

## CHAPTER SIX

### THERMOCHEMISTRY

#### Questions

9. A coffee-cup calorimeter is at constant (atmospheric) pressure. The heat released or gained at constant pressure is  $\Delta H$ . A bomb calorimeter is at constant volume. The heat released or gained at constant volume is  $\Delta E$ .

10. Plot a represents an exothermic reaction. In an exothermic process, the bonds in the product molecules are stronger (on average) than those in the reactant molecules. The net result is that the quantity of energy  $\Delta(\text{PE})$  is transferred to the surroundings as heat when reactants are converted to products.

For an endothermic process, energy flows into the system as heat to increase the potential energy of the system. In an endothermic process, the products have higher potential energy (weaker bonds on average) than the reactants.

11. The specific heat capacities are:  $0.89 \text{ J/g}\cdot^\circ\text{C}$  (Al) and  $0.45 \text{ J/g}\cdot^\circ\text{C}$  (Fe)  
Al would be the better choice. It has a higher heat capacity and a lower density than Fe. Using Al, the same amount of heat could be dissipated by a smaller mass, keeping the mass of the amplifier down.
12.  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ ; Heat must be added to boil water so  $q$  is positive. Since a certain quantity of  $\text{H}_2\text{O}(\text{g})$  occupies a much larger volume than the same quantity of  $\text{H}_2\text{O}(\text{l})$ , an expansion will occur as  $\text{H}_2\text{O}(\text{l})$  is converted to  $\text{H}_2\text{O}(\text{g})$ . Therefore,  $w$  will be negative for this process, i.e., the system does work on the surroundings when the expansion occurs.
13. A state function is a function whose change depends only on the initial and final states and not on how one got from the initial to the final state. If  $H$  and  $E$  were not state functions, the law of conservation of energy (first law) would not be true.
14. If Hess's law were not true it would be possible to create energy by reversing a reaction using a different series of steps. This violates the law of conservation of energy (first law). Thus, Hess's law is another statement of the law of conservation of energy.
15. In order to compare values of  $\Delta H$  to each other, a common reference (or zero) point must be chosen. The definition of  $\Delta H_f^\circ$  establishes the pure elements in their standard states as that common reference point.
16. Advantages:  $\text{H}_2$  burns cleanly (less pollution) and gives a lot of energy per gram of fuel.

Disadvantages: Expense and storage.

## Exercises

### Potential and Kinetic Energy

17.  $KE = \frac{1}{2}mv^2$ ; Convert mass and velocity to SI units.  $1 \text{ J} = \frac{1 \text{ kg m}^2}{\text{s}^2}$

$$\text{Mass} = 5.25 \text{ oz} \times \frac{1 \text{ lb}}{16 \text{ oz}} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 0.149 \text{ kg}$$

$$\text{Velocity} = \frac{1.0 \times 10^2 \text{ mi}}{\text{hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1760 \text{ yd}}{\text{mi}} \times \frac{1 \text{ m}}{1.094 \text{ yd}} = \frac{45 \text{ m}}{\text{s}}$$

$$KE = \frac{1}{2}mv^2 = \frac{1}{2} \times 0.149 \text{ kg} \times \left( \frac{45 \text{ m}}{\text{s}} \right)^2 = 150 \text{ J}$$

18.  $KE = \frac{1}{2}mv^2 = \frac{1}{2} \times \left( 1.0 \times 10^{-5} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} \right) \times \left( \frac{2.0 \times 10^5 \text{ cm}}{\text{sec}} \times \frac{1 \text{ m}}{100 \text{ cm}} \right)^2 = 2.0 \times 10^{-2} \text{ J}$

19.  $KE = \frac{1}{2}mv^2 = \frac{1}{2} \times 2.0 \text{ kg} \times \left( \frac{1.0 \text{ m}}{\text{s}} \right)^2 = 1.0 \text{ J}$ ;  $KE = \frac{1}{2}mv^2 = \frac{1}{2} \times 1.0 \text{ kg} \times \left( \frac{2.0 \text{ m}}{\text{s}} \right)^2 = 2.0 \text{ J}$

The 1.0 kg object with a velocity of 2.0 m/s has the greater kinetic energy.

20. Ball A:  $PE = mgz = 2.00 \text{ kg} \times \frac{9.80 \text{ m}}{\text{s}^2} \times 10.0 \text{ m} = \frac{196 \text{ kg m}^2}{\text{s}^2} = 196 \text{ J}$

At Point I: All of this energy is transferred to Ball B. All of B's energy is kinetic energy at this point.  $E_{\text{total}} = KE = 196 \text{ J}$ . At point II, the sum of the total energy will equal 196 J.

At Point II:  $PE = mgz = 4.00 \text{ kg} \times \frac{9.80 \text{ m}}{\text{s}^2} \times 3.00 \text{ m} = 118 \text{ J}$

$$KE = E_{\text{total}} - PE = 196 \text{ J} - 118 \text{ J} = 78 \text{ J}$$

### Heat and Work

21. a.  $\Delta E = q + w = 51 \text{ kJ} + (-15 \text{ kJ}) = 36 \text{ kJ}$

b.  $\Delta E = 100. \text{ kJ} + (-65 \text{ kJ}) = 35 \text{ kJ}$       c.  $\Delta E = -65 + (-20.) = -85 \text{ kJ}$

d. When the system delivers work to the surroundings,  $w < 0$ . This is the case in all these examples, a, b and c.

