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:

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

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

$$\frac{170 \text{ kcal}}{1 \text{ serving}} \bullet \frac{1000 \text{ calorie}}{1 \text{ kcal}} \bullet \frac{4.184 \text{ J}}{1 \text{ cal}} \bullet \frac{1 \text{ kJ}}{1000 \text{ J}} = 710 \text{ kJoules/serving}$$

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. $28.1\dfrac{\text{J}}{\text{mol} \bullet \text{K}} \bullet \dfrac{1 \text{ mol}}{200.59 \text{ g}} = 0.140 \dfrac{\text{J}}{\text{g} \bullet \text{K}}$

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

Heat = mass x heat capacity x ΔT

For copper = $(168 \text{ g})(\dfrac{0.385 \text{ J}}{g \bullet K})[25.6°\text{C}-(-12.2)°\text{C}] \bullet \dfrac{1 \text{ K}}{1 \text{ °C}} = 2.44 \times 10^3 \text{ J}$ 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 $_{Fe}$ = (mass)(heat capacity)(ΔT)

$2.25 \times 10^3 \text{ J} = (344 \text{ g})(0.449 \dfrac{\text{J}}{\text{g} \bullet \text{K}})(x)$ and solving for x we get:

14.57 K = x and since 1K = 1°C, ΔT = 14.57 °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_{copper} = $-q_{water}$

Using the heat capacities of H_2O and copper, and expressing the temperatures in Kelvin (K = °C + 273.15) we can write:

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

Simplifying each side gives:

$$17.52 \frac{J}{K} \bullet T_{final} - 6533 \text{ J} = -636.0 \frac{J}{K} \bullet T_{final} + 185,480 \text{ J}$$

$$653.52 \frac{J}{K} \bullet T_{final} = 192013 \text{ J}$$

$$T_{final} = 293.81 \text{ K or } (293.81 - 273.15) \text{ or } 20.7 \text{ °C}$$

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_{water} (at 95 °C) = $-q_{water}$ (at 22 °C)

$$(85.2 \text{ g})(4.184 \frac{J}{g \bullet K})(T_{final} - 368.15 \text{ K}) = -(156 \text{ g})(4.184 \frac{J}{g \bullet K})(T_{final} - 295.15 \text{ K}) \text{ or}$$

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

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

rearranging: 241.2 J/K • T_{final} = 77409.78 J so 321.0 K = T_{final} or 47.8 °C

17. Here the warmer Zn is losing heat to the water: 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: $\Delta T = T_{final} - T_{initial} = (27.1 - 98.8)$ or -71.7°C or –71.7 K.

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

$$(13.8 \text{ g})(C_{metal})(-71.7 \text{ K}) = -(45.0 \text{ g})(4.184 \frac{J}{g \bullet K})(2.1 \text{ K})$$

$$- 989.46 \text{ g} \bullet \text{K}(C_{metal}) = - 395 \text{ J}$$

$$C_{metal} = 0.40 \frac{J}{g \cdot K} \text{ (to 2 significant figures)}$$

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: $1000 \text{ g ice} \cdot \frac{333 \text{ J}}{1.000 \text{ g ice}} = 333. \times 10^3 \text{ J or } 330 \text{ kJ (to 2sf)}$

21. Heat required to vaporize (convert liquid to gas) 125 g C_6H_6:

The heat of vaporization of benzene is 30.8 kJ/mol.

Convert mass of benzene to moles of benzene: 125 g • 78.11 g/mol = 1.60 mol
Heat required: 1.60 mol C_6H_6 • 30.8 kJ/mol = 49.3 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 • 13.6 g/mL = 13.6 g Hg   (Recall:1 cm^3 = 1 mL)
1) The energy to cool 13.6 g of Hg from 23.0 °C to liquid at – 38.8 °C is:
     ΔT = (234.35 K - 296.15 K) or - 61.8 K
     $13.6 \text{ g Hg} \cdot 0.140 \frac{J}{g \cdot K} \cdot - 61.8 \text{ K} = -118 \text{ J}$
2) To convert liquid mercury to solid Hg at this temperature:
          - 11.4 J/g • 13.6 g = - 155 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
$q_{mercury} = - q_{surroundings}$ 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 ($\Delta T = 58.29$ 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:

$(2.44 \dfrac{J}{g \cdot K})(1000 \text{ g})(58.29 \text{ K}) = 142{,}227.6 \text{ J}$ (142,000 J to 3 sf)

To boil the ethanol at 78.29 ˚C, we need:

$855 \dfrac{J}{g} \cdot 1000 \text{ g} = 855{,}000 \text{ J}$

The total heat energy needed (in J) is $(142{,}000 + 855{,}000) = 997{,}000$ or 9.97×10^5 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 $\Delta H°$ 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:

$1.25 \text{ g NO} \cdot \dfrac{1 \text{ mol NO}}{30.01 \text{ g NO}} \cdot \dfrac{-114.1 \text{ kJ}}{2 \text{ mol NO}} = -2.38 \text{ kJ}$

29. The combustion of isooctane (IO) is **exothermic**. The molar mass of IO is: 114.2 g/mol.

The heat evolved is:

$1.00 \text{ L of IO} \cdot \dfrac{0.69 \text{ g IO}}{1 \text{mL}} \cdot \dfrac{1 \times 10^3 \text{ mL}}{1 \text{ L}} \cdot \dfrac{1 \text{ mol IO}}{114.2 \text{ g IO}} \cdot \dfrac{-10922 \text{ kJ}}{2 \text{ mol IO}} = -3.3 \times 10^4 \text{ kJ}$

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:

$q = (4.2 \text{ J/g} \cdot \text{K})(150. \text{ g})(24.28 °\text{C} - 22.50°\text{C})$ [and since $1.78°\text{C} = 1.78$ K]

$q = (4.2 \text{ J/g} \cdot \text{K})(150. \text{ g})(1.78 \text{ K})$

$q = 1120 \text{ J}$

The molar enthalpy of neutralization is: $\dfrac{-1120 \text{ J}}{0.0200 \text{ mol CsOH}} = -56000$ 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 : $\Delta T = T_{final} - T_{initial} = (24.3 - 99.5)$ or $- 75.2°C$ or $-75.2K$.

For the water: $\Delta T = T_{final} - T_{initial} = (24.3 - 21.7)$ or $2.6°C$ or 2.6 K (recalling that a Celsius degrees and a Kelvin are the same "size".

