Chapter 5
Principles of Chemical Reactivity:
Energy and Chemical Reactions

PRACTICING SKILLS

Energy

1. To move the lever, one uses mechanical energy. The energy resulting is manifest in electrical energy (which produces light); thermal energy would be released as the bulb in the flashlight glows.

Energy Units

3. Express the energy of a 1200 Calories/day diet in joules:

\[
\frac{1200 \text{ Cal}}{1 \text{ day}} \cdot \frac{1000 \text{ calorie}}{1 \text{ Cal}} \cdot \frac{4.184 \text{ J}}{1 \text{ cal}} = 5.0 \times 10^6 \text{ Joules/day}
\]

5. Compare 170 kcal/serving and 280 kJ/serving.

\[
\frac{170 \text{ kcal}}{1 \text{ serving}} \cdot \frac{1000 \text{ calorie}}{1 \text{ kcal}} \cdot \frac{4.184 \text{ J}}{1 \text{ cal}} \cdot \frac{1 \text{ kJ}}{1000 \text{ J}} = 710 \text{ kJoules/serving}
\]

So 170 kcal/serving has a greater energy content.

Specific Heat Capacity

7. What is the specific heat capacity of mercury, if the molar heat capacity is 28.1 J/mol • K?

Note that the difference in units of these two quantities is in the amount of substance. In one case, moles, while in the other grams.

\[
28.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \frac{1 \text{ mol}}{200.59 \text{ g}} = 0.140 \frac{\text{J}}{\text{g} \cdot \text{K}}
\]

9. Heat energy to warm 168 g copper from -12.2 °C to 25.6 °C:

\[
\text{Heat} = \text{mass} \times \text{heat capacity} \times \Delta T
\]

For copper = (168 g)\(\frac{0.385 \text{ J}}{\text{g} \cdot \text{K}}\)[25.6°C−(−12.2)°C]\(\times \frac{1 \text{ K}}{1 \text{ °C}}\) = 2.44 x 10³ J or 2.44 kJ

11. The final temperature of a 344 g sample of iron when 2.25 kJ of heat are added to a sample originally at 18.2 °C. The energy added is:

\[
q_{Fe} = (\text{mass})(\text{heat capacity})(\Delta T)
\]

\[
2.25 \times 10^3 \text{ J} = (344 \text{ g})(0.449 \frac{\text{J}}{\text{g} \cdot \text{K}})(x)\]

and solving for x we get:

\[
14.57 \text{ K} = x \quad \text{and since 1K = 1°C,} \quad \Delta T = 14.57 \text{ °C.}
\]

The final temperature is (14.57 + 18.2)°C or 32.8°C.
13. Final T of copper-water mixture:

We must assume that no energy will be transferred to or from the beaker containing the water. Then the magnitude of energy lost by the hot copper and the energy gained by the cold water will be equal (but opposite in sign).

\[ q_{\text{copper}} = -q_{\text{water}} \]

Using the heat capacities of \( \text{H}_2\text{O} \) and copper, and expressing the temperatures in Kelvin \( (K = ^\circ C + 273.15) \) we can write:

\[ (45.5 \text{ g})(0.385 \frac{\text{J}}{\text{g} \cdot \text{K}})(T_{\text{final}} - 372.95 \text{ K}) = -(152. \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot \text{K}})(T_{\text{final}} - 291.65 \text{K}) \]

Simplifying each side gives:

\[ 17.52 \frac{\text{J}}{\text{K}} \cdot T_{\text{final}} - 6533 \text{ J} = -636.0 \frac{\text{J}}{\text{K}} \cdot T_{\text{final}} + 185,480 \text{ J} \]

\[ 653.52 \frac{\text{J}}{\text{K}} \cdot T_{\text{final}} = 192013 \text{ J} \]

Don’t forget: Round numbers only at the end.

15. Final temperature of water mixture:

This problem is solved almost exactly like question 13. The difference is that both samples are samples of water. From a mechanical standpoint, the heat capacity of both samples will be identical—and can be omitted from both sides of the equation:

\[ q_{\text{water}} (\text{at } 95 \text{ }^\circ \text{C}) = -q_{\text{water}} (\text{at } 22 \text{ }^\circ \text{C}) \]

\[ (85.2 \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot \text{K}})(T_{\text{final}} - 368.15 \text{ K}) = -(156 \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot \text{K}})(T_{\text{final}} - 295.15 \text{K}) \]

or

\[ (85.2 \text{ g})(T_{\text{final}} - 368.15 \text{ K}) = -(156 \text{ g})(T_{\text{final}} - 295.15 \text{K}) \]

or

\[ 85.2 \text{ J/K} \cdot T_{\text{final}} - 31366.38 \text{ J} = -156 \text{ J/K} \cdot T_{\text{final}} + 46043.4 \text{ J} \]

rearranging:

\[ 241.2 \text{ J/K} \cdot T_{\text{final}} = 77409.78 \text{ J} \]

so

\[ 321.0 \text{ K} = T_{\text{final}} \text{ or } 47.8 \text{ }^\circ \text{C} \]

17. Here the warmer Zn is losing heat to the water: \( q_{\text{metal}} = -q_{\text{water}} \)

Remembering that \( \Delta T = T_{\text{final}} - T_{\text{initial}} \), we can calculate the change in temperature for the water and the metal. Further, since we know the final and initial for both the metal and the water, we can calculate the temperature difference in units of Celsius degrees, since the change in temperature on the Kelvin scale would be numerically identical.

For the metal: \( \Delta T = T_{\text{final}} - T_{\text{initial}} = (27.1 - 98.8) \) or \(-71.7 \text{ }^\circ \text{C} \) or \(-71.7 \text{ K} \).

For the water: \( \Delta T = T_{\text{final}} - T_{\text{initial}} = (27.1 - 25.0) \text{ or } 2.1 \text{ }^\circ \text{C} \text{ or } 2.1 \text{ K} \) (recalling that a Celsius degrees and a Kelvin are the same “size”).

\[ (13.8 \text{ g})(C_{\text{metal}})(-71.7 \text{ K}) = -(45.0 \text{ g})(4.184 \frac{\text{J}}{\text{g} \cdot \text{K}})(2.1 \text{ K}) \]

\[ -989.46 \text{ g} \cdot \text{K}(C_{\text{metal}}) = -395 \text{ J} \]
Changes of State

19. Quantity of energy evolved when 1.0 L of water at 0 °C solidifies to ice:
   The mass of water involved: If we assume a density of liquid water of 1.000 g/mL,
   1.0 L of water (1000 mL) would have a mass of 1000 g.
   To freeze 1000 g water: 1000 g ice \( \times \frac{333 \text{ J}}{1.000 \text{ g ice}} = 333 \times 10^3 \text{ J} \) or 330 kJ (to 2sf)

21. Heat required to vaporize (convert liquid to gas) 125 g C\textsubscript{6}H\textsubscript{6}:
   The heat of vaporization of benzene is 30.8 kJ/mol.
   Convert mass of benzene to moles of benzene: 125 g \( \times \frac{78.11 \text{ g/mol}}{125 \text{ g}} = 1.60 \text{ mol} \)
   Heat required: 1.60 mol C\textsubscript{6}H\textsubscript{6} \( \times \frac{30.8 \text{ kJ/mol}}{1.60 \text{ mol}} = 49.3 \text{ kJ} \)
   NOTE: No sign has been attached to the amount of heat, since we wanted to know the amount. If we want to assign a direction of heat flow in this question, then we would add a (+) to 49.3 kJ to indicate that heat is being added to the liquid benzene.