22. a.  $\Delta E = q + w = -47 \text{ kJ} + 88 \text{ kJ} = 41 \text{ kJ}$

b.  $\Delta E = 82 + 47 = 129 \text{ kJ}$

c.  $\Delta E = 47 + 0 = 47 \text{ kJ}$

d. When the surroundings deliver work to the system,  $w > 0$ . This is the case for a and b.

23.  $\Delta E = q + w = -125 + 104 = -21 \text{ kJ}$

24. Step 1:  $\Delta E_1 = q + w = 72 \text{ J} + 35 \text{ J} = 107 \text{ J}$ ; Step 2:  $\Delta E_2 = 35 \text{ J} - 72 \text{ J} = -37 \text{ J}$

$$\Delta E_{\text{overall}} = \Delta E_1 + \Delta E_2 = 107 \text{ J} - 37 \text{ J} = 70. \text{ J}$$

25.  $w = -P\Delta V = -P \times (V_f - V_i) = -2.0 \text{ atm} \times (5.0 \times 10^{-3} \text{ L} - 5.0 \text{ L}) = -2.0 \text{ atm} \times (-5.0 \text{ L}) = 10. \text{ L atm}$

We can also calculate the work in Joules.

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 1.013 \times 10^5 \frac{\text{kg}}{\text{m s}^2}; \quad 1 \text{ L} = 1000 \text{ cm}^3 = 1 \times 10^{-3} \text{ m}^3$$

$$1 \text{ L atm} = 1 \times 10^{-3} \text{ m}^3 \times 1.013 \times 10^5 \frac{\text{kg}}{\text{m s}^2} = 101.3 \frac{\text{kg m}^2}{\text{s}^2} = 101.3 \text{ J}$$

$$w = 10. \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = 1013 \text{ J} = 1.0 \times 10^3 \text{ J}$$

26. In this problem  $q = w = -950. \text{ J}$

$$-950. \text{ J} \times \frac{1 \text{ L atm}}{101.3 \text{ J}} = -9.38 \text{ L atm of work done by the gases.}$$

$$w = -P\Delta V, \quad -9.38 \text{ L atm} = \frac{-650.}{760} \text{ atm} \times (V_f - 0.040 \text{ L}), \quad V_f - 0.040 = 11.0 \text{ L}, \quad V_f = 11.0 \text{ L}$$

27.  $q = \text{molar heat capacity} \times \text{mol} \times \Delta T = \frac{20.8 \text{ J}}{^\circ\text{C mol}} \times 39.1 \text{ mol} \times (38.0 - 0.0) ^\circ\text{C} = 30,900 \text{ J} = 30.9 \text{ kJ}$

$$w = -P\Delta V = -1.00 \text{ atm} \times (998 \text{ L} - 876 \text{ L}) = -122 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -12,400 \text{ J} = -12.4 \text{ kJ}$$

$$\Delta E = q + w = 30.9 \text{ kJ} + (-12.4 \text{ kJ}) = 18.5 \text{ kJ}$$

28.  $\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)}$ ;  $\Delta E = q + w$ ;  $q = -40.66 \text{ kJ}$ ;  $w = -P\Delta V$

$$\text{Volume of 1 mol H}_2\text{O(l)} = 1 \text{ mol H}_2\text{O(l)} \times \frac{18.02 \text{ g}}{\text{mol}} \times \frac{1 \text{ cm}^3}{0.996 \text{ g}} = 18.1 \text{ cm}^3 = 18.1 \text{ mL}$$

$$w = -P\Delta V = -1.00 \text{ atm} \times (0.0181 \text{ L} - 30.6 \text{ L}) = 30.6 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = 3.10 \times 10^3 \text{ J} = 3.10 \text{ kJ}$$

$$\Delta E = q + w = -40.66 \text{ kJ} + 3.10 \text{ kJ} = -37.56 \text{ kJ}$$

### Properties of Enthalpy

29. This is an endothermic reaction so heat must be absorbed in order to convert reactants into products.

The high temperature environment of internal combustion engines provides the heat.

30. One should try to cool the reaction mixture or provide some means of removing heat since the reaction is very exothermic (heat is released). The  $\text{H}_2\text{SO}_4(\text{aq})$  will get very hot and possibly boil unless cooling is provided.
31. a. Heat is absorbed from the water (it gets colder) as  $\text{KBr}$  dissolves, so this is an endothermic process.
- b. Heat is released as  $\text{CH}_4$  is burned, so this is an exothermic process.
- c. Heat is released to the water (it gets hot) as  $\text{H}_2\text{SO}_4$  is added, so this is an exothermic process.
- d. Heat must be added (absorbed) to boil water, so this is an endothermic process.
32. a. The combustion of gasoline releases heat, so this is an exothermic process.
- b.  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ ; Heat is released when water vapor condenses, so this is an exothermic process.
- c. To convert a solid to a gas, heat must be absorbed, so this is an endothermic process.
- d. Heat must be added (absorbed) in order to break a bond, so this is an endothermic process.
33.  $4 \text{ Fe}(\text{s}) + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ Fe}_2\text{O}_3(\text{s}) \quad \Delta H = -1652 \text{ kJ}$ ; Note that 1652 kJ of heat are released when 4 mol Fe react with 3 mol  $\text{O}_2$  to produce 2 mol  $\text{Fe}_2\text{O}_3$ .
- a.  $4.00 \text{ mol Fe} \times \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} = -1650 \text{ kJ heat released}$
- b.  $1.00 \text{ mol Fe}_2\text{O}_3 \times \frac{-1652 \text{ kJ}}{2 \text{ mol Fe}_2\text{O}_3} = -826 \text{ kJ heat released}$
- c.  $1.00 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} \times \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} = -7.39 \text{ kJ heat released}$
- d.  $10.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g}} = 0.179 \text{ mol Fe}$ ;  $2.00 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g}} = 0.0625 \text{ mol O}_2$
- $0.179 \text{ mol Fe} / 0.0625 \text{ mol O}_2 = 2.86$ ; The balanced equation requires a 4 mol Fe/3 mol  $\text{O}_2 = 1.33$  mol ratio.  $\text{O}_2$  is limiting since the actual mol Fe/mol  $\text{O}_2$  ratio is less than the required mol ratio.
- $0.0625 \text{ mol O}_2 \times \frac{-1652 \text{ kJ}}{3 \text{ mol O}_2} = -34.4 \text{ kJ heat released}$
34. a.  $1.00 \text{ mol H}_2\text{O} \times \frac{-572 \text{ kJ}}{2 \text{ mol H}_2\text{O}} = -286 \text{ kJ heat released}$