$(20.8$ g$)(C_{metal})(-75.2$ K$) = -(75.0$ g$)(4.184 \frac{J}{g \cdot K})(2.6$ K$)$

$- 1564.16$ 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_4NO_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

$(155.4$ g$)(4.2 \frac{J}{g \cdot K})(- 2.4$ K$) = -1566$ J or $–1600$ J(to 2 sf)

Calculate the amount of NH_4NO_3: 5.44 g NH_4NO_3 $\bullet \frac{1 \text{ mol } NH_4NO_3}{80.04 \text{ g } NH_4NO_3} = 0.0680$ mol

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:

Enthalpy of dissolving $= \dfrac{1.566 \text{ kJ}}{0.0680 \text{ mol}} = 23.0$ 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 g $\bullet$ 4.184 $\frac{J}{g \cdot K}$ $\bullet (26.72 - 21.25)°C\bullet$ 1K/1°C $= 18,700$ J

2) Calculate the heat transferred to the bomb calorimeter

923 J/K $\bullet (26.72 - 21.25)°C\bullet$ 1K/1°C $= 5,050.$J

3) Amount of sulfur present: 2.56 g $\bullet \dfrac{1 \text{ mol } S_8}{256.536 \text{ g } S_8} = 0.010$ 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:

$\dfrac{(18,700 \text{ J } + 5,050 \text{ J})}{0.08 \text{ mol } SO_2} = 297,000$ J/mol SO_2 or 297 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:

       $775 \text{ g} \cdot 4.184 \dfrac{\text{J}}{\text{g} \cdot \text{K}} \cdot (31.69 - 22.50\ )\text{°C} \cdot 1\text{K}/1\text{°C} = 29{,}800 \text{ J}$

    2) Calculate the heat transferred to the bomb calorimeter

       $893 \text{ J/K} \cdot (31.69 - 22.50\ )\text{°C} \cdot 1\text{K}/1\text{°C} = 8{,}210 \text{ J}$

    3) Amount of benzoic acid:

       $1.500 \text{ g benzoic acid} \cdot \dfrac{1 \text{ mol benzoic acid}}{122.1 \text{ g benzoic acid}} = 1.229 \times 10^{-2} \text{ mol benzoic acid}$

    4) Heat evolved per mol of benzoic acid is:

       $\dfrac{(29{,}800 \text{ J} + 8{,}210 \text{ J})}{1.229 \times 10^{-2} \text{ mol}} = 3.09 \times 10^{6} \text{ J/mol or } 3.09 \times 10^{3} \text{ kJ/mol}$

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

    Since this energy (1180 J) is released by the metal, we can calculate the heat capacity of the metal: heat   =   heat capacity x mass x ΔT

       -1180 J =   C x 50.0 g x (273.2 K - 373 K) [Note that ΔT is negative!]

    $0.236 \dfrac{\text{J}}{\text{g} \cdot \text{K}}$ =   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)

CH_4 (g) + 2 O_2 (g) $\rightarrow CO_2$ (g) + 2 H_2O (g)	$\Delta H° = -\ 802.4 \text{ kJ}$
CO_2 (g) + 2 H_2O (g) $\rightarrow CH_3OH$(g) + 3/2 O_2 (g)	$\Delta H° = +\ 676 \text{ kJ}$
CH_4 (g) + 1/2 O_2 (g) $\rightarrow CH_3OH$(g)	$\Delta H° = -\ 126 \text{ kJ}$
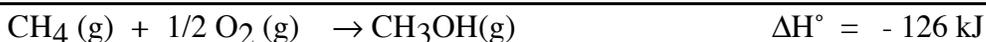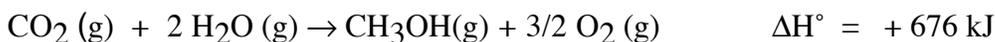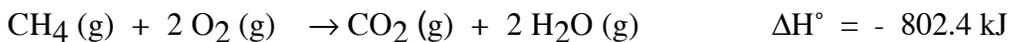
(b) A graphic description of the energy change:

$$CH_4 (g) \ + \ 1/2 \ O_2 (g)$$

$\Delta H° \ = \ - \ 126.4 \ kJ$

$+ \ 3/2 \ O_2 (g)$

$CH_3 OH(g)$

$\Delta H° \ = \ - \ 802.4 \ kJ$

$\Delta H° \ = \ + \ 676 \ kJ$

$$CO_2(g) \ + \ 2 \ H_2O \ (\ell)$$
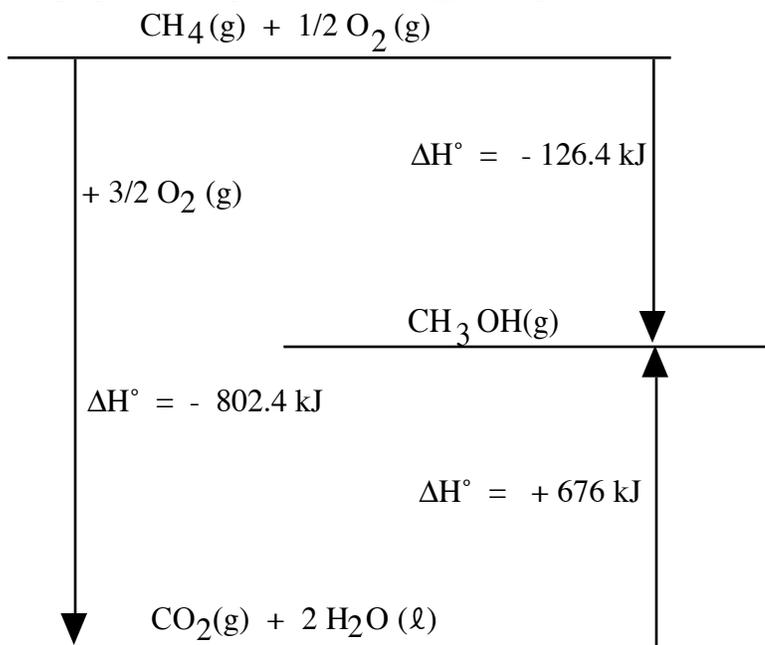
45. The overall enthalpy change for $1/2 \ N_2 (g) + 1/2 \ O_2 (g) \rightarrow NO \ (g)$

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:

$2 \ N_2 (g) + 6 \ H_2 (g) \rightarrow 4 \ NH_3 (g)$ $\quad\quad\quad\quad\quad \Delta H \ = (2)(- 91.8 \ kJ)$

The second equation has NO on the right side :

$4 \ NH_3 (g) + \ 5 \ O_2 (g) \rightarrow 4 \ NO(g) \ + \ 6 \ H_2O \ (g)$ $\quad\quad \Delta H \ = \ - \ 906.2kJ$

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

$6 \ H_2O \ (g) \rightarrow 6 \ H_2 (g) + 3 \ O_2 (g)$ $\quad\quad\quad\quad\quad \Delta H \ = \ (+241.8)(6) \ kJ$

Adding these 3 equations gives

$2 \ N_2 (g) + \ 2 \ O_2 (g) \rightarrow 4 \ NO(g)$ $\quad\quad\quad\quad\quad \Delta H \ = 361 \ kJ$

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

a $\Delta H \ = \ +361 \bullet 0.25 \ kJ$ or $90.3 \ kJ$

Standard Enthalpies of Formation

47. The equation requested requires that we form **one** mol of product liquid CH_3OH from its elements—each in their standard state.