23. To calculate the quantity of heat for the process described, think of the problem in two steps:
   1) cool liquid from 23.0 °C to liquid at –38.8 °C
   2) freeze the liquid at its freezing point (–38.8 °C)
   Note that the specific heat capacity is expressed in units of mass, so convert the volume of liquid mercury to mass. 1.00 mL \( \times \frac{13.6 \text{ g/mL}}{1.00 \text{ mL}} = 13.6 \text{ g Hg} \) (Recall: 1 cm\textsuperscript{3} = 1 mL)
   1) The energy to cool 13.6 g of Hg from 23.0 °C to liquid at –38.8 °C is:
      \[
      \Delta T = (234.35 \text{ K} - 296.15 \text{ K}) \text{ or } -61.8 \text{ K}
      \]
      \[
      13.6 \text{ g Hg} \times \frac{0.140 \text{ J}}{\text{g \cdot K}} \times -61.8 \text{ K} = -118 \text{ J}
      \]
   2) To convert liquid mercury to solid Hg at this temperature:
      - 11.4 J/g \( \times \frac{13.6 \text{ g}}{13.6 \text{ g}} = -155 \text{ J} \) (The (-) sign indicates that heat is being removed from the Hg.
      The total energy released by the Hg is: [-118 J + -155 J] = -273 J and since \( q_{\text{mercury}} = -q_{\text{surroundings}} \), the amount released to the surroundings is 273 J.
25. To accomplish the process, one must:
   1) heat the ethanol from 20.0 °C to 78.29 °C (ΔT = 58.29 K)
   2) boil the ethanol (convert from liquid to gas) at 78.29 °C
Using the specific heat for ethanol, the energy for the first step is:
\[ \frac{2.44}{g \cdot K} \times 1000 \, g \times 58.29 \, K = 142,227.6 \, J \] (142,000 J to 3 sf)
To boil the ethanol at 78.29 °C, we need:
\[ 855 \frac{J}{g} \times 1000 \, g = 855,000 \, J \]
The total heat energy needed (in J) is (142,000 + 855,000) = 997,000 or 9.97 x 10^5 J

**Enthalpy Changes**

*Note that in this chapter, I have left negative signs with the value for heat released*
*(heat released = - ; heat absorbed = +)*

27. For a process in which the ΔH° is negative, that process is **exothermic**.
   To calculate heat released when 1.25 g NO react, note that the energy shown (-114.1 kJ) is released when 2 moles of NO react, so we’ll need to account for that:
\[ 1.25 \, g \, NO \times \frac{1 \, mol \, NO}{30.01 \, g \, NO} \times \frac{-114.1 \, kJ}{2 \, mol \, NO} = -2.38 \, kJ \]

29. The combustion of isoctane (IO) is **exothermic**. The molar mass of IO is: 114.2 g/mol.
   The heat evolved is:
\[ 1.00 \, L \, of \, IO \times \frac{0.69 \, g \, IO}{1 \, mL} \times \frac{1 \times 10^3 \, mL}{1 \, L} \times \frac{1 \, mol \, IO}{114.2 \, g \, IO} \times \frac{-10922 \, kJ}{2 \, mol \, IO} = -3.3 \times 10^4 \, kJ \]

**Calorimetry**

31. 100.0 mL of 0.200 M CsOH and 50.0 mL of 0.400 M HCl each supply 0.0200 moles of base and acid respectively. If we assume the specific heat capacities of the solutions are 4.2 J/g • K, the **heat evolved** for 0.200 moles of CsOH is:
\[ q = (4.2 \, J/g \cdot K)(150. \, g)(24.28 \, °C - 22.50°C) \] [and since 1.78°C = 1.78 K]
\[ q = (4.2 \, J/g \cdot K)(150. \, g)(1.78 \, K) \]
\[ q = 1120 \, J \]
The molar enthalpy of neutralization is:
\[ \frac{-1120 \, J}{0.0200 \, mol \, CsOH} = -56000 \, J/mol \] (to 2 sf)
or -56 kJ/mol
33. For the problem, we’ll assume that the coffee-cup calorimeter absorbs no heat.
   Since $q_{metal} = -q_{water}$
   Remembering that $\Delta T = T_{final} - T_{initial}$, we can calculate the change in temperature for the water and the metal. Further, since we know the final and initial for both the metal and the water, we can calculate the temperature difference in units of Celsius degrees, since the change in temperature on the Kelvin scale would be numerically identical.
   For the metal: $\Delta T = T_{final} - T_{initial} = (24.3 - 99.5) \text{ or } -75.2^\circ C \text{ or } -75.2 K$.
   For the water: $\Delta T = T_{final} - T_{initial} = (24.3 - 21.7) \text{ or } 2.6^\circ C \text{ or } 2.6 K$ (recalling that a Celsius degrees and a Kelvin are the same “size”).
   \[(20.8 \text{ g})(C_{metal})(-75.2 \text{ K}) = -(75.0 \text{ g})(4.184 \frac{J}{g \cdot K})(2.6 \text{ K})\]
   \[-1564.16 \text{ g} \cdot K(C_{metal}) = -816 J\]
   \[C_{metal} = 0.52 \frac{J}{g \cdot K} \text{ (to 2 significant figures)}\]

35. Enthalpy change when 5.44 g of NH$_4$NO$_3$ is dissolved in 150.0 g water at 18.6 °C.
   Calculate the heat released by the solution: $\Delta T = (16.2 - 18.6)$ or -2.4 °C or -2.4 K
   \[(155.4 \text{ g})(4.2 \frac{J}{g \cdot K})(-2.4 \text{ K}) = -1566 J \text{ or } -1600 J \text{ (to 2 sf)}\]
   Calculate the amount of NH$_4$NO$_3$: 5.44 g NH$_4$NO$_3$ • $\frac{1 \text{ mol NH}_4\text{NO}_3}{80.04 \text{ g NH}_4\text{NO}_3} = 0.0680 \text{ mol} $NH$_4$NO$_3$
   Recall that the energy that was released by the solution is absorbed by the ammonium nitrate, so we change the sign from (-) to (+). The enthalpy change has been requested in units of kJ, so divide the energy (in J) by 1000:
   \[\text{Enthalpy of dissolving} = \frac{1.566 \text{ kJ}}{0.0680 \text{ mol}} = 23.0 \text{ kJ/mol or 23 kJ/mol (to 2 sf)}\]

37. Calculate the heat evolved (per mol SO$_2$) for the reaction of sulfur with oxygen to form SO$_2$
   There are several steps:
   1) Calculate the heat transferred to the water:
      \[815 \text{ g} \cdot 4.184 \frac{J}{g \cdot K} \cdot (26.72 - 21.25) \text{ } ^\circ C \cdot 1K/1^\circ C = 18,700 J\]
   2) Calculate the heat transferred to the bomb calorimeter
      \[923 \text{ J/K } \cdot (26.72 - 21.25) \text{ } ^\circ C \cdot 1K/1^\circ C = 5,050 J\]
   3) Amount of sulfur present: \[2.56 \text{ g} \cdot \frac{1 \text{ mol S}_8}{256.536 \text{ g } S_8} = 0.010 \text{ mol } S_8\]
   Note from the equation that 8 mol of SO$_2$ form from each mole of S$_8$
   4) Calculating the quantity of heat related per mol of SO$_2$ yields:
      \[\frac{18,700 J + 5,050 J}{0.08 \text{ mol SO}_2} = 297,000 \text{ J/mol SO}_2 \text{ or } 297 \text{ kJ/mol SO}_2\]
39. Quantity of heat evolved in the combustion of benzoic acid:
   As in study question 37, we can approach this in several steps:

   1) Calculate the heat transferred to the water:
      \[ 775 \text{ g} \cdot 4.184 \frac{\text{J}}{\text{g} \cdot \text{K}} \cdot (31.69 - 22.50) \text{ } ^\circ\text{C} \cdot 1\text{K}/1{\text{^\circ}\text{C}} = 29,800 \text{ J} \]

   2) Calculate the heat transferred to the bomb calorimeter
      \[ 893 \text{ J/K} \cdot (31.69 - 22.50) \text{ } ^\circ\text{C} \cdot 1\text{K}/1{\text{^\circ}\text{C}} = 8,210 \text{ J} \]