$$\text{b. } 4.03 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{-572 \text{ kJ}}{2 \text{ mol H}_2} = -572 \text{ kJ heat released}$$

$$\text{c. } 186 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{-572 \text{ kJ}}{\text{mol O}_2} = -3320 \text{ kJ heat released}$$

$$\text{d. } n_{\text{H}_2} = \frac{PV}{RT} = \frac{1.0 \text{ atm} \times 2.0 \times 10^8 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times 298 \text{ K}} = 8.2 \times 10^6 \text{ mol H}_2$$

$$8.2 \times 10^6 \text{ mol H}_2 \times \frac{-572 \text{ kJ}}{2 \text{ mol H}_2} = -2.3 \times 10^9 \text{ kJ heat released}$$

35. From Sample Exercise 6.3,  $q = 1.3 \times 10^8 \text{ J}$ . Since the heat transfer process is only 60.%

efficient, the total energy required is:  $1.3 \times 10^8 \text{ J} \times \frac{100. \text{ J}}{60. \text{ J}} = 2.2 \times 10^8 \text{ J}$

$$\text{mass C}_3\text{H}_8 = 2.2 \times 10^8 \text{ J} \times \frac{1 \text{ mol C}_3\text{H}_8}{2221 \times 10^3 \text{ J}} \times \frac{44.09 \text{ g C}_3\text{H}_8}{\text{mol C}_3\text{H}_8} = 4.4 \times 10^3 \text{ g C}_3\text{H}_8$$

$$36. \text{ a. } 1.00 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{-891 \text{ kJ}}{\text{mol CH}_4} = -55.5 \text{ kJ}$$

$$\text{b. } PV = nRT, n = \frac{PV}{RT} = \frac{\frac{740.}{760} \text{ atm} \times 1.00 \times 10^3 \text{ L}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times 298 \text{ K}} = 39.8 \text{ mol}$$

$$39.8 \text{ mol} \times \frac{-891 \text{ kJ}}{\text{mol}} = -3.55 \times 10^4 \text{ kJ}$$

### Calorimetry and Heat Capacity

37. Specific heat capacity is defined as the amount of heat necessary to raise the temperature of one gram of substance by one degree Celsius. Therefore,  $\text{H}_2\text{O(l)}$  with the largest heat capacity value requires the largest amount of heat for this process. The amount of heat for  $\text{H}_2\text{O(l)}$  is:

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

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

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

38. a.  $s = \text{specific heat capacity} = \frac{0.24 \text{ J}}{\text{g } ^\circ\text{C}} = \frac{0.24 \text{ J}}{\text{g K}}$  since  $\Delta T(\text{K}) = \Delta T(^{\circ}\text{C})$ .

$$\text{energy} = s \times m \times \Delta T = \frac{0.24 \text{ J}}{\text{g } ^\circ\text{C}} \times 150.0 \text{ g} \times (298 \text{ K} - 273 \text{ K}) = 9.0 \times 10^2 \text{ J}$$

b.  $\text{molar heat capacity} = \frac{0.24 \text{ J}}{\text{g } ^\circ\text{C}} \times \frac{107.9 \text{ g Ag}}{\text{mol Ag}} = \frac{26 \text{ J}}{\text{mol } ^\circ\text{C}}$

c.  $1250 \text{ J} = \frac{0.24 \text{ J}}{\text{g } ^\circ\text{C}} \times m \times (15.2^{\circ}\text{C} - 12.0^{\circ}\text{C}), m = \frac{1250}{0.24 \times 3.2} = 1.6 \times 10^3 \text{ g Ag}$

39. The units for specific heat capacity ( $s$ ) are  $\text{J/g}\cdot^{\circ}\text{C}$ .  $s = \frac{78.2 \text{ J}}{45.6 \text{ g} \times 13.3^{\circ}\text{C}} = \frac{0.129 \text{ J}}{\text{g } ^\circ\text{C}}$

$$\text{Molar heat capacity} = \frac{0.129 \text{ J}}{\text{g } ^\circ\text{C}} \times \frac{207.2 \text{ g}}{\text{mol Pb}} = \frac{26.7 \text{ J}}{\text{mol } ^\circ\text{C}}$$

40.  $s = \frac{585 \text{ J}}{125.6 \text{ g} \times (53.5 - 20.0)^{\circ}\text{C}} = 0.139 \text{ J/g}\cdot^{\circ}\text{C}$

$$\text{Molar heat capacity} = \frac{0.139 \text{ J}}{\text{g } ^\circ\text{C}} \times \frac{200.6 \text{ g}}{\text{mol Hg}} = \frac{27.9 \text{ J}}{\text{mol } ^\circ\text{C}}$$

41.  $|\text{Heat loss by hot water}| = |\text{Heat gain by cooler water}|$

The magnitude of heat loss and heat gain are equal in calorimetry problems. The only difference is the sign (positive or negative). To avoid sign errors, keep all quantities positive and, if necessary, deduce the correct signs at the end of the problem. Water has a specific heat capacity  $= s = 4.18 \text{ J/}^{\circ}\text{C}\cdot\text{g} = 4.18 \text{ J/K}\cdot\text{g}$  ( $\Delta T$  in  $^{\circ}\text{C} = \Delta T$  in K).