Begin by writing a balanced equation:

$2 \ C \ (s,graphite) \ + \ O_2(g) + 4 \ H_2(g) \rightarrow \ 2 \ CH_3OH(l)$
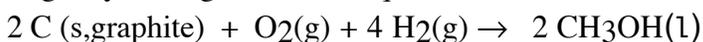
Now express the reaction so that you form one mole of CH3OH—divide coefficients by 2.

C (s) + 1/2 O2(g) + 2 H2(g) →   CH3OH(l)

And from Appendix L, the $\Delta_fH°$ is reported as –238.4 kJ/mol

49. (a) The equation of the formation of Cr2O3 (s) from the elements:

   2 Cr (s) + 3/2 O2 (g) → Cr2O3 (s)
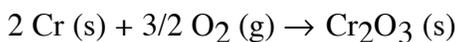
   from Appendix L $\Delta_fH°$ is reported as: -1134.7 kJ/mol for the oxide.

   (b) The enthalpy change if 2.4 g of Cr is oxidized to Cr2O3 (g) is:

   $2.4 \text{ g Cr} \cdot \dfrac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \cdot \dfrac{-1134.7 \text{ kJ}}{2 \text{ mol Cr}} = -26 \text{ kJ}$ (to 2 sf)

51. Calculate $\Delta_rH°$ for the following processes:

   (a) 1.0 g of white phosphorus burns:

   P4 (s) + 5 O2 (g) → P4O10 (s) from Appendix L: $\Delta_fH°$ -2984.0 kJ/mol
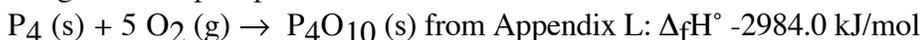
   $1.0 \text{ g P}_4 \cdot \dfrac{1.0 \text{ mol P}_4}{123.89 \text{ g P}_4} \cdot \dfrac{-2984.0 \text{ kJ}}{1 \text{ mol P}_4} = -24 \text{ kJ}$

   (b) 0.20 mol NO (g) decomposes to N2 (g) and O2 (g):

   From Appendix L: $\Delta_fH°$ for NO = 90.29 kJ/mol

   Since the reaction requested is the **reverse** of $\Delta_fH°$, we change the sign to – 90.29 kJ/mol.

   The enthalpy change is then $\dfrac{-90.29 \text{ kJ}}{1 \text{ mol}} \cdot 0.20 \text{ mol} = -18 \text{ kJ}$

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

   From Appendix L: $\Delta_fH°$ for NaCl (s) = - 411.12 kJ/mol

   The amount of NaCl is: $2.40 \text{ g NaCl} \cdot \dfrac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.0411 \text{ mol}$

   The overall energy change is: -411.12 kJ/mol • 0.0411 mol = - 16.9 kJ

   (d) 250 g of Fe oxidized to Fe2O3 (s):

   From Appendix L: $\Delta_fH°$ for Fe2O3 (s) = - 824.2 kJ/mol

   The overall energy change is:

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

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

	4 NH3(g) +	5 O2(g)	→	4 NO(g) +	6 H2O(g)
$\Delta_f H°$ (kJ/mol)	-45.90	0		+90.29	-241.83
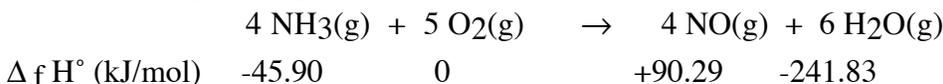
$\Delta _rH° = [(4 \text{ mol})(+90.29 \frac{kJ}{mol}) + (6 \text{ mol})(-241.83 \frac{kJ}{mol})] -$

$$[(4 \text{ mol})(-45.90 \frac{kJ}{mol}) + (5 \text{ mol})(0)]$$

= (-1089.82 kJ) - (-183.6 kJ)

= -906.2 kJ   **The reaction is exothermic.**

(b) Heat **evolved** when 10.0 g NH_3 react:

The balanced equation shows that 4 mol NH_3 result in the release of 906.2 kJ.

$$10.0 \text{ g } NH_3 \bullet \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} \bullet \frac{-906.2 \text{ kJ}}{4 \text{ mol } NH_3} = \text{ -133 kJ}$$

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

$2 BaO_2 (s)$ $\rightarrow$ $2 BaO (s) + O_2 (g)$

Given $\Delta _f H°$ for BaO is: - 553.5 kJ/mol and $\Delta _f H°$ for BaO_2 is: -634.3 kJ/mol

This equation can be seen as the summation of the two equations:

(1) $2 Ba (s) + O_2 (g) \rightarrow 2 BaO (s)$

(2) $2 \underline{BaO_2 (s) \rightarrow 2 Ba (s) + O_2 (g)}$
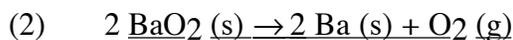
Equation (1) corresponds to the formation of BaO x 2 while equation(2) corresponds to (2x) the **reverse** of the formation of BaO_2

$$\Delta _rH° = (2\Delta _fH° \text{ for BaO}) + -2(\Delta _fH° \text{ for } BaO_2) =$$

$\Delta _rH°$ = 161.6 kJ and the reaction is **endothermic**.

(b) Energy level diagram for the equations in question:

Ba (s) + 1/2 O_2 (g)   Ba (s) + O_2 (g)

$\Delta H°$ = - 553.5 kJ $\Delta H°$ = - 634.3 kJ

▼BaO (s)   + 1/2 O_2(g)

$\Delta H°$rxn = + 80.8 kJ

BaO_2(s)▼
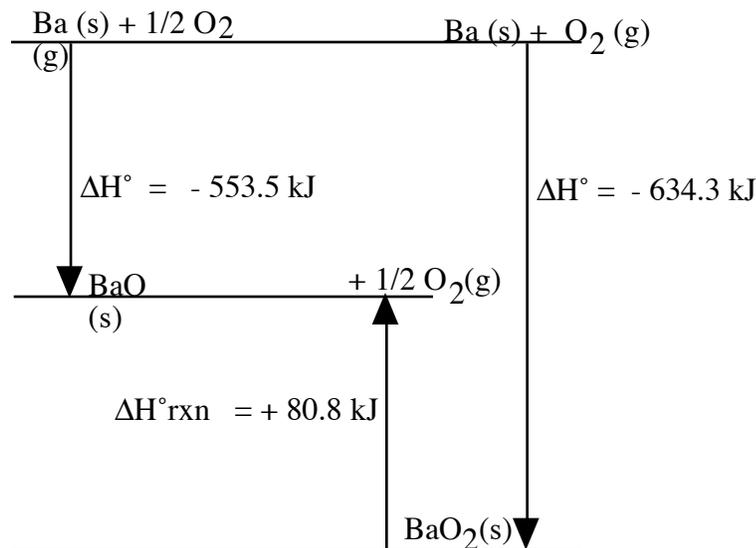
57. The molar enthalpy of formation of naphthalene can be calculated since we're given the
enthalpic change for the reaction:

$$C_{10}H_8 \text{ (s)} + 12\ O_2(g) \rightarrow 10\ CO_2(g) + 4\ H_2O(\ell)$$

$\Delta H°_f$(kJ/mol)   **?**   0   -393.509   -285.83
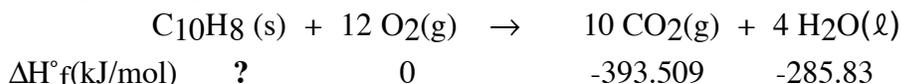
$\Delta H°_{rxn}$ $= \sum \Delta H°_f$ products $- \sum \Delta H°_f$ reactants