   3) Amount of benzoic acid:
      \[ 1.500 \text{ g benzoic acid} \cdot \frac{1 \text{ mol benzoic acid}}{122.1 \text{ g benzoic acid}} = 1.229 \times 10^{-2} \text{ mol benzoic acid} \]

   4) Heat evolved per mol of benzoic acid is:
      \[ \frac{29,800 \text{ J} + 8,210 \text{ J}}{1.229 \times 10^{-2} \text{ mol}} = 3.09 \times 10^6 \text{ J/mol or } 3.09 \times 10^3 \text{ kJ/mol} \]

41. Heat absorbed by the ice: \[ \frac{333 \text{ J}}{1.00 \text{ g ice}} \cdot 3.54 \text{ g ice} = 1,180 \text{ J} \] (to 3 sf)

   Since this energy (1180 J) is released by the metal, we can calculate the heat capacity of the metal:
   \[ \text{heat} = \text{heat capacity} \times \text{mass} \times \Delta T \]
   \[ -1180 \text{ J} = C \times 50.0 \text{ g} \times (273.2 \text{ K} - 373 \text{ K}) \] [Note that \( \Delta T \) is negative!]
   \[ 0.236 \frac{\text{J}}{\text{g} \cdot \text{K}} = C \]

   Note that the heat released (left side of equation) has a negative sign to indicate the directional flow of the energy.

Hess’s Law

43. (a) Hess’ Law allows us to calculate the overall enthalpy change by the appropriate combination of several equations. In this case we add the two equations, reversing the second one (with the concomitant reversal of sign)

\[
\begin{align*}
\text{CH}_4 (g) + 2 \text{O}_2 (g) & \rightarrow \text{CO}_2 (g) + 2 \text{H}_2\text{O} (g) \quad \Delta H^\circ = -802.4 \text{ kJ} \\
\text{CO}_2 (g) + 2 \text{H}_2\text{O} (g) & \rightarrow \text{CH}_3\text{OH} (g) + 3/2 \text{O}_2 (g) \quad \Delta H^\circ = +676 \text{ kJ} \\
\text{CH}_4 (g) + 1/2 \text{O}_2 (g) & \rightarrow \text{CH}_3\text{OH} (g) \quad \Delta H^\circ = -126 \text{ kJ}
\end{align*}
\]
(b) A graphic description of the energy change:
\[
\text{CH}_4 (g) + \frac{1}{2} \text{O}_2 (g) + \frac{3}{2} \text{O}_2 (g) \rightarrow \text{CH}_3 \text{OH}(g)
\]
\[
\Delta H^\circ = -126.4 \text{ kJ}
\]
\[
\Delta H'' = -802.4 \text{ kJ}
\]
\[
\Delta H^\circ = +676 \text{ kJ}
\]
\[
\text{CO}_2(g) + 2 \text{ H}_2 \text{O}(l)
\]

45. The overall enthalpy change for \(\frac{1}{2} \text{N}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{NO} (g)\)

For the overall equation, note that elemental nitrogen and oxygen are on the “left” side of the equation, and NO on the “right” side of the equation. Noting that equation 2 has 4 ammonia molecules consumed, let’s multiply equation 1 by 2:

\[
2 \text{N}_2 (g) + 6 \text{H}_2 (g) \rightarrow 4 \text{NH}_3 (g) \quad \Delta H = (2)(-91.8 \text{ kJ})
\]

The second equation has NO on the right side:

\[
4 \text{NH}_3 (g) + 5 \text{O}_2 (g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2 \text{O}(g) \quad \Delta H = -906.2 \text{kJ}
\]

The third equation has water as a product, and we need to “consume” the water formed in equation two, so let’s reverse equation 3—changing the sign—AND multiply it by 6

\[
6 \text{H}_2 \text{O}(g) \rightarrow 6 \text{H}_2 (g) + 3 \text{O}_2 (g) \quad \Delta H = (+241.8)(6) \text{kJ}
\]

Adding these 3 equations gives

\[
2 \text{N}_2 (g) + 2 \text{O}_2 (g) \rightarrow 4 \text{NO}(g) \quad \Delta H = 361 \text{ kJ}
\]

So, dividing all the coefficients by 4 provides the desired equation with

\[
\Delta H = +361 \cdot 0.25 \text{ kJ} \text{ or } 90.3 \text{ kJ}
\]

**Standard Enthalpies of Formation**

47. The equation requested requires that we form one mol of product liquid CH\(_3\)OH from its elements—each in their standard state.

Begin by writing a balanced equation:

\[
2 \text{C (s, graphite)} + \text{O}_2(g) + 4 \text{H}_2(g) \rightarrow 2 \text{CH}_3\text{OH}(l)
\]
Now express the reaction so that you form one mole of CH₃OH—divide coefficients by 2.

\[
C (s) + \frac{1}{2}O_2(g) + 2H_2(g) \rightarrow CH_3OH(1)
\]

And from Appendix L, the \( \Delta_f H^\circ \) is reported as \(-238.4 \text{ kJ/mol} \)

49. (a) The equation of the formation of \( \text{Cr}_2\text{O}_3 \) (s) from the elements:

\[
2 \text{Cr} (s) + \frac{3}{2}O_2 (g) \rightarrow \text{Cr}_2\text{O}_3 (s)
\]

from Appendix L \( \Delta_f H^\circ \) is reported as: \(-1134.7 \text{ kJ/mol} \) for the oxide.

(b) The enthalpy change if 2.4 g of Cr is oxidized to \( \text{Cr}_2\text{O}_3 \) (g) is:

\[
2.4 \text{ g Cr} \cdot \frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \cdot \frac{-1134.7 \text{ kJ}}{2 \text{ mol Cr}} = -26 \text{ kJ} \quad \text{(to 2 sf)}
\]

51. Calculate \( \Delta_r H^\circ \) for the following processes:

(a) 1.0 g of white phosphorus burns:

\[
P_4 (s) + 5O_2 (g) \rightarrow P_4O_{10} (s) \text{ from Appendix L: } \Delta_f H^\circ = -2984.0 \text{ kJ/mol}
\]

\[
1.0 \text{ g } P_4 \cdot \frac{1.0 \text{ mol } P_4}{123.89 \text{ g } P_4} \cdot \frac{-2984.0 \text{ kJ}}{1 \text{ mol } P_4} = -24 \text{ kJ}
\]

(b) 0.20 mol NO (g) decomposes to \( \text{N}_2 \) (g) and \( \text{O}_2 \) (g):

From Appendix L: \( \Delta_f H^\circ \) for NO = 90.29 kJ/mol

Since the reaction requested is the reverse of \( \Delta_f H^\circ \), we change the sign to \(-90.29 \text{ kJ/mol} \)

The enthalpy change is then \( \frac{-90.29 \text{ kJ}}{1 \text{ mol}} \cdot 0.20 \text{ mol} = -18 \text{ kJ} \)

(c) 2.40 g NaCl is formed from elemental Na and elemental Cl₂:

From Appendix L: \( \Delta_f H^\circ \) for NaCl (s) = - 411.12 kJ/mol

The amount of NaCl is: \( \frac{2.40 \text{ g NaCl}}{58.44 \text{ g NaCl}} \cdot 1 \text{ mol NaCl} = 0.0411 \text{ mol} \)

The overall energy change is: \(-411.12 \text{ kJ/mol} \cdot 0.0411 \text{ mol} = -16.9 \text{ kJ} \)

(d) 250 g of Fe oxidized to \( \text{Fe}_2\text{O}_3 \) (s):

From Appendix L: \( \Delta_f H^\circ \) for \( \text{Fe}_2\text{O}_3 \) (s) = - 824.2 kJ/mol

The overall energy change is:

\[
250 \text{ g Fe} \cdot \frac{1 \text{ mol Fe}}{55.8847 \text{ g Fe}} \cdot \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}} \cdot \frac{-824.2 \text{ kJ}}{1 \text{ mol Fe}_2\text{O}_3} = -1.8 \times 10^3 \text{ kJ}
\]