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

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

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

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

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

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

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

$$= \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times 97.3 \text{ g H}_2\text{O} \times (T_f - 22.0^\circ\text{C})$$

$$4.5(100.0 - T_f) + 4.5(100.0 - T_f) = 407(T_f - 22.0), \quad 450 - 4.5 T_f + 450 - 4.5 T_f = 407 T_f - 8950$$

$$416 T_f = 9850, \quad T_f = 23.7^\circ\text{C}$$

43. Heat gained by water = heat loss by metal =  $s \times m \times \Delta T$  where  $s$  = specific heat capacity.

$$\text{Heat gain} = \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times 150.0 \text{ g} \times (18.3^\circ\text{C} - 15.0^\circ\text{C}) = 2100 \text{ J}$$

A common error in calorimetry problems is sign errors. Keeping all quantities positive helps eliminate sign errors.

$$\text{heat loss} = 2100 \text{ J} = s \times 150.0 \text{ g} \times (75.0^\circ\text{C} - 18.3^\circ\text{C}), \quad s = \frac{2100 \text{ J}}{150.0 \text{ g} \times 56.7^\circ\text{C}} = 0.25 \text{ J/g}^\circ\text{C}$$

44. Heat gain by water = heat loss by Cu; Keeping all quantities positive to avoid sign errors:

$$\frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times m \times (24.9^\circ\text{C} - 22.3^\circ\text{C}) = \frac{0.20 \text{ J}}{\text{g}^\circ\text{C}} \times 110. \text{ g Cu} \times (82.4^\circ\text{C} - 24.9^\circ\text{C})$$

$$11 m = 1300, \quad m = 120 \text{ g H}_2\text{O}$$

45.  $50.0 \times 10^{-3} \text{ L} \times 0.100 \text{ mol/L} = 5.00 \times 10^{-3} \text{ mol}$  of both  $\text{AgNO}_3$  and  $\text{HCl}$  are reacted. Thus,  $5.00 \times 10^{-3} \text{ mol}$  of  $\text{AgCl}$  will be produced since there is a 1:1 mol ratio between reactants.

Heat lost by chemicals = Heat gained by solution

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

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

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

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

46.  $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \quad \Delta H = ?$ ; mass of solution =  $75.0 \text{ g} + 1.60 \text{ g} = 76.6 \text{ g}$

Heat lost by solution = Heat gained as  $\text{NH}_4\text{NO}_3$  dissolves. To help eliminate sign errors, we will keep all quantities positive ( $q$  and  $\Delta T$ ), then deduce the correct sign for  $\Delta H$  at the end of the problem. Here, since temperature decreases as  $\text{NH}_4\text{NO}_3$  dissolves, heat is absorbed as  $\text{NH}_4\text{NO}_3$

dissolves, so it is an endothermic process ( $\Delta H$  is positive).

$$\text{Heat lost by solution} = \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times 76.6 \text{ g} \times (25.00 - 23.34)^\circ\text{C} = 532 \text{ J} = \text{heat gained as } \text{NH}_4\text{NO}_3 \text{ dissolves}$$

$$\Delta H = \frac{532 \text{ J}}{1.60 \text{ g } \text{NH}_4\text{NO}_3} \times \frac{80.05 \text{ g } \text{NH}_4\text{NO}_3}{\text{mol } \text{NH}_4\text{NO}_3} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 26.6 \text{ kJ/mol } \text{NH}_4\text{NO}_3 \text{ dissolving}$$

47. Since  $\Delta H$  is exothermic, the temperature of the solution will increase as  $\text{CaCl}_2(\text{s})$  dissolves. Keeping all quantities positive:

$$\text{Heat loss as } \text{CaCl}_2 \text{ dissolves} = 11.0 \text{ g } \text{CaCl}_2 \times \frac{1 \text{ mol } \text{CaCl}_2}{110.98 \text{ g } \text{CaCl}_2} \times \frac{81.5 \text{ kJ}}{\text{mol } \text{CaCl}_2} = 8.08 \text{ kJ}$$

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

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

48.  $0.100 \text{ L} \times \frac{0.500 \text{ mol HCl}}{\text{L}} = 5.00 \times 10^{-2} \text{ mol HCl}$

$$0.300 \text{ L} \times \frac{0.100 \text{ mol Ba(OH)}_2}{\text{L}} = 3.00 \times 10^{-2} \text{ mol Ba(OH)}_2$$

To react with all the HCl present,  $5.00 \times 10^{-2}/2 = 2.50 \times 10^{-2} \text{ mol Ba(OH)}_2$  are required. Since  $3.00 \times 10^{-2} \text{ mol Ba(OH)}_2$  are present, HCl is the limiting reactant.