-5156.1 kJ $= [(10\ mol)(-393.509\ \frac{kJ}{mol}) + (4\ mol)(-285.83\ \frac{kJ}{mol})] - [\Delta H°_f\ C_{10}H_8]$

-5156.1 kJ $= (-5078.41\ kJ) - \Delta H°_f\ C_{10}H_8$

- 77.7 kJ $= -\Delta H°_f\ C_{10}H_8$

77.7 kJ $= \Delta H°_f\ C_{10}H_8$

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
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, ΔH.

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 (N_2) = 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), O_2 (g), O_3 (g).

Substance	$\Delta_f H$ (at 298K) kJ/mol
O(g)	249.170
O_2 (g)	0
O_3 (g)	142.67

What is the standard state of O_2? The standard state of oxygen (O_2) is as a gas.

Is the formation of O from O_2 exothermic?

$\Delta_r H = \Sigma \Delta_f H_{products} - \Sigma \Delta_f H_{reactants}$ ($O_2 \rightarrow 2O$)

$\Delta_r H = (2\,mol)(249.170) - (1\,mol)(0) = 498.340$ kJ (endothermic)

What is the ΔH for 3/2 O_2(g) $\rightarrow O_3$ (g)

$\Delta_r H = \Sigma \Delta_f H_{products} - \Sigma \Delta_f H_{reactants}$

$\Delta_r H = (1\,mol)(142.67\ kJ/mol) - (3/2\,mol)(0) = 142.67$ kJ

65. To calculate the formation of $SnCl_4(\ell)$ and $TiBr_2(s)$ from $SnBr_2(s) + TiCl_4(\ell)$ we can use Hess' Law to add a series of appropriate equations. A screen capture from the CD-ROM shows the overall process:

Reactions   **ΔH° (kJ)**

Select a reaction by clicking and dragging the reaction into one of the spaces below.

1. $SnCl_2(s) + TiBr_2(s) \longrightarrow SnBr_2(s) + TiCl_2(s)$ +4.2
2. $SnCl_2(s) + Cl_2(g) \longrightarrow SnCl_4(\ell)$ -195
3. $TiCl_2(s) + Cl_2(g) \longrightarrow TiCl_4(\ell)$ -273

                                                                              ΔH° (kJ)

Clear	Reverse	$SnBr_2(s) + TiCl_2(s) \longrightarrow SnCl_2(s) + TiBr_2(s)$	-4.2
Clear	Reverse	$SnCl_2(s) + Cl_2(g) \longrightarrow SnCl_4(\ell)$	-195
Clear	Reverse	$TiCl_4(\ell) \longrightarrow TiCl_2(s) + Cl_2(g)$	+273

Net Reaction: $SnBr_2(s) + TiCl_4(\ell) \longrightarrow$ $\Delta H^\circ_{net} = 73.8$ kJ

$TiBr_2(s) + SnCl_4(\ell)$

Given the integral values for "Reaction 2", $\Delta H^\circ = 74$ 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 $q = m \cdot c \cdot \Delta t$; so 187 J = 93.45 g • c • (27.0 – 18.5)°C. and

$$C_{Ag} = \frac{187 \text{ J}}{93.45 \text{ g} \bullet (27.0 - 18.5)°C} = 0.24 \text{ J/g} \bullet K$$

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 $q_{water} = -q_{ice}$

The melting of ice can be expressed with the heat of fusion of ice, 333 J/g, as $q = m \bullet 333$ J/g. The cooling of the water may be expressed: $q = m \bullet c \bullet \Delta T$. Setting these quantities equal gives:

$m \bullet c \bullet \Delta T = m \bullet 333$ J/g or 100.0 g • (4.184 J/g •K) • (0 – 60)K = -x g • 333 J/g

[x = quantity of ice that melts. Note that since Celsius degrees and kelvin are the same "size", Δt is –60°C or –60 K]

100.0 g • (4.184 J/g •K) • (0 – 60)K = -x • 333 J/g

- 25104 J = - x • 333 J/g or $\dfrac{-25104 \text{ J}}{- 333 \text{ J/g}}$ = x or 75.4 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_{water} = -q_{ice} and we can set up the expression.

$m \bullet c \bullet \Delta T$ = - m • 333 J/g 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:
$m_{tea} \bullet c \bullet \Delta T_{tea}$ = - [$m_{ice} \bullet$ 333 J/g + $m_{ice} \bullet c \bullet \Delta T_{ice}$]

500. g • (4.184 J/g•K) • (F – 293.2 K) = -[(90 g • 333 J/g) +

(90 g •(4.184 J/g•K) • (F -273.2 K))]
where F is the final temperature of the tea and melted ice.

2092F 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 $\Delta H°_f$. The definition is the

enthalpy change associated with the formation of **one mole** of the substance (in this case
B_2H_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 B (s) + 3/2 O_2 (g) → B_2O_3 (s) $\Delta H°$ = 1/2(-2543.8 kJ) = -1271.9 kJ

The formation of 1 mole of B_2H_6 will require the use of 6 moles of H (or 3 moles of H_2),

so multiply the second equation by 3 to give:
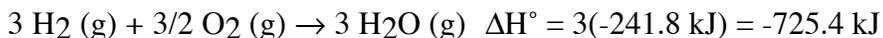
3 H_2 (g) + 3/2 O_2 (g) → 3 H_2O (g) $\Delta H°$ = 3(-241.8 kJ) = -725.4 kJ
Finally the third equation given has B_2H_6 as a **reactant and not a product**. So reverse
the third equation to give:

 B_2O_3 (s) + 3 H_2O (g) → B_2H_6 (g) + 3 O_2 (g) $\Delta H°$ = -(-2032.9 kJ)= +2032.9kJ
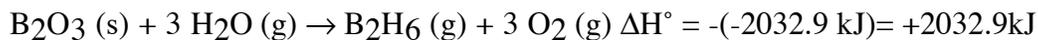
(b) Adding the three equations gives the equation:

2 B (s) +3 H_2 (g) → B_2H_6 (g) with a $\Delta H°$ = (-1271.9 + -725.4 + 2032.9)kJ
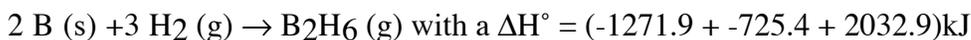
or a $\Delta H°$ for B_2H_6 (g) of + 35.6 kJ