53. (a) The enthalpy change for the reaction:

\[
4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)
\]

\[
\Delta_f H^\circ (\text{kJ/mol}) \quad -45.90 \quad 0 \quad +90.29 \quad -241.83
\]
\[ \Delta rH^\circ = [(4 \text{ mol})(+90.29 \text{ kJ/mol}) + (6 \text{ mol})(-241.83 \text{ kJ/mol})] -
[(4 \text{ mol})(-45.90 \text{ kJ/mol}) + (5 \text{ mol})(0)]
= (-1089.82 \text{ kJ}) - (-183.6 \text{ kJ})
= -906.2 \text{ kJ} \quad \text{The reaction is exothermic.}

(b) Heat evolved when 10.0 g NH\textsubscript{3} react:
The balanced equation shows that 4 mol NH\textsubscript{3} result in the release of 906.2 kJ.

\[
10.0 \text{ g NH}_3 \cdot \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \cdot \frac{-906.2 \text{ kJ}}{4 \text{ mol NH}_3} = -133 \text{ kJ}
\]

55. (a) The enthalpy change for the reaction:
2 BaO\textsubscript{2} (s) \rightarrow 2 \text{ BaO (s)} + \text{ O}_2 (g)
Given \(\Delta_f H^\circ\) for BaO is: -553.5 kJ/mol and \(\Delta_f H^\circ\) for BaO\textsubscript{2} is: -634.3 kJ/mol
This equation can be seen as the summation of the two equations:
(1) 2 Ba (s) + O\textsubscript{2} (g) \rightarrow 2 \text{ BaO (s)}
(2) 2 BaO\textsubscript{2} (s) \rightarrow 2 \text{ Ba (s)} + O\textsubscript{2} (g)
Equation (1) corresponds to the formation of BaO x 2 while equation(2) corresponds to (2x) the reverse of the formation of BaO\textsubscript{2}
\[ \Delta rH^\circ = (2\Delta_f H^\circ \text{ for BaO}) + -2(\Delta_f H^\circ \text{ for BaO}_2) = \]
\[ \Delta rH^\circ = 161.6 \text{ kJ} \text{ and the reaction is endothermic.} \]

(b) Energy level diagram for the equations in question:
57. The molar enthalpy of formation of naphthalene can be calculated since we’re given the enthalpic change for the reaction:

\[ \text{C}_{10}\text{H}_8(\text{s}) + 12 \text{O}_2(\text{g}) \rightarrow 10 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\ell) \]

\[ \Delta H^\circ_{f}(\text{kJ/mol}) \quad ? \quad 0 \quad -393.509 \quad -285.83 \]

\[ \Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{f} \text{products} - \sum \Delta H^\circ_{f} \text{reactants} \]

\[ -5156.1 \text{ kJ} = [(10 \text{ mol})(-393.509 \text{ kJ/mol}) + (4 \text{ mol})(-285.83 \text{ kJ/mol})] - [\Delta H^\circ_{f} \text{C}_{10}\text{H}_8] \]

\[ -5156.1 \text{ kJ} = (-5078.41 \text{ kJ}) - \Delta H^\circ_{f} \text{C}_{10}\text{H}_8 \]

\[ 77.7 \text{ kJ} = - \Delta H^\circ_{f} \text{C}_{10}\text{H}_8 \]

\[ 77.7 \text{ kJ} = \Delta H^\circ_{f} \text{C}_{10}\text{H}_8 \]

**GENERAL QUESTIONS ON THERMOCHEMISTRY**

59. Define and give an example of:

(a) Exothermic and Endothermic—the suffix “thermic” talks about heat, and the prefixes “exo” and “endo” tell us whether heat is ADDED to the surroundings from the system (exo) or REMOVED from the surroundings to the system (endo). Combustion reactions (e.g. gasoline burning in your automobile) are EXOthermic reactions, while ice melting is an ENDOthermic reaction.

(b) System and Surroundings—The “system” is the reactant(s) and product(s) of a reaction, while the “surroundings” is EVERYTHING else. Suppose we burn gasoline in an internal combustion engine. The gasoline (and air) in the cylinder(s) composes the “system”, while the engine, and the air contacting the engine is the “surroundings”. Together the “system” and “surroundings” compose the “universe”—at least in thermodynamics.

(c) Specific heat capacity—is the quantity of heat required to change the temperature of 1g of a substance by 1 degree Celsius. Water has a specific heat capacity of about 4.2 J/g*K, meaning that 1 gram of water at 15 degrees C, to which 4.2 J of energy is added, will have a temperature of 16 degrees C. (or 14 degrees C—if 4.2 J of energy is removed).

(d) State function—Any parameter which is dependent ONLY on the initial and final states. Chemists typically use CAPITAL letters to indicate state functions (e.g. H, S, ) while non-state functions are indicated with LOWER CASE letters (e.g. q, w). Your checking account balance is a state function!

(e) Standard state—Defined as the MOST STABLE (PHYSICAL) STATE for a substance at a pressure of 1 bar and at a specified temperature. (Typically 298K) The standard state for elemental nitrogen at 25 °C (298K) is gas.

(f) Enthalpy change—the heat transferred in a process that is carried out under constant pressure conditions is the enthalpy change, \( \Delta H \).
The enthalpy change upon the formation of 1 mol of water(ℓ) is \(-285.8\) kJ, meaning that 285.8 kJ is released upon the formation of 1 mol of liquid water from 1 mol of hydrogen (g) and 1/2 mol oxygen (g).

(g) Standard Enthalpy of Formation—the enthalpy change for the formation of 1 mol of a compound directly from its component elements, each in their standard states. The standard enthalpy of formation of nitrogen gas (N₂) = 0 kJ/mol.

61. Define system and surroundings for each of the following, and give direction of heat transfer:
   (a) Methane is burning in a gas furnace in your home:
       (System) methane + oxygen (Surroundings) components of furnace and the air in your home. The heat flows from the methane + oxygen to the furnace and air.
   (b) Water drops on your skin evaporate:
       (System) water droplets (Surroundings) your skin and the surrounding air. The heat flows from your skin and the air to the water droplet.
   (c) Liquid water at 25 °C is placed in freezer:
       (System) water (Surroundings) freezer. The heat flows from the water to the freezer.
   (d) Aluminum and FeO react in a flask on a lab bench:
       (System) Al and FeO (Surroundings) flask, lab bench, and air around flask. The heat flows from the reaction of Al and FeO into the surroundings.

63. Standard Enthalpies of Formation for O(g), O₂ (g), O₃ (g).

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔfH (at 298K) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(g)</td>
<td>249.170</td>
</tr>
<tr>
<td>O₂ (g)</td>
<td>0</td>
</tr>
<tr>
<td>O₃ (g)</td>
<td>142.67</td>
</tr>
</tbody>
</table>

What is the standard state of O₂? The standard state of oxygen (O₂) is as a gas.

Is the formation of O from O₂ exothermic?

\[ \Delta_fH = \Sigma \Delta_fH_{products} - \Sigma \Delta_fH_{reactants} \quad (O_2 \rightarrow 2O) \]

\[ \Delta_fH = (2 \text{ mol})(249.170) - (1 \text{ mol})(0) = 498.340 \text{ kJ (endothermic)} \]

What is the ΔH for 3/2 O₂(g) → O₃ (g)

\[ \Delta_fH = \Sigma \Delta_fH_{products} - \Sigma \Delta_fH_{reactants} \]

\[ \Delta_fH = (1 \text{ mol})(142.67 \text{ kJ/mol}) - (3/2 \text{ mol})(0) = 142.67 \text{ kJ} \]
65. To calculate the formation of SnCl₄(ℓ) and TiBr₂(s) from SnBr₂(s) + TiCl₄(ℓ) we can use Hess’ Law to add a series of appropriate equations. A screen capture from the CD-ROM shows the overall process:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>ΔH° (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. SnCl₂(s) + TiBr₂(s) → SnBr₂(s) + TiCl₄(s)</td>
<td>+4.2</td>
</tr>
<tr>
<td>2. SnCl₂(s) + Cl₂(g) → SnCl₄(ℓ)</td>
<td>-195</td>
</tr>
<tr>
<td>3. TiCl₂(s) + Cl₂(g) → TiCl₄(ℓ)</td>
<td>-273</td>
</tr>
</tbody>
</table>

Net Reaction: SnBr₂(s) + TiCl₄(ℓ) → TiBr₂(s) + SnCl₄(ℓ)  
ΔH°ₙₑᵗ = 73.8 kJ

Given the integral values for “Reaction 2”, ΔH° = 74 kJ.