$$5.00 \times 10^{-2} \text{ mol HCl} \times \frac{118 \text{ kJ}}{2 \text{ mol HCl}} = 2.95 \text{ kJ of heat is evolved by reaction.}$$

$$\text{Heat gained by solution} = 2.95 \times 10^3 \text{ J} = \frac{4.18 \text{ J}}{\text{g}^\circ\text{C}} \times 400.0 \text{ g} \times \Delta T$$

$$\Delta T = 1.76^\circ\text{C} = T_f - T_i = T_f - 25.0^\circ\text{C}, \quad T_f = 26.8^\circ\text{C}$$

49. First, we need to get the heat capacity of the calorimeter from the combustion of benzoic acid.

Heat lost by combustion = Heat gained by calorimeter

$$\text{Heat loss} = 0.1584 \text{ g} \times \frac{26.42 \text{ kJ}}{\text{g}} = 4.185 \text{ kJ}$$

$$\text{Heat gain} = 4.185 \text{ kJ} = C_{\text{cal}} \times \Delta T, \quad C_{\text{cal}} = \frac{4.185 \text{ kJ}}{2.54^\circ\text{C}} = 1.65 \text{ kJ/}^\circ\text{C}$$

Now we can calculate the heat of combustion of vanillin. Heat loss = Heat gain

$$\text{Heat gain by calorimeter} = \frac{1.65 \text{ kJ}}{^\circ\text{C}} \times 3.25^\circ\text{C} = 5.36 \text{ kJ}$$

Heat loss = 5.36 kJ, which is the heat evolved by the combustion of the vanillin.



$$\Delta E_{\text{comb}} = \frac{-5.36 \text{ kJ}}{0.2130 \text{ g}} = -25.2 \text{ kJ/g}; \quad \Delta E_{\text{comb}} = \frac{-25.2 \text{ kJ}}{\text{g}} \times \frac{152.14 \text{ g}}{\text{mol}} = -3830 \text{ kJ/mol}$$

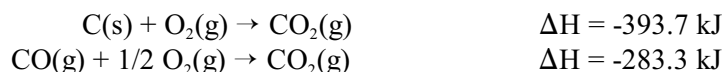
50. Heat gain by calorimeter =  $\frac{1.56 \text{ kJ}}{^{\circ}\text{C}} \times 3.2^{\circ}\text{C} = 5.0 \text{ kJ} = \text{heat loss by quinone}$

Heat loss = 5.0 kJ, which is the heat evolved (exothermic reaction) by the combustion of 0.1964 g of quinone.

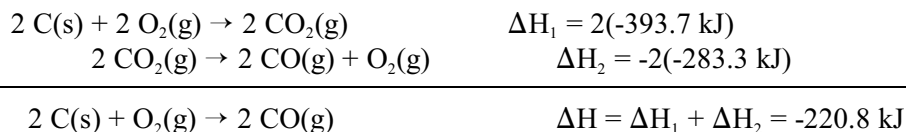
$$\Delta E_{\text{comb}} = \frac{-5.0 \text{ kJ}}{0.1964 \text{ g}} = -25 \text{ kJ/g}; \quad \Delta E_{\text{comb}} = \frac{-25 \text{ kJ}}{\text{g}} \times \frac{108.09 \text{ g}}{\text{mol}} = -2700 \text{ kJ/mol}$$

### Hess's Law

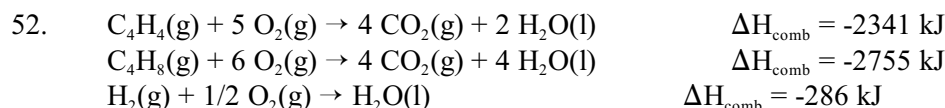
51. Information given:



Using Hess's Law:

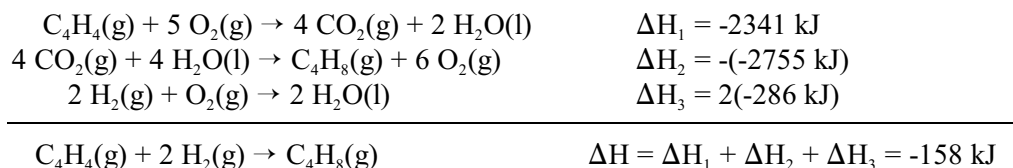


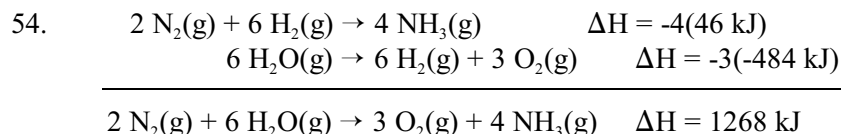
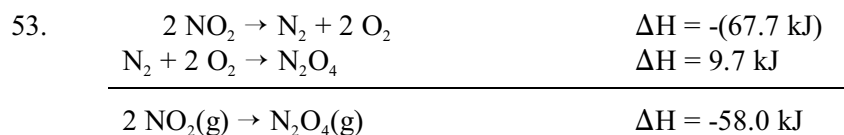
Note: The enthalpy change for a reaction that is reversed is the negative quantity of the enthalpy change for the original reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of  $\Delta H$  is multiplied by the same integer.