(c) Energy level diagram for the reactions:

B_2H_6(g)

$\Delta H° = + 35.6$ kJ

2 B (s) $+ 3\, H_2$ (g)

$- 3\, O_2$(g)

$\Delta H° = +2032.9$kJ

$+ 3/2\, O_2$ (g)

$+ 3/2\, O_2$ (g)

$\Delta H° = -1271.9$ kJ $\Delta H° = -725.4$ kJ

B_2O_3 (s)   + $3\, H_2O$ (g) B_2O_3 (s) $+ 3\, H_2O$ (g)
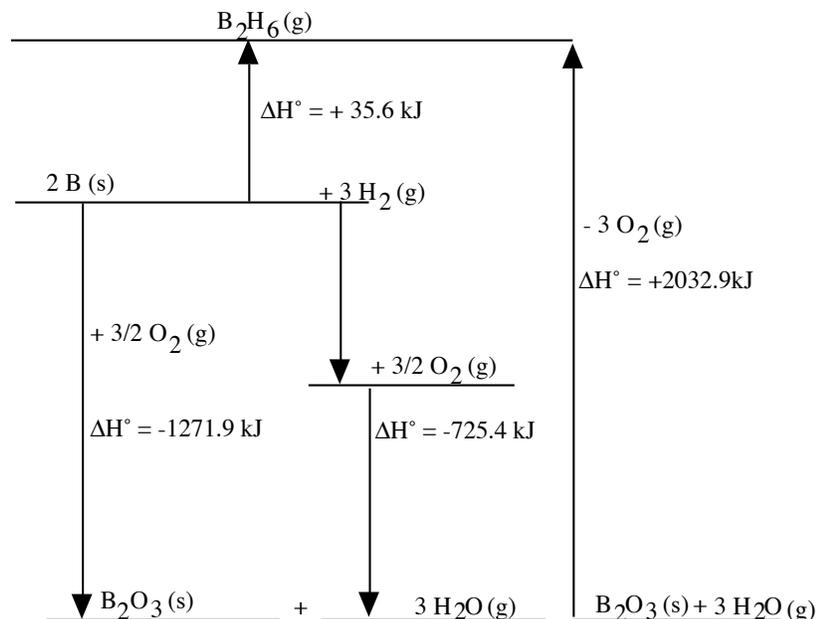
(d) Formation of B_2H_6 (g) is **reactant-favored**

75. (a) Enthalpy change for:

$$C(s) +\quad H_2O(g) \quad\rightarrow\quad CO(g) +\quad H_2(g)$$

$\Delta H°_f$(kJ/mol)   0   -241.83   -110.525   0
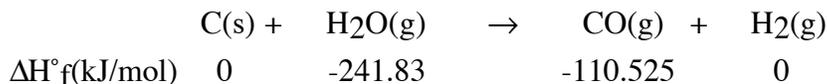
$$\Delta H°_{rxn} = [(1\ mol)(-110.525\ \tfrac{kJ}{mol}) + 0] - [\,0\ +\ (1\ mol)(-241.83\ \tfrac{kJ}{mol})]$$

$$= +131.31\ kJ$$

(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:

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

77. For the combustion of C_8H_{18}:

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(l)$$
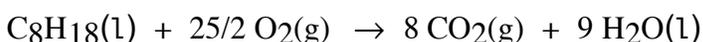
$$\Delta_r H° = [(8\ mol)(-393.509\ \tfrac{kJ}{mol}) + (9\ mol)(-285.83\ \tfrac{kJ}{mol})] - [(1\ mol)(-259.2\ \tfrac{kJ}{mol}) + 0]$$

$$\Delta_r H° = -5461.3\ kJ$$

Expressed on a gram basis: $-5461.3\ \dfrac{kJ}{mol} \bullet \dfrac{1\ mol\ C_8H_{18}}{114.2\ g\ C_8H_{18}} = -47.81\ kJ/g$

For the combustion of CH_3OH:

$$2\ CH_3OH(l) + 3\ O_2\ (g) \rightarrow 2\,CO_2\ (g) + 4\ H_2O(l)$$
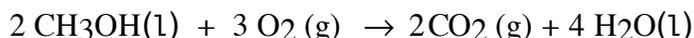
$\Delta_r H° = [(2\,mol)(-393.509\ kJ/mol) + (4\ mol)(-285.83\ kJ/mol)]$

$- [(2\,mol)(-238.4\ kJ/mol) + 0]$

$$= [(- 787.0) + (- 967.2)] + 477.4 \text{ kJ}$$

$$= - 1453.5 \text{ kJ or } -726.77 \text{ kJ/mol}$$

Express this on a per mol and per gram basis:

$$\frac{-1453.5 \text{ kJ}}{2 \text{ mol CH}_3\text{OH}} \bullet \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} = - 22.682 \text{ kJ/g}$$

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
        Sr (s) + C (graphite) + 3/2 O2 (g) → SrCO3 (s) using the data:

Sr(s) + 1/2 O2 (g) →SrO(s)	$\Delta_f H° = -592$ kJ/mol-rxn
SrO(s) + CO2 (g) →SrCO3 (s)	$\Delta_r H° = -234$ kJ/mol-rxn
C (graphite) + O2 (g) →CO2 (g)	$\Delta_f H° = -394$ kJ/mol-rxn
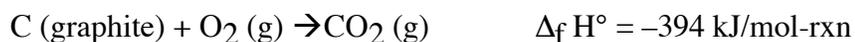
Let's add the equations to give our desired overall equation.

Sr(s) + 1/2 O2 (g) → SrO(s)	$\Delta_f H° = -592$ kJ/mol-rxn
S̶r̶O̶(s) + C̶O̶2̶(g) → S̶rCO3 (s)	$\Delta_r H° = -234$ kJ/mol-rxn
C (graphite) + O2 (g) → C̶O̶2 (g)	$\Delta_f H° = -394$ kJ/mol-rxn
Sr (s) + C (graphite) + 3/2 O2 (g) → SrCO3 (s)	$\Delta_r H° = -1220.$ kJ/mol-rxn
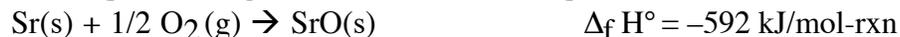
(b) Energy diagram relating the energy quantities:

Sr (s) + 1/2O2 (g) + C (graphite) + O2 (g)

ΔH°f = –394 kJ

ΔH°f = –592 kJ   CO2

SrO (s)