67. If 187 J raises the temperature of 93.45 g of Ag from 18.5 to 27.0°C, what is the specific heat capacity of silver?
Recall that q = m•c•Δt; so

\[ C_{Ag} = \frac{187 \text{ J}}{93.45 \text{ g} \cdot (27.0 - 18.5) \text{°C}} = 0.24 \text{ J/g • K} \]

69. Addition of 100.0 g of water at 60 °C to 100.0 g of ice at 0.00 °C. The water cools to 0.00 °C. How much ice has melted?
As the ice absorbs heat from the water, two processes occur: (1) the ice melts and (2) the water cools. We can express this with the equation qₜₐₜₜ = qₗₐₜₜ
The melting of ice can be expressed with the heat of fusion of ice, 333 J/g, as q = m • 333 J/g.
The cooling of the water may be expressed: q = m • c • ΔT. Setting these quantities equal gives:

\[ m \cdot c \cdot ΔT = m \cdot 333 \text{ J/g} + 100.0 \text{ g} \cdot (4.184 \text{ J/g • K}) \cdot (0 - 60) \text{K} = -x \cdot 333 \text{ J/g} \]

\[ x = \text{quantity of ice that melts. Note that since Celsius degrees and kelvin are the same “size”, } \Delta t \text{ is } -60^\circ \text{C or } -60 \text{ K} \]

\[ 100.0 \text{ g} \cdot (4.184 \text{ J/g • K}) \cdot (0 - 60) \text{K} = -x \cdot 333 \text{ J/g} \]

\[ -25104 \text{ J} = -x \cdot 333 \text{ J/g or } \frac{-25104 \text{ J}}{-333 \text{ J/g}} = x \text{ or } 75.4 \text{ g of ice.} \]
71. 90 g (two 45 g cubes) of ice cubes (at 0 °C) are dropped into 500. mL tea at 20.0 °C (Assume a density of 1.00 g/mL for tea). What is the final temperature of the mixture if all the ice melts?

Since \( q_{\text{water}} = -q_{\text{ice}} \) and we can set up the expression.

\[
m \cdot c \cdot \Delta T = - m \cdot 333 \text{ J/g} \quad \text{NOTE however, that not only does all the ice melt, but the melted ice warms to a temperature above 0 °C. We add a term to account for that:}
\]

\[
m_{\text{tea}} \cdot c \cdot \Delta T_{\text{tea}} = - [m_{\text{ice}} \cdot 333 \text{ J/g} + m_{\text{ice}} \cdot c \cdot \Delta T_{\text{ice}} ]
\]

500. g \cdot (4.184 \text{ J/g} \cdot \text{K}) \cdot (F - 293.2 \text{ K}) = -[(90 \text{ g} \cdot 333 \text{ J/g}) + (90 \text{ g} \cdot (4.184 \text{ J/g} \cdot \text{K}) \cdot (F - 273.2 \text{ K}))]

where F is the final temperature of the tea and melted ice.

2092 F J - 613,374 J = -[29970 J + 377F J - 102,876 J] Simplifying:

2092F J - 613,374 J + 29970 J + 377F J - 102,876 J = 0

(2092F J + 377F J) + (-613,374 J + 29970 J - 102,876 J) = 0

2469 F J + -686,280 = 0 or 2469 F J = 686,280 and F = (686,280/2469) = 278 K

and noting that 45 g of ice cube has 2 sf, we report a final temperature of 280 K.

73. One can arrive at the desired answer if you recall the definition of \( \Delta H^\circ_f \). The definition is the enthalpy change associated with the formation of one mole of the substance (in this case \( \text{B}_2\text{H}_6 \)) from its elements — each in their standard state (s for boron and g for hydrogen).

(a) Note that the 1st equation given uses four moles of B as a reactant — and we’ll need only 2, so divide the first equation by 2 to give:

\[
2 \text{ B (s)} + 3/2 \text{ O}_2 (g) \rightarrow \text{B}_2\text{O}_3 (s) \quad \Delta H^\circ = 1/2(-2543.8 \text{ kJ}) = -1271.9 \text{ kJ}
\]

The formation of 1 mole of \( \text{B}_2\text{H}_6 \) will require the use of 6 moles of H (or 3 moles of \( \text{H}_2 \)), so multiply the second equation by 3 to give:

\[
3 \text{ H}_2 (g) + 3/2 \text{ O}_2 (g) \rightarrow 3 \text{ H}_2\text{O} (g) \quad \Delta H^\circ = 3(-241.8 \text{ kJ}) = -725.4 \text{ kJ}
\]

Finally the third equation given has \( \text{B}_2\text{H}_6 \) as a reactant and not a product. So reverse the third equation to give:

\[
\text{B}_2\text{O}_3 (s) + 3 \text{ H}_2\text{O} (g) \rightarrow \text{B}_2\text{H}_6 (g) + 3 \text{ O}_2 (g) \Delta H^\circ = -(-2032.9 \text{ kJ}) = +2032.9 \text{ kJ}
\]

(b) Adding the three equations gives the equation:

\[
2 \text{ B (s)} + 3 \text{ H}_2 (g) \rightarrow \text{B}_2\text{H}_6 (g) \quad \text{with a } \Delta H^\circ = (-1271.9 + -725.4 + 2032.9) \text{kJ}
\]

or a \( \Delta H^\circ \) for \( \text{B}_2\text{H}_6 \) of +35.6 kJ

(c) Energy level diagram for the reactions:
Chapter 5  Energy and Chemical Reactions

(d) Formation of $\text{B}_2\text{H}_6 \text{ (g)}$ is **reactant-favored**

75. (a) Enthalpy change for:

$$\text{C(s) + H}_2\text{O(g)} \rightarrow \text{CO(g) + H}_2\text{(g)}$$

$\Delta H^\circ _\text{f}(\text{kJ/mol})$  
$\begin{array}{ccc}
0 & -241.83 & -110.525 & 0 \\
\end{array}$

$\Delta H^\circ _\text{rxn} = \left[ (1 \text{ mol})(-110.525 \frac{\text{kJ}}{\text{mol}}) + 0 \right] - \left[ 0 + (1 \text{ mol})(-241.83 \frac{\text{kJ}}{\text{mol}}) \right]$

$\Delta H^\circ _\text{rxn} = +131.31 \text{ kJ}$

(b) The process is **endothermic**, so the reaction is **reactant-favored**.