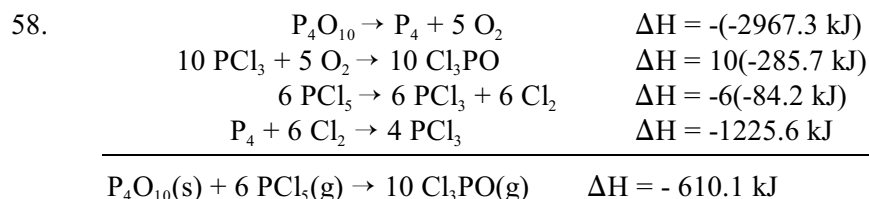
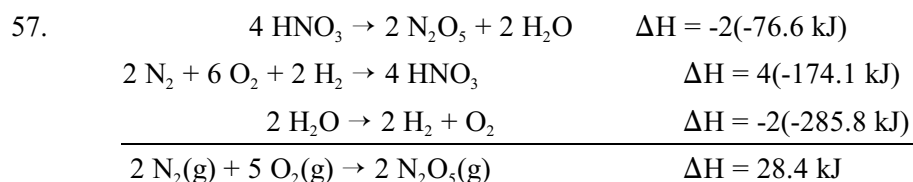
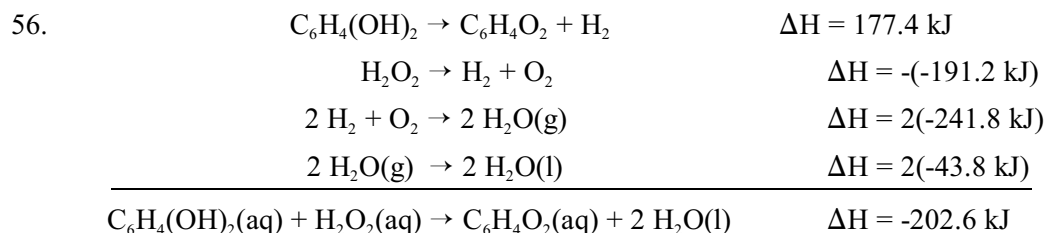
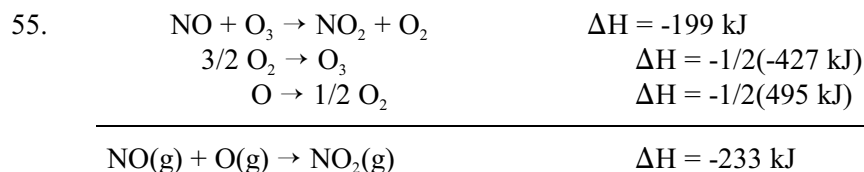
By convention,  $\text{H}_2\text{O(l)}$  is produced when enthalpies of combustion are given and, since per mol quantities are given, the combustion reaction refers to 1 mol of that quantity reacting with  $\text{O}_2(\text{g})$ .

Using Hess's Law to solve:



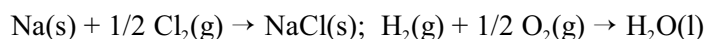


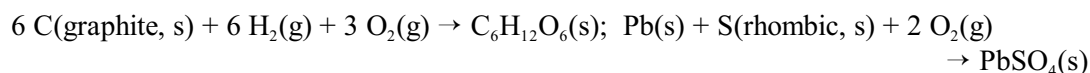
No, since the reaction is very endothermic (requires a lot of heat), it would not be a practical way of making ammonia due to the high energy costs required.



### Standard Enthalpies of Formation

59. The change in enthalpy that accompanies the formation of one mole of a compound from its elements, with all substances in their standard states, is the standard enthalpy of formation for a compound. The reactions that refer to  $\Delta H_f^\circ$  are:





60. a. aluminum oxide =  $\text{Al}_2\text{O}_3$ ;  $2 \text{ Al(s)} + 3/2 \text{ O}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{s})$
- b.  $\text{C}_2\text{H}_5\text{OH(l)} + 3 \text{ O}_2(\text{g}) \rightarrow 2 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O(l)}$
- c.  $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)}$
- d.  $2 \text{ C(graphite, s)} + 3/2 \text{ H}_2(\text{g}) + 1/2 \text{ Cl}_2(\text{g}) \rightarrow \text{C}_2\text{H}_3\text{Cl(g)}$
- e.  $\text{C}_6\text{H}_6(\text{l}) + 15/2 \text{ O}_2(\text{g}) \rightarrow 6 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O(l)}$

Note:  $\Delta H_{\text{comb}}$  values assume one mol of compound combusted.

- f.  $\text{NH}_4\text{Br(s)} \rightarrow \text{NH}_4^+(\text{aq}) + \text{Br}^-(\text{aq})$
61. In general:  $\Delta H^\circ = \sum n_p \Delta H_f^\circ \text{ products} - \sum n_r \Delta H_f^\circ \text{ reactants}$  and all elements in their standard state have  $\Delta H_f^\circ = 0$  by definition.

- a. The balanced equation is:  $2 \text{ NH}_3(\text{g}) + 3 \text{ O}_2(\text{g}) + 2 \text{ CH}_4(\text{g}) \rightarrow 2 \text{ HCN(g)} + 6 \text{ H}_2\text{O(g)}$

$$\Delta H^\circ = [2 \text{ mol HCN} \times \Delta H_f^\circ \text{ HCN} + 6 \text{ mol H}_2\text{O(g)} \times \Delta H_f^\circ \text{ H}_2\text{O}] - [2 \text{ mol NH}_3 \times \Delta H_f^\circ \text{ NH}_3 + 2 \text{ mol CH}_4 \times \Delta H_f^\circ \text{ CH}_4]$$