ΔH°rxn = –234 kJ

ΔH°rxn = –1220. kJ

SrCO3 (s)
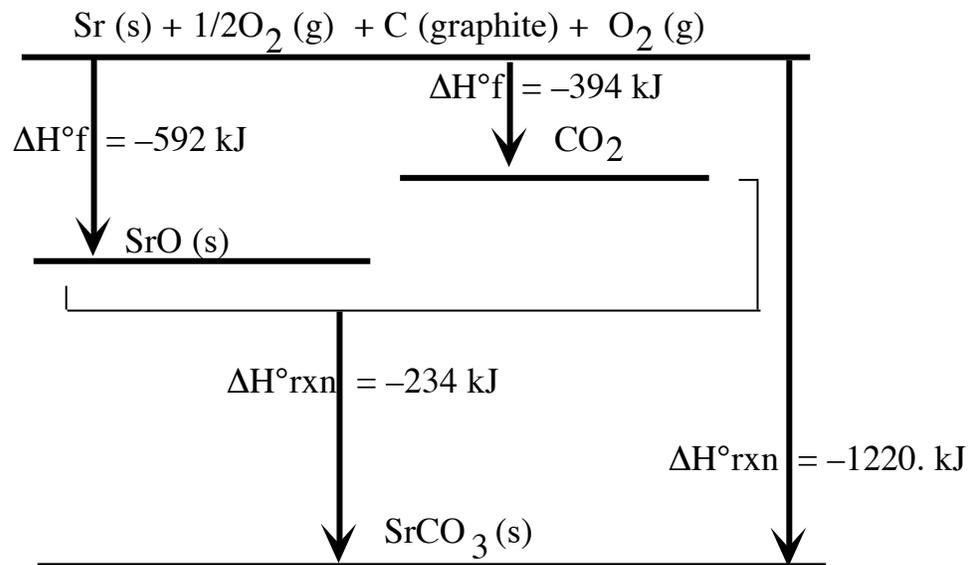
81. The desired equation is: CH_4 (g) + 3 Cl_2 (g) → 3 HCl (g) + $CHCl_3$ (g)

Begin with equation 1 (the combustion of methane)

CH_4 (g) + 2 O_2 (g) → 2 H_2O (l) + CO_2 (g)   ΔH= -890.4 kJ = -890.4 kJ/mol-rxn
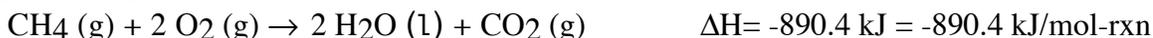
Noting that we form HCl as one of the products, using the second equation, we need to **reverse** it and (to adjust the coefficient of HCl to 3), multiply by 3/2 to give:

3/2 H_2 (g) + 3/2 Cl_2 (g) → 3 HCl   ΔH = -3/2(+184.6) kJ/mol-rxn = - 276.9 kJ

Note that CO_2 formed in equation 1 doesn't appear in the overall equation so let's use the equation for the formation of CO_2 (reversed) to "consume" the CO_2:

CO_2 (g) → C (graphite) + O_2 (g)   ΔH = -1(-393.5) kJ = + 393.5 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 H_2O (l) → 2 H_2 (g) + O_2 (g)   ΔH = -2(-285.8) kJ = + 571.6 kJ

and finally we need to produce $CHCl_3$ which we can do with the equation that represents the $ΔH_f$ for $CHCl_3$:

C(graphite) + 1/2 H_2 (g) + 3/2 Cl_2 (g) → $CHCl_3$ (g)   ΔH = -103.1 kJ
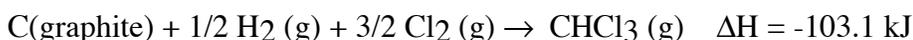
The overall enthalpy change would then be:

ΔH = -890.4 kJ - 276.9 kJ + 393.5 kJ + 571.6 kJ -103.1 kJ = -305.3 kJ

IN THE LABORATORY

83. q_{metal} = heat capacity x mass x ΔT

q_{metal} = C_{metal} • 27.3 g • (299.47 K - 372.05 K)

Note that ΔT is negative, since T_{final} of the metal is LESS THAN $T_{initial}$

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

Setting q_{metal} = - q_{water}

C_{metal} • 27.3 g • (-72.58 K) = - 239.7 J and solving for C gives:

$C_{metal} = 0.121 \dfrac{J}{g \cdot K}$

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

1) How much AgCl is being formed?

250. mL of 0.16 M $AgNO_3$ will contain (0.250L • 0.16 mol/L) 0.040 mol of $AgNO_3$

125 mL of 0.32 M NaCl will contain (0.125L • 0.32 mol/L) 0.040 mol of NaCl.

Given the stoichiometry of the process, we anticipate the formation of 0.040 mol of AgCl.

2) How much energy is evolved?

[(250 +125ml) • 1g/mL = 375g of water

$375 \text{ g} \bullet 4.2 \dfrac{J}{g \bullet K} \bullet (296.05 \text{ K} - 294.30) \text{ K} = 2{,}800 \text{ J (to 2 sf)}$

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

The change in kJ/mol is $\dfrac{2800 \text{ J}}{0.040 \text{ mol}} \bullet \dfrac{1 \text{ kJ}}{1000 \text{ J}} = -69 \text{ kJ/mol}$

87. Heat evolved when ammonium nitrate is decomposed:

$\Delta T = (20.72\text{-}18.90) = 1.82 \text{ °C (or 1.82 K)}$.

Heat absorbed by the calorimeter: $155 \text{ J/K} \bullet 1.82\text{K} = 282 \text{ J}$

Heat absorbed by the water: $415 \text{ g} \bullet 4.18 \dfrac{J}{g \bullet K} \bullet 1.82 \text{ K} = 3160 \text{ J}$

Total heat **released** by the decomposition: $3160 \text{ J} + 282 \text{ J} = 3{,}440 \text{ J (to 3 sf)}$

With 7.647 g $NH_4NO_3 = 0.09554$ mol, heat released $= \dfrac{3440 \text{ J}}{0.09554 \text{ mol}} = 36.0 \text{ kJ/mol}$

89. The enthalpy change for the reaction:

$$Mg(s) + 2\ H_2O(l) \quad \rightarrow \quad Mg(OH)_2\ (s) + H_2(g)$$

$\Delta_fH°$ (kJ/mol) 0   -285.83   -924.54   0
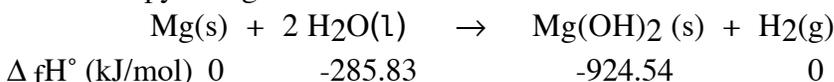
$\Delta_rH° \quad = (1 \text{ mol})(\text{-}924.54\ \tfrac{kJ}{mol}) - (2 \text{ mol})(\text{-}285.83\ \tfrac{kJ}{mol})$

$\qquad\qquad = \text{-}352.88 \text{ kJ or } \text{-}3.5288 \times 10^5 \text{ J}$

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.

heat   = heat capacity x mass x ΔT

$\qquad = (4.184\ \tfrac{kJ}{mol})(25 \text{ mL})(\tfrac{1.00 \text{ g}}{1 \text{ mL}})(60 \text{ K})$

$\qquad = 6276 \text{ or } 6300 \text{ J} \quad \text{or } 6.3 \text{ kJ (to 2 sf)}$