(c) Heat involved when 1.0 metric ton (1000.0 kg) of C is converted to coal gas:

$$1000.0 \text{ kg C} \cdot \frac{1000 \text{ g C}}{1 \text{ kg C}} \cdot \frac{1 \text{ mol C}}{12.011 \text{ g C}} \cdot \frac{+131.31 \text{ kJ}}{1 \text{ mol C}} = 1.0932 \times 10^7 \text{ kJ}$$

77. For the combustion of $\text{C}_8\text{H}_{18}$:

$$\text{C}_8\text{H}_{18(1)} + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8 \text{ CO}_2(\text{g}) + 9 \text{ H}_2\text{O}(\text{l})$$

$\Delta_f H^\circ = \left[ (8 \text{ mol})(-393.509 \frac{\text{kJ}}{\text{mol}}) + (9 \text{ mol})(-285.83 \frac{\text{kJ}}{\text{mol}}) \right] - [(1 \text{ mol})(-259.2 \frac{\text{kJ}}{\text{mol}}) + 0]$

$\Delta_f H^\circ = -5461.3 \text{ kJ}$

Expressed on a gram basis: $-5461.3 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1 \text{ mol C}_8\text{H}_{18}}{114.2 \text{ g C}_8\text{H}_{18}} = -47.81 \text{ kJ/g}$

For the combustion of $\text{CH}_3\text{OH}$:

$$2 \text{ CH}_3\text{OH(1)} + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$$

$\Delta_f H^\circ = \left[ (2\text{ mol})(- 393.509 \text{ kJ/mol}) + (4 \text{ mol})(- 285.83 \text{ kJ/mol}) \right] - [(2\text{ mol})(- 238.4 \text{ kJ/mol}) + 0]$

$\Delta_f H^\circ = -1343.3 \text{ kJ}$

$\Delta_f H^\circ = -77.15 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1 \text{ mol C}_8\text{H}_{18}}{114.2 \text{ g C}_8\text{H}_{18}} = -0.67 \text{ kJ/g}$
Express this on a per mol and per gram basis:
\[
\frac{-1453.5 \text{ kJ}}{2 \text{ mol CH}_3\text{OH}} \cdot \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} = -22.682 \text{ kJ/g}
\]
On a per gram basis, octane liberates the greater amount of heat energy.

79. (a) Enthalpy change for formation of 1.00 mol of SrCO₃

\[
\text{Sr (s) + C (graphite) + } \frac{3}{2} \text{ O}_2 (g) \rightarrow \text{SrCO}_3 (s) \text{ using the data:}
\]

\[
\text{Sr(s) + 1/2 O}_2 (g) \rightarrow \text{SrO(s)} \quad \Delta_f H^\circ = -592 \text{ kJ/mol-rxn}
\]
\[
\text{SrO(s) + CO}_2 (g) \rightarrow \text{SrCO}_3 (s) \quad \Delta_r H^\circ = -234 \text{ kJ/mol-rxn}
\]
\[
\text{C (graphite) + O}_2 (g) \rightarrow \text{CO}_2 (g) \quad \Delta_f H^\circ = -394 \text{ kJ/mol-rxn}
\]

Let’s add the equations to give our desired overall equation.

\[
\text{Sr (s) + C (graphite) + } \frac{3}{2} \text{ O}_2 (g) \rightarrow \text{SrCO}_3 (s) \quad \Delta_r H^\circ = -1220. \text{ kJ/mol-rxn}
\]

(b) Energy diagram relating the energy quantities:
81. The desired equation is: \( \text{CH}_4 (g) + 3 \text{Cl}_2 (g) \rightarrow 3 \text{HCl} (g) + \text{CHCl}_3 (g) \)

Begin with equation 1 (the combustion of methane)

\[
\text{CH}_4 (g) + 2 \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l) + \text{CO}_2 (g) \quad \Delta H = -890.4 \text{ kJ} = -890.4 \text{ kJ/mol-react} 
\]

Noting that we form HCl as one of the products, using the second equation, we need to **reverse** it and (to adjust the coefficient of HCl to 3), multiply by \( \frac{3}{2} \) to give:

\[
3/2 \text{H}_2 (g) + 3/2 \text{Cl}_2 (g) \rightarrow 3 \text{HCl} \quad \Delta H = -3/2(+184.6) \text{ kJ/mol-react} = -276.9 \text{ kJ}
\]

Note that \( \text{CO}_2 \) formed in equation 1 doesn’t appear in the overall equation so let’s use the equation for the formation of \( \text{CO}_2 \) (reversed) to “consume” the \( \text{CO}_2 \):

\[
\text{CO}_2 (g) \rightarrow \text{C (graphite)} + \text{O}_2 (g) \quad \Delta H = -1(-393.5) \text{ kJ} = +393.5 \text{ kJ}
\]

Noting also that equation 1 produces 2 water molecules, let’s “consume” them by using the equation for the formation of water (reversed) multiplied by 2:

\[
2 \text{H}_2\text{O} (l) \rightarrow 2 \text{H}_2 (g) + \text{O}_2 (g) \quad \Delta H = -2(-285.8) \text{ kJ} = +571.6 \text{ kJ}
\]

and finally we need to produce \( \text{CHCl}_3 \) which we can do with the equation that represents the \( \Delta H_f \) for \( \text{CHCl}_3 \):

\[
\text{C (graphite)} + 1/2 \text{H}_2 (g) + 3/2 \text{Cl}_2 (g) \rightarrow \text{CHCl}_3 (g) \quad \Delta H = -103.1 \text{ kJ}
\]

The overall enthalpy change would then be:

\[
\Delta H = -890.4 \text{ kJ} - 276.9 \text{ kJ} + 393.5 \text{ kJ} + 571.6 \text{ kJ} -103.1 \text{ kJ} = -305.3 \text{ kJ}
\]

**IN THE LABORATORY**

83. \( q_{\text{metal}} = \text{heat capacity} \times \text{mass} \times \Delta T \)

\[
q_{\text{metal}} = C_{\text{metal}} \times 27.3 \text{ g} \times (299.47 - 372.05) \text{ K}
\]

Note that \( \Delta T \) is negative, since \( T_{\text{final}} \) of the metal is LESS THAN \( T_{\text{initial}} \)

and \( q_{\text{water}} = 15.0 \text{ g} \times \frac{4.184 \text{ J}}{\text{g} \cdot \text{K}} \times (299.47 - 295.65) \text{ K} = 239.7 \text{ J} \)

Setting \( q_{\text{metal}} = -q_{\text{water}} \)

\[
C_{\text{metal}} \times 27.3 \text{ g} \times (-72.58 \text{ K}) = -239.7 \text{ J} \quad \text{and solving for } C \text{ gives:}
\]

\[
C_{\text{metal}} = 0.121 \frac{\text{J}}{\text{g} \cdot \text{K}}
\]

85. Calculate the enthalpy change for the precipitation of \( \text{AgCl} \) (in kJ/mol):

1) How much \( \text{AgCl} \) is being formed?

- 250. mL of 0.16 M \( \text{AgNO}_3 \) will contain \((0.250 \text{ L} \cdot 0.16 \text{ mol/L}) \cdot 0.040 \text{ mol of } \text{AgNO}_3 \)
- 125 mL of 0.32 M \( \text{NaCl} \) will contain \((0.125 \text{ L} \cdot 0.32 \text{ mol/L}) \cdot 0.040 \text{ mol of } \text{NaCl} \).

Given the stoichiometry of the process, we anticipate the formation of 0.040 mol of \( \text{AgCl} \).
2) How much energy is evolved?

\[
375 \text{ g} \cdot \frac{4.2 \text{ J}}{\text{g} \cdot \text{K}} \cdot (296.05 \text{ K} - 294.30 \text{ K}) = 2,800 \text{ J (to 2 sf)}
\]

The enthalpy change is then -2800 J (since the reaction releases heat).