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

- b.  $\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 3 \text{ H}_2\text{SO}_4(\text{l}) \rightarrow 3 \text{ CaSO}_4(\text{s}) + 2 \text{ H}_3\text{PO}_4(\text{l})$

$$\Delta H^\circ = \left[ 3 \text{ mol CaSO}_4 \left( \frac{-1433 \text{ kJ}}{\text{mol}} \right) + 2 \text{ mol H}_3\text{PO}_4(\text{l}) \left( \frac{-1267 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 1 \text{ mol Ca}_3(\text{PO}_4)_2 \left( \frac{-4126 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol H}_2\text{SO}_4(\text{l}) \left( \frac{-814 \text{ kJ}}{\text{mol}} \right) \right]$$

$$\Delta H^\circ = -6833 \text{ kJ} - (-6568 \text{ kJ}) = -265 \text{ kJ}$$

- c.  $\text{NH}_3(\text{g}) + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$

$$\Delta H^\circ = [1 \text{ mol NH}_4\text{Cl} \times \Delta H_f^\circ \text{ NH}_4\text{Cl}] - [1 \text{ mol NH}_3 \times \Delta H_f^\circ \text{ NH}_3 + 1 \text{ mol HCl} \times \Delta H_f^\circ \text{ HCl}]$$

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

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

62. a. The balanced equation is:  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$

$$\begin{aligned}\Delta H^\circ &= \left[ 2 \text{ mol} \left( \frac{-393.5 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol} \left( \frac{-242 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 1 \text{ mol} \left( \frac{-278 \text{ kJ}}{\text{mol}} \right) \right] \\ &= -1513 \text{ kJ} - (-278 \text{ kJ}) = -1235 \text{ kJ}\end{aligned}$$

- b.  $\text{SiCl}_4(\text{l}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4 \text{HCl}(\text{aq})$

Since  $\text{HCl}(\text{aq})$  is  $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ , then  $\Delta H_f^\circ = 0 - 167 = -167 \text{ kJ/mol}$ .

$$\Delta H^\circ = \left[ 4 \text{ mol} \left( \frac{-167 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-911 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 1 \text{ mol} \left( \frac{-687 \text{ kJ}}{\text{mol}} \right) + 2 \text{ mol} \left( \frac{-286 \text{ kJ}}{\text{mol}} \right) \right]$$

$$\Delta H^\circ = -1579 \text{ kJ} - (-1259 \text{ kJ}) = -320. \text{ kJ}$$

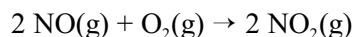
- c.  $\text{MgO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mg}(\text{OH})_2(\text{s})$

$$\Delta H^\circ = \left[ 1 \text{ mol} \left( \frac{-925 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 1 \text{ mol} \left( \frac{-602 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-286 \text{ kJ}}{\text{mol}} \right) \right]$$

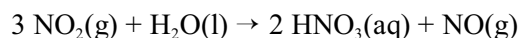
$$\Delta H^\circ = -925 \text{ kJ} - (-888 \text{ kJ}) = -37 \text{ kJ}$$

63. a.  $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g}); \Delta H^\circ = \sum n_p \Delta H_{f, \text{products}}^\circ - \sum n_r \Delta H_{f, \text{reactants}}^\circ$

$$\Delta H^\circ = \left[ 4 \text{ mol} \left( \frac{90. \text{ kJ}}{\text{mol}} \right) + 6 \text{ mol} \left( \frac{-242 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 4 \text{ mol} \left( \frac{-46 \text{ kJ}}{\text{mol}} \right) \right] = -908 \text{ kJ}$$

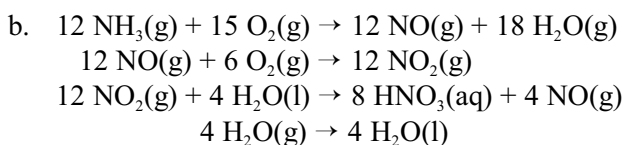


$$\Delta H^\circ = \left[ 2 \text{ mol} \left( \frac{34 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 2 \text{ mol} \left( \frac{90. \text{ kJ}}{\text{mol}} \right) \right] = -112 \text{ kJ}$$

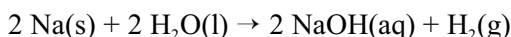
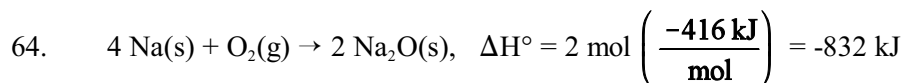


$$\begin{aligned}\Delta H^\circ &= \left[ 2 \text{ mol} \left( \frac{-207 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{90. \text{ kJ}}{\text{mol}} \right) \right] \\ &\quad - \left[ 3 \text{ mol} \left( \frac{34 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-286 \text{ kJ}}{\text{mol}} \right) \right] = -140. \text{ kJ}\end{aligned}$$

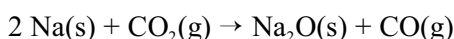
Note: All  $\Delta H_f^\circ$  values are assumed  $\pm 1 \text{ kJ}$ .



The overall reaction is exothermic since each step is exothermic.