Magnesium required:

$6.3 \text{ kJ} \bullet \dfrac{1 \text{ mol Mg}}{352.88 \text{ kJ}} \bullet \dfrac{24.3 \text{ g Mg}}{1 \text{mol Mg}} = 0.43 \text{ g Mg}$

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 ΔH for the reaction:
$$Ca(s) + 1/8\ S_8\ (s) + 2\ O_2(g) \rightarrow CaSO_4(s)$$
   Imagine this as the sum of several processes:
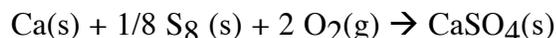
   1) $Ca(s) + 1/2\ O_2(g) \rightarrow CaO(s)$
   2) $1/8\ S_8\ (s) + 3/2\ O_2(g) \rightarrow SO_3(g)$
   3) $CaO(s) + SO_3(g) \rightarrow CaSO_4(s)$ $\Delta H = -402.7\ kJ$

   Note that the SUM of the three processes is the DESIRED equation (the formation of $CaSO_4(s)$). The OVERALL ΔH is then the SUM of the ΔH for process (1) and ΔH for process (2). We know that the $\Delta_r H°$ for (3) = -402.7 kJ or

   $\Delta_r H° = \Delta_f H° \ CaSO_4(s) – [\Delta \ _f H° \ CaO(s) + \Delta \ _f H° \ SO_3(g)]$. Since we know the $\Delta_r H°$ and

   BOTH the $\Delta_f H°$ for $CaO(s)$ and $SO_3(g)$, we can calculate the $\Delta_f H° \ CaSO_4(s)$.

   From Appendix L we find,

   $\Delta_f H°$ for $CaO(s) = -635.09$ kJ/mol and $\Delta_f H°$ for $SO_3(g) = - 395.77$ kJ/mol

   $\Delta_r H° = \Delta_f H° \ CaSO_4(s) – [\Delta_f H° \ CaO(s) + \Delta_f H° \ SO_3(g)]$

   $- 402.7\ kJ = \Delta_f H° \ CaSO_4(s) – [-635.09\ kJ/mol + - 395.77\ kJ/mol]$

   $- 1,433.6\ kJ = \Delta_f H° \ CaSO_4(s)$

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

$$0.897\ \frac{J}{g \bullet K} \quad \bullet \quad \frac{26.98\ g\ Al}{1\ mol\ Al} = 24.2\ \frac{J}{mol \bullet K}$$

$$0.449\ \frac{J}{g \bullet K} \quad \bullet \quad \frac{55.85\ gFe}{1\ mol\ Fe} = 25.1\ \frac{J}{mol \bullet K}$$

$$0.385\ \frac{J}{g \bullet K} \quad \bullet \quad \frac{63.55\ g\ Cu}{1\ mol\ Cu} = 24.5\ \frac{J}{mol \bullet K}$$

$$0.129\ \frac{J}{g \bullet K} \quad \bullet \quad \frac{197.0\ g\ Au}{1\ mol\ Au} = 25.4\ \frac{J}{mol \bullet K}$$
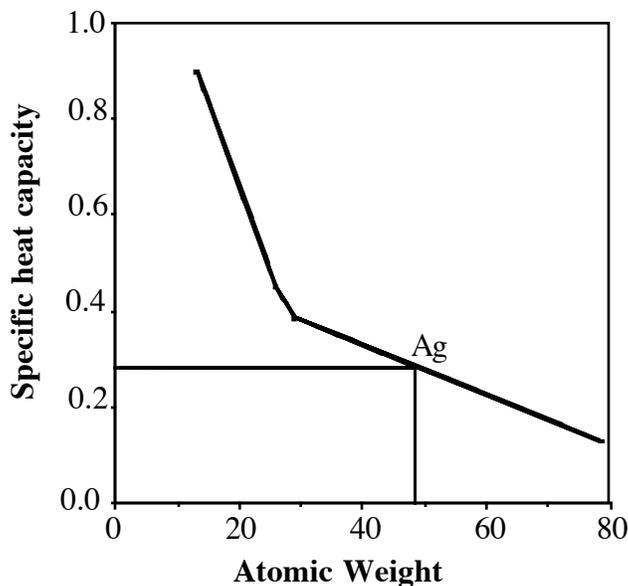
Atomic Weight

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:

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

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:

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

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

$$2.90 \ x \ 10^4 \ mol \ air \bullet \ 29.1 \frac{J}{mol \ \bullet \ K} \ \bullet \ 7.0 \ K \ = \ 5.9 \ x \ 10^6 \ J$$

What quantity of energy does the combustion of methane provide?
The reaction may be written: $CH_4 \ (g) + 2 \ O_2 \ (g) \rightarrow 2 \ H_2O \ (g) + CO_2 \ (g)$

Using data from Appendix L:

$\Delta_r H = [(2 \text{ mol})(-241.83 \text{ kJ/mol}) + (1 \text{mol})(-393.509 \text{ kJ/mol})]$

$- [(1 \text{ mol})(-74.87 \text{ kJ/mol}) + (2 \text{ mol})(0)] = -802.3 \text{ kJ}$

The amount of methane necessary is:

$$5.9 \times 10^6 \text{ J} \bullet \frac{1 \text{ kJ}}{1000 \text{ J}} \bullet \frac{1 \text{ mol CH}_4}{802.3 \text{ kJ}} \bullet \frac{16.0 \text{ g CH}_4}{1 \text{ mol CH}_4} = 120 \text{ g CH}_4 \text{ (2 sf)}$$

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 1mi^2 in cm^2

[1 km = 0.62137 mi and 1 km = 10^5 cm.]

$$\frac{1 \text{ mi}^2}{1} \bullet \frac{(1 \text{ km})^2}{(0.62137 \text{ mi})^2} \bullet \frac{(10^5 \text{ cm})^2}{(1 \text{ km})^2} = \frac{10^{10} \text{cm}^2}{0.38610} = 2.59 \times 10^{10} \text{ cm}^2$$

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

The mass of water is: 6.6 x 10^{10} cm^3 x 1.0 g/cm^3 or 6.6 x 10^{10} g of water.