The change in kJ/mol is

\[
\frac{2800 \text{ J}}{0.040 \text{ mol}} \cdot \frac{1 \text{ kJ}}{1000 \text{ J}} = -69 \text{ kJ/mol}
\]

87. Heat evolved when ammonium nitrate is decomposed:

\[
\Delta T = (20.72-18.90) = 1.82 ^\circ \text{C} \text{ (or 1.82 K)}.
\]

Heat absorbed by the calorimeter: 155 J/K \cdot 1.82K = 282 J

Heat absorbed by the water: 415 g \cdot \frac{4.18 \text{ J}}{\text{g} \cdot \text{K}} \cdot 1.82 \text{ K} = 3160 J

Total heat released by the decomposition: 3160 J + 282 J = 3,440 J (to 3 sf)

With 7.647 g NH\textsubscript{4}NO\textsubscript{3} = 0.09554 mol, heat released = \frac{3440 J}{0.09554 \text{ mol}} = 36.0 \text{ kJ/mol}

89. The enthalpy change for the reaction:

\[
\text{Mg(s)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2 (s) + \text{H}_2(g)
\]

\[
\Delta_fH^\circ (\text{kJ/mol}) \quad 0 \quad -285.83 \quad -924.54 \quad 0
\]

\[
\Delta_rH^\circ = (1 \text{ mol})(-924.54 \frac{\text{kJ}}{\text{mol}}) - (2 \text{ mol})(-285.83 \frac{\text{kJ}}{\text{mol}}) = -352.88 \text{ kJ or } -3.5288 \times 10^5 \text{ J}
\]

Each mole of magnesium releases 352.88 kJ of heat energy.

Calculate the heat required to warm 25 mL of water from 25 to 85 °C.

\[
\text{heat} = \text{heat capacity} \times \text{mass} \times \Delta T
\]

\[
= (4.184 \frac{\text{kJ}}{\text{mol} \cdot \text{°C}})(25 \text{ mL})(\frac{1.00 \text{ g}}{\text{mL}})(60 \text{ K}) = 6276 \text{ or } 6300 \text{ J \ or } 6.3 \text{ kJ (to 2 sf)}
\]

Magnesium required:

\[
6.3 \text{ kJ} \cdot \frac{1 \text{ mol Mg}}{352.88 \text{ kJ}} \cdot \frac{24.3 \text{ g Mg}}{1 \text{ mol Mg}} = 0.43 \text{ g Mg}
\]
SUMMARY AND CONCEPTUAL QUESTIONS

91. Without doing calculations, decide whether each is product- or reactant-favored:
   (a) combustion of natural gas—oxidation reactions of carbon and hydrogen are typically product-favored. This process is exothermic as well.
   (b) Decomposition of sugar to carbon and water- Sugar does not naturally decompose into carbon and water, hence we predict the reaction to be reactant-favored.

93. Determine the value of $\Delta H$ for the reaction:
   $$\text{Ca}(s) + 1/8 \text{S}_8 (s) + 2 \text{O}_2(g) \rightarrow \text{CaSO}_4(s)$$
   Imagine this as the sum of several processes:
   1) Ca(s) + 1/2 O$_2$(g) $\rightarrow$ CaO(s)
   2) 1/8 S$_8$ (s) + 3/2 O$_2$(g) $\rightarrow$ SO$_3$(g)
   3) CaO(s) + SO$_3$(g) $\rightarrow$ CaSO$_4$(s) $\Delta H = -402.7 \text{ kJ}$

   Note that the SUM of the three processes is the DESIRED equation (the formation of CaSO$_4$(s)). The OVERALL $\Delta H$ is then the SUM of the $\Delta H$ for process (1) and $\Delta H$ for process (2). We know that the $\Delta_f H^\circ$ for (3) = -402.7 kJ or $\Delta_f H^\circ = [\Delta_f H^\circ \text{CaSO}_4(s) - \Delta_f H^\circ \text{CaO(s)} + \Delta_f H^\circ \text{SO}_3(g)]$. Since we know the $\Delta_f H^\circ$ and BOTH the $\Delta_f H^\circ$ for CaO(s) and SO$_3$(g), we can calculate the $\Delta_f H^\circ$ CaSO$_4$(s).

   From Appendix L we find,
   $\Delta_f H^\circ$ for CaO(s) = -635.09 kJ/mol and $\Delta_f H^\circ$ for SO$_3$(g) = -395.77 kJ/mol

   $\Delta_f H^\circ = [\Delta_f H^\circ \text{CaSO}_4(s) - \Delta_f H^\circ \text{CaO(s)} + \Delta_f H^\circ \text{SO}_3(g)]$

   - 402.7 kJ = $\Delta_f H^\circ$ CaSO$_4$(s) - [-635.09 kJ/mol + -395.77 kJ/mol]

   - 1,433.6 kJ = $\Delta_f H^\circ$ CaSO$_4$(s)

95. The molar heat capacities for Al, Fe, Cu, and Au are:

   $\frac{0.897}{\text{g} \cdot \text{K}} \cdot \frac{26.98}{\text{g Al}} = \frac{24.2}{\text{mol} \cdot \text{K}}$

   $\frac{0.449}{\text{g} \cdot \text{K}} \cdot \frac{55.85}{\text{g Fe}} = \frac{25.1}{\text{mol} \cdot \text{K}}$

   $\frac{0.385}{\text{g} \cdot \text{K}} \cdot \frac{63.55}{\text{g Cu}} = \frac{24.5}{\text{mol} \cdot \text{K}}$

   $\frac{0.129}{\text{g} \cdot \text{K}} \cdot \frac{197.0}{\text{g Au}} = \frac{25.4}{\text{mol} \cdot \text{K}}$
The graph shown is a plot of specific heat capacity versus atomic weight. As you can see, no simple linear relationship exists for these metals. The plot of the specific heat of Cu (atomic weight 63.55) and Au (atomic weight 197) does show a decreasing value of specific heat capacity as the atomic weight of the element increases. If you estimate the atomic weight to be about 100 (exact value is about 108), one could estimate a value of approximately 0.28 as the specific heat (compared to the experimental value of 0.236).

Alternatively, a quick examination of the values for the four metals above indicates that they are quite similar, with an average of 24.8 J/mol • K. This translates into:

$$\frac{24.8 \text{ J/mol} \cdot \text{K}}{1 \text{ mol Au}} = \frac{1 \text{ mol Au}}{107.9 \text{ g Au}} = 0.230 \text{ J/g} \cdot \text{K}$$

97. Mass of methane needed to heat the air from 15.0 to 22.0 °C:

Calculate the volume of air, then with the density and average molar mass, the moles of air present:

$$275 \text{ m}^2 \cdot 2.50 \text{ m} \cdot \frac{1000 \text{ L}}{1 \text{ m}^3} \cdot \frac{1.22 \text{ g air}}{1 \text{ L air}} \cdot \frac{1 \text{ mol air}}{28.9 \text{ g air}} = 2.90 \times 10^4 \text{ mol air}$$

The energy needed to change the temperature of that amount of air by (22.0 – 15.0)°C:

$$2.90 \times 10^4 \text{ mol air} \cdot \frac{29.1 \text{ J}}{\text{ mol} \cdot \text{ K}} \cdot 7.0 \text{ K} = 5.9 \times 10^6 \text{ J}$$

What quantity of energy does the combustion of methane provide?

The reaction may be written: CH₄ (g) + 2 O₂ (g) → 2 H₂O (g) + CO₂ (g)
Using data from Appendix L:
\[ \Delta_f H = [(2 \text{ mol})(-241.83 \text{ kJ/mol}) + (1 \text{ mol})(-393.509 \text{ kJ/mol})] \\
- [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (2 \text{ mol})(0)] = -802.3 \text{ kJ} \]

The amount of methane necessary is:
\[ 5.9 \times 10^6 \text{ J} \cdot \frac{1 \text{ kJ}}{1000 \text{ J}} \cdot \frac{1 \text{ mol} \text{ CH}_4}{802.3 \text{ kJ}} \cdot \frac{16.0 \text{ g} \text{ CH}_4}{1 \text{ mol} \text{ CH}_4} = 120 \text{ g CH}_4 \ (2 \text{ sf}) \]

99. Calculate the quantity of heat transferred to the surroundings from the water vapor condensation as rain falls.

Calculate the volume of water that falls, and then the mass of that water:

From the conversion factors listed in your textbook, calculate the area of 1 mi² in cm²
[1 km = 0.62137 mi and 1 km = 10⁵ cm.]
\[ \frac{1 \text{ mi}^2}{1} \cdot \frac{(1 \text{ km})^2}{(0.62137 \text{ mi})^2} \cdot \frac{(10^5 \text{ cm})^2}{(1 \text{ km})^2} = \frac{10^{10} \text{ cm}^2}{0.38610} = 2.59 \times 10^{10} \text{ cm}^2 \]

1 in = 2.54 cm so the VOLUME of water is 2.59 \times 10^{10} \text{ cm}^2 \times 2.54 \text{ cm} = 6.6 \times 10^{10} \text{ cm}^3.

