T_f) = 407(T_f - 22.0)$, $450 - 4.5\ T_f + 450 - 4.5\ T_f$

$= 407\ T_f - 8950$

$416\ T_f = 9850$, $T_f = 23.7°\text{C}$

51. $50.0 \times 10^{-3}\ \text{L} \times 0.100\ \text{mol/L} = 5.00 \times 10^{-3}$ mol of both $AgNO_3$ and HCl are reacted. Thus,

5.00×10^{-3} mol of AgCl will be produced since there is a 1:1 mole ratio between reactants.

Heat lost by chemicals = Heat gained by solution

$$\text{Heat gain} = \frac{4.18\text{ J}}{\text{g }^\circ\text{C}} \times 100.0\text{ g} \times (23.40 - 22.60)^\circ\text{C} = 330\text{ J}$$

Heat loss = 330 J; This is the heat evolved (exothermic reaction) when 5.00×10^{-3} mol of AgCl is produced. So q = -330 J and ΔH (heat per mol AgCl formed) is negative with a value of:

$$\Delta H = \frac{-330\text{ J}}{5.00 \times 10^{-3}\text{ mol}} \times \frac{1\text{ kJ}}{1000\text{ J}} = -66\text{ kJ/mol}$$

Note: Sign errors are common with calorimetry problems. However, the correct sign for ΔH can easily be determined from the ΔT data, i.e., if ΔT of the solution increases, then the reaction is exothermic since heat was released, and if ΔT of the solution decreases, then the reaction is endothermic since the reaction absorbed heat from the water. For calorimetry problems, keep all quantities positive until the end of the calculation, then decide the sign for ΔH. This will help eliminate sign errors.

53. Since ΔH is exothermic, the temperature of the solution will increase as $CaCl_2(s)$ dissolves.

Keeping all quantities positive:

$$\text{Heat loss as } CaCl_2 \text{ dissolves} = 11.0\text{ g } CaCl_2 \times \frac{1\text{ mol } CaCl_2}{110.98\text{ g } CaCl_2} \times \frac{81.5\text{ kJ}}{\text{mol } CaCl_2} = 8.08\text{ kJ}$$

$$\text{Heat gain by solution} = 8.08 \times 10^3\text{ J} = \frac{4.18\text{ J}}{\text{g }^\circ\text{C}} \times (125 + 11.0)\text{ g} \times (T_f - 25.0^\circ\text{C})$$

$$T_f - 25.0^\circ\text{C} = \frac{8.08 \times 10^3}{4.18 \times 136} = 14.2^\circ\text{C},\ \ T_f = 14.2^\circ\text{C} + 25.0^\circ\text{C} = 39.2^\circ\text{C}$$

55. a. heat gain by calorimeter = heat loss by CH_4 = $6.79\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.04\text{ g}} \times \frac{802\text{ kJ}}{\text{mol}}$ = 340. kJ

$$\text{heat capacity of calorimeter} = \frac{340.\text{ kJ}}{10.8\ ^\circ\text{C}} = 31.5\text{ kJ/}^\circ\text{C}$$

b. heat loss by C_2H_2 = heat gain by calorimeter = $16.9^\circ\text{C} \times \frac{31.5\text{ kJ}}{^\circ\text{C}}$ = 532 kJ

$$\Delta E_{comb} = \frac{-532\text{ kJ}}{12.6\text{ g } C_2H_2} \times \frac{26.04\text{ g}}{\text{mol } C_2H_2} = -1.10 \times 10^3\text{ kJ/mol}$$

Hess's Law

57. Information given:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.7 \text{ kJ}$$
$$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -283.3 \text{ kJ}$$

Using Hess's Law:

$$2\ C(s) + 2\ O_2(g) \rightarrow 2\ CO_2(g) \qquad \Delta H_1 = 2(-393.7 \text{ kJ})$$
$$2\ CO_2(g) \rightarrow 2\ CO(g) + O_2(g) \qquad \Delta H_2 = -2(-283.3 \text{ kJ})$$

$$2\ C(s) + O_2(g) \rightarrow 2\ CO(g) \qquad \Delta H = \Delta H_1 + \Delta H_2 = -220.8 \text{ kJ}$$

Note: The enthalpy change for a reaction that is reversed is the negative quantity of the enthalpy change for the original reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer while the sign stays the same.

Standard Enthalpies of Formation

65. The change in enthalpy that accompanies the formation of one mole of a compound from its elements, with all substances in their standard states, is the standard enthalpy of formation for a compound. The reactions that refer to ΔH_f^o are:

$Na(s) + 1/2\ Cl_2(g) \rightarrow NaCl(s)$; $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$6\ C(\text{graphite, s}) + 6\ H_2(g) + 3\ O_2(g) \rightarrow C_6H_{12}O_6(s)$

$Pb(s) + S(\text{rhombic, s}) + 2\ O_2(g) \rightarrow PbSO_4(s)$

67. In general: $\Delta H° = 3n_p \Delta H^\circ_{f,\text{ products}} - 3n_r \Delta H^\circ_{f,\text{ reactants}}$ and all elements in their standard state have $\Delta H^\circ_f = 0$ by definition.

a. The balanced equation is: $2\ NH_3(g) + 3\ O_2(g) + 2\ CH_4(g) \rightarrow 2\ HCN(g) + 6\ H_2O(g)$

$$\Delta H° = [\ 2 \text{ mol HCN} \times \Delta H^\circ_{f,\,HCN} + 6 \text{ mol } H_2O(g) \times \Delta H^\circ_{f,\,H_2O}\,]$$

$$-\ [2 \text{ mol } NH_3 \times \Delta H^\circ_{f,\,NH_3} + 2 \text{ mol } CH_4 \times \Delta H^\circ_{f,\,CH_4}\,]$$

$$\Delta H° = [2(135.1) + 6(-242)] - [2(-46) + 2(-75)] = -940.\text{ kJ}$$

c. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

$\Delta H° = [1 \text{ mol } NH_4Cl \times \Delta H^{\circ}_{f,\, NH_4Cl}] - [1 \text{ mol } NH_3 \times \Delta H^{\circ}_{f,\, NH_3} + 1 \text{ mol } HCl \times \Delta H^{\circ}_{f,\, HCl}]$

$$\Delta H° = \left[1\,\text{mol}\left(\frac{-314\text{ kJ}}{\text{mol}}\right)\right] - \left[1\,\text{mol}\left(\frac{-46\text{ kJ}}{\text{mol}}\right) + 1\,\text{mol}\left(\frac{-92\text{ kJ}}{\text{mol}}\right)\right]$$

$\Delta H° = -314 \text{ kJ} + 138 \text{ kJ} = -176 \text{ kJ}$