The amount of heat: $\dfrac{6.6 \times 10^{10} \text{g water}}{1} \bullet \dfrac{1 \text{ mol water}}{18.02 \text{ g water}} \bullet \dfrac{44.0 \text{ kJ}}{1 \text{ mol water}} = 1.6 \times 10^{11} \text{ kJ}$

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

101. (a) The diagram is:
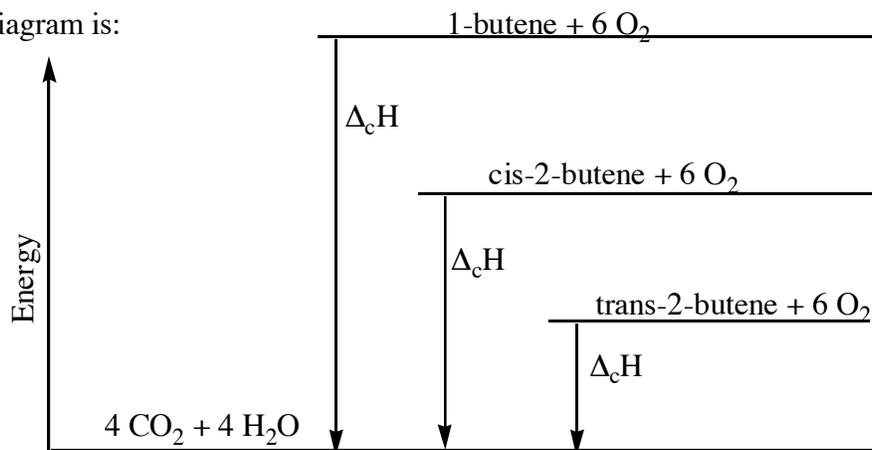
(b) For the combustion reaction: $C_4H_8(g) + 6 O_2(g) \rightarrow 4 CO_2(g) + 4 H_2O(g)$

$\Delta_c H° = 4 \bullet \Delta_f H° (CO_2) + 4 \bullet \Delta_f H° (H_2O) - \Delta_f H° (C_4H_8) + 6 \bullet \Delta_f H°(O_2)$ Note that the last term will be 0 in all cases. Substitute the thermodynamic data for each of the three isomers:

cis-2-butene:

$\Delta_c H° = 4•\Delta_f H° (CO_2) + 4•\Delta_f H°(H_2O) - \Delta_f H°(C_4H_8)$

1 mol • -2687.5kJ/mol =

   4 mol • -393.509kJ/mol+ 4 mol • -241.83 kJmol – 1 mol • $\Delta_f H°(C_4H_8)$ = 146.1 kJ

trans-2-butene:

1 mol • -2684.2kJ/mol =

   4 mol • -393.509kJ/mol+ 4 mol • -241.83 kJmol – 1 mol • $\Delta_f H°(C_4H_8)$ = 142.8 kJ

1-butene:

1 mol • -2696.7kJ/mol =

   4 mol • -393.509kJ/mol+ 4 mol • -241.83 kJmol – 1 mol • $\Delta_f H°(C_4H_8)$ = 155.3 kJ

(c)Relation of Enthalpies of Isomers to the elements:
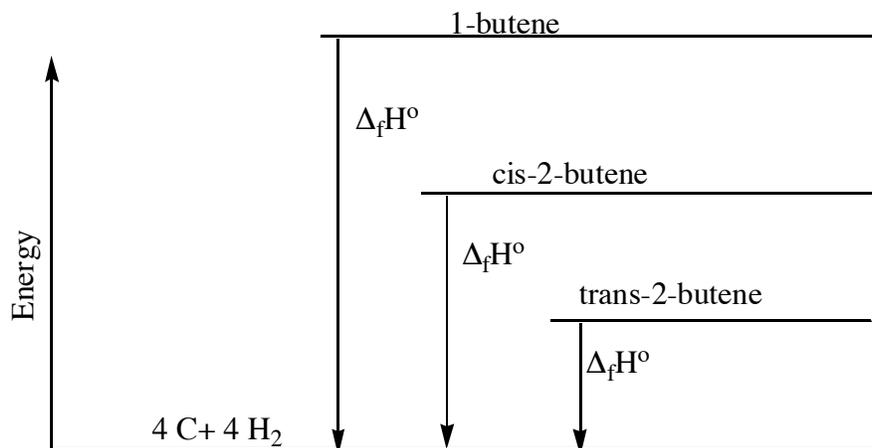
   (d)Enthalpy change of cis-2-butene to trans-2-butene:

   $\Delta_r H° = \Delta_f H°$ (trans-2-butene) - $\Delta_f H°$(cis-2-butene) = 142.8 kJ-146.1 kJ = -3.3 kJ

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

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

        kJ/mol

   (b) Final temperature of water and bomb calorimeter:

        Heat evolved = - Heat absorbed

        -25400 J = -(820 J/K)ΔT + (750.g)(4.184 J/g•K)ΔT

        -25400 J = -(820 J/K)ΔT + (3138 J/K)ΔT and –25400 J = -3958 J/K ΔT

        -25400 J/-3958 J/K = 6.41 K   (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.
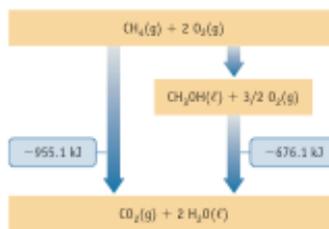
   (b) Energy per gram:

   For methane: $\dfrac{-955.1 \text{ kJ}}{1 \text{ mol}} \bullet \dfrac{1 \text{ mol}}{16.04 \text{ g}} = -59.54 \text{ kJ/g}$

   For methanol: $\dfrac{-676.1 \text{ kJ}}{1 \text{ mol}} \bullet \dfrac{1 \text{ mol}}{32.04 \text{ g}} = -21.10 \text{kJ/g}$

   (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 ΔH = -955.1 kJ – (-676.1 kJ) = - 279 kJ/mol

   (d) The equation for conversion of methane to methanol: $CH_4(g) + 1/2\ O_2(g) \rightarrow CH_3OH(l)$

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.
     $-(100.0 \text{ g})(0.9002 \text{ J/g}\bullet\text{K})(T_f - 373) =$

                    $(50.0 \text{ g})(0.1289 \text{ J/g}\bullet\text{K})(T_f\text{-}263) + (300.\text{g})(4.184 \text{ J/g}\bullet\text{K})(T_f\text{-}294)$
     $-90.02T_f + 33577 = 6.445T_f\text{-}1695.035 + 1255.2T_f\text{-} 369028.8$
     Collecting T_f terms:
     $-90.02T_f + -6.445T_f + - 1255.2T_f = - 369028.8 + -33577 + -1695.035$ or
     $-1351.665\ T_f = - 404300.835$ and a $T_f = 299.1$K or (299- 273) = 26°C

(b) Process is similar to that in (a) but we want *minimal* T change:

Consider the following table of data and calculations:

Specific heat	Mass	Heat Capacity	**Metal**	ΔT for metal heated to 100°C	ΔT for metal cooled to - 10°C	Heat lost upon cooling to 21 °C	Heat gained upon warming to 21°C
0.9002	50.0	45.0	**Al**	79	31	3555.79	**1395.31**
0.3860	50.0	19.3	**Zn**	79	31	**1524.7**	598.3

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 g)(0.3860 J/g•K)(T$_f$ – 373) =

$\quad\quad\quad\quad\quad$ (50.0 g)(0.9002 J/g•K)(T$_f$-263) + (300.g)(4.184 J/g•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 or

-1319.54 T$_f$ = - 388065.3 and a T$_f$= 294K or (294- 273) = 21°C