The mass of water is: 6.6 \times 10^{10} \text{ cm}^3 \times 1.0 \text{ g/cm}^3 = 6.6 \times 10^{10} \text{ g} \text{ of water.}

The amount of heat:
\[ \frac{6.6 \times 10^{10} \text{ g water}}{1} \cdot \frac{1 \text{ mol water}}{18.02 \text{ g water}} \cdot \frac{44.0 \text{ kJ}}{1 \text{ mol water}} = 1.6 \times 10^{11} \text{ kJ} \]

Note the much larger energy for this process than for the detonation of a ton of dynamite.

101. (a) The diagram is:

(b) For the combustion reaction: \( \text{C}_4\text{H}_8(\text{g}) + 6 \text{ O}_2(\text{g}) \rightarrow 4 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{g}) \)
\[ \Delta H^\circ = 4\Delta H^\circ (\text{CO}_2) + 4\Delta H^\circ (\text{H}_2\text{O}) - \Delta H^\circ (\text{C}_4\text{H}_8) + 6\Delta H^\circ (\text{O}_2) \]
Note that the last term will be 0 in all cases. Substitute the thermodynamic data for each of the three isomers:
cis-2-butene:
\[ \Delta_f H^\circ = 4 \Delta H^\circ (\text{CO}_2) + 4 \Delta H^\circ (\text{H}_2\text{O}) - \Delta H^\circ (\text{C}_4\text{H}_8) \]
1 mol • -2687.5 kJ/mol =
4 mol • -393.509 kJ/mol + 4 mol • -241.83 kJ/mol – 1 mol • \( \Delta_f H^\circ (\text{C}_4\text{H}_8) \) = 146.1 kJ

trans-2-butene:
1 mol • -2684.2 kJ/mol =
4 mol • -393.509 kJ/mol + 4 mol • -241.83 kJ/mol – 1 mol • \( \Delta_f H^\circ (\text{C}_4\text{H}_8) \) = 142.8 kJ

1-butene:
1 mol • -2696.7 kJ/mol =
4 mol • -393.509 kJ/mol + 4 mol • -241.83 kJ/mol – 1 mol • \( \Delta_f H^\circ (\text{C}_4\text{H}_8) \) = 155.3 kJ

(c) Relation of Enthalpies of Isomers to the elements:
\[ \Delta f H^\circ = \Delta f H^\circ (\text{trans-2-butene}) - \Delta f H^\circ (\text{cis-2-butene}) = 142.8 \text{ kJ} - 146.1 \text{ kJ} = -3.3 \text{ kJ} \]

103. (a) A sample of 0.850 g Mg corresponds to 0.0350 mol Mg.

The amount of heat (evolved) is -25.4 kJ, corresponding to 25.4 kJ/0.0350 mol Mg = -726 kJ/mol

(b) Final temperature of water and bomb calorimeter:

Heat evolved = - Heat absorbed
\[-25400 \text{ J} = -(820 \text{ J/K})\Delta T + (750.\text{ g})(4.184 \text{ J/g°C})\Delta T\]
\[-25400 \text{ J} = -(820 \text{ J/K})\Delta T + (3138 \text{ J/K})\Delta T\] and \[-25400 \text{ J} = -3958 \text{ J/K} \Delta T\]
\[-25400 \text{ J}/-3958 \text{ J/K} = 6.41 \text{ K} \quad \text{(or 6.41°C — since a K and a °C are the same “size”)}

The new temperature of water will be 18.6 °C + 6.41°C = 25.0 °C
105. (a) The energy diagram shown here indicates that methane liberates 955.1 kJ/mol while methanol liberates only 676.1 kJ/mol.

(b) Energy per gram:

For methane:
\[
\frac{-955.1 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{16.04 \text{ g}} = -59.54 \text{ kJ/g}
\]

For methanol:
\[
\frac{-676.1 \text{ kJ}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{32.04 \text{ g}} = -21.10 \text{ kJ/g}
\]

(c) Enthalpy conversion from methane to methanol: The diagram indicates that the difference in enthalpy for these two substances is the difference between the two “top boxes”.

Hence \(\Delta H = -955.1 \text{ kJ} - (-676.1 \text{ kJ}) = -279 \text{ kJ/mol}\)

(d) The equation for conversion of methane to methanol: \(\text{CH}_4(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})\)

107. (a) Piece of metal to heat? To cool to achieve a maximum T? Final temperature of water?

To convey maximum heat per gram, one needs a metal with the greatest specific heat—so of these 3 metals, Al, is the best candidate, and the larger piece of metal (1) would convey MORE heat than the smaller piece (2) of Al. To minimize the heat absorbed by the “cooler” metal, one needs a metal with the lesser specific heat—and the smaller the better—so the smaller piece of Au (4) is a prime candidate. As to final T:

Heat loss (by warm metal) = Heat gain (by cool metal and water)

Note that the SIGNS of the two will be opposite, so let’s (arbitrarily) place a (-) sign in front of the “heat loss” side.

\[-(100.0 \text{ g})(0.9002 \text{ J/g•K})(T_f - 373) = \]
\[-(50.0 \text{ g})(0.1289 \text{ J/g•K})(T_f - 263) + (300.0 \text{ g})(4.184 \text{ J/g•K})(T_f - 294)\]
\[-90.02T_f + 33577 = 6.445T_f - 1695.035 + 1255.2T_f - 369028.8\]

Collecting \(T_f\) terms:
\[-90.02T_f + 6.445T_f + 1255.2T_f = -1351.665 T_f = -404300.835\] and a \(T_f = 299.1\text{K}\) or \(299 - 273 = 26^\circ\text{C}\)
(b) Process is similar to that in (a) but we want minimal $T$ change:
Consider the following table of data and calculations:

<table>
<thead>
<tr>
<th>Specific heat</th>
<th>Mass</th>
<th>Heat Capacity</th>
<th>Metal</th>
<th>$\Delta T$ for metal heated to 100°C</th>
<th>$\Delta T$ for metal cooled to 0°C</th>
<th>Heat lost upon cooling to 21°C</th>
<th>Heat gained upon warming to 21°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9002</td>
<td>50.0</td>
<td>45.0</td>
<td>Al</td>
<td>79</td>
<td>31</td>
<td>3555.79</td>
<td>1395.31</td>
</tr>
<tr>
<td>0.3860</td>
<td>50.0</td>
<td>19.3</td>
<td>Zn</td>
<td>79</td>
<td>31</td>
<td>1524.7</td>
<td>598.3</td>
</tr>
</tbody>
</table>

Note that the amount of heat lost by cooling 50.0g Zn and the heat gained by warming 50.0g of Al is approximately equal. Obviously you could do these calculations for all the combinations of metals (both type and mass). Let’s see how these two compute!

- Heat lost = Heat gained

\[-(50.0 \text{ g})(0.3860 \text{ J/g}\cdot\text{K})(T_f - 373) = \]
\[-(50.0 \text{ g})(0.9002 \text{ J/g}\cdot\text{K})(T_f - 263) + (300.0 \text{ g})(4.184 \text{ J/g}\cdot\text{K})(T_f - 294)\]
\[-19.3T_f + 71989 = 45.01T_f + 11837.6 + 1255.2T_f + 369028.8\]
Collecting $T_f$ terms:
\[-19.3T_f + -45.01T_f + -1255.2T_f = -369028.8 + -11837.6 + 71989 \text{ or} \]
\[-1319.54 T_f = -388065.3 \text{ and a } T_f = 294K \text{ or (294 - 273)} = 21°C \]