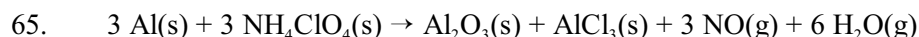


$$\Delta H^\circ = \left[ 2 \text{ mol} \left( \frac{-470. \text{ kJ}}{\text{mol}} \right) \right] - \left[ 2 \text{ mol} \left( \frac{-286 \text{ kJ}}{\text{mol}} \right) \right] = -368 \text{ kJ}$$

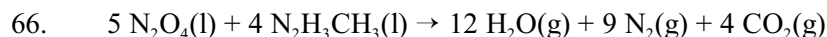


$$\Delta H^\circ = \left[ 1 \text{ mol} \left( \frac{-416 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-110.5 \text{ kJ}}{\text{mol}} \right) \right] - \left[ 1 \text{ mol} \left( \frac{-393.5 \text{ kJ}}{\text{mol}} \right) \right] = -133 \text{ kJ}$$

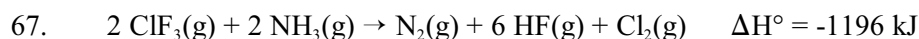
In both cases, sodium metal reacts with the "extinguishing agent." Both reactions are exothermic and each reaction produces a flammable gas,  $\text{H}_2$  and  $\text{CO}$ , respectively.



$$\begin{aligned}\Delta H^\circ = & \left[ 6 \text{ mol} \left( \frac{-242 \text{ kJ}}{\text{mol}} \right) + 3 \text{ mol} \left( \frac{90. \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-704 \text{ kJ}}{\text{mol}} \right) + 1 \text{ mol} \left( \frac{-1676 \text{ kJ}}{\text{mol}} \right) \right] \\ & - \left[ 3 \text{ mol} \left( \frac{-295 \text{ kJ}}{\text{mol}} \right) \right] = -2677 \text{ kJ}\end{aligned}$$



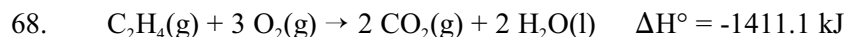
$$\begin{aligned}\Delta H^\circ = & \left[ 12 \text{ mol} \left( \frac{-242 \text{ kJ}}{\text{mol}} \right) + 4 \text{ mol} \left( \frac{-393.5 \text{ kJ}}{\text{mol}} \right) \right] \\ & - \left[ 5 \text{ mol} \left( \frac{-20. \text{ kJ}}{\text{mol}} \right) + 4 \text{ mol} \left( \frac{54 \text{ kJ}}{\text{mol}} \right) \right] = -4594 \text{ kJ}\end{aligned}$$



$$\Delta H^\circ = [6 \Delta H_{\text{f, HF}}^\circ] - [2 \Delta H_{\text{f, ClF}_3}^\circ + 2 \Delta H_{\text{f, NH}_3}^\circ]$$

$$-1196 \text{ kJ} = 6 \text{ mol} \left( \frac{-271 \text{ kJ}}{\text{mol}} \right) - 2 \Delta H_{\text{f, ClF}_3}^\circ - 2 \text{ mol} \left( \frac{-46 \text{ kJ}}{\text{mol}} \right)$$

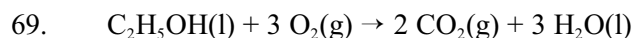
$$-1196 \text{ kJ} = -1626 \text{ kJ} - 2 \Delta H_{\text{f, ClF}_3}^\circ + 92 \text{ kJ}, \Delta H_{\text{f, ClF}_3}^\circ = \frac{(-1626 + 92 + 1196) \text{ kJ}}{2 \text{ mol}} = \frac{-169 \text{ kJ}}{\text{mol}}$$



$$\Delta H^\circ = -1411.1 \text{ kJ} = 2(-393.5) \text{ kJ} + 2(-285.8) \text{ kJ} - \Delta H_{\text{f, C}_2\text{H}_4}^\circ$$

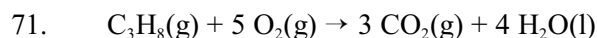
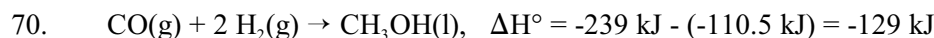
$$-1411.1 \text{ kJ} = -1358.6 \text{ kJ} - \Delta H_{\text{f, C}_2\text{H}_4}^\circ, \Delta H_{\text{f, C}_2\text{H}_4}^\circ = 52.5 \text{ kJ/mol}$$

### Energy Consumption and Sources



$$\Delta H^\circ = [2(-393.5 \text{ kJ}) + 3(-286 \text{ kJ})] - (-278 \text{ kJ}) = -1367 \text{ kJ/mol ethanol}$$

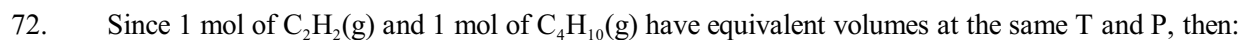
$$\frac{-1367 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = -29.67 \text{ kJ/g}$$



$$\Delta H^\circ = [3(-393.5 \text{ kJ}) + 4(-286 \text{ kJ})] - [-104 \text{ kJ}] = -2221 \text{ kJ/mol C}_3\text{H}_8$$

$$\frac{-2221 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{44.09 \text{ g}} = \frac{-50.37 \text{ kJ}}{\text{g}} \text{ vs. } -47.7 \text{ kJ/g for octane (Sample Exercise 6.11)}$$

The fuel values are very close. An advantage of propane is that it burns more cleanly. The boiling point of propane is  $-42^\circ\text{C}$ . Thus, it is more difficult to store propane and there are extra safety hazards associated with using high pressure compressed gas tanks.



$$\frac{\text{enthalpy of combustion per volume of C}_2\text{H}_2}{\text{enthalpy of combustion per volume of C}_4\text{H}_{10}} = \frac{\text{enthalpy of combustion per mol C}_2\text{H}_2}{\text{enthalpy of combustion per mol C}_4\text{H}_{10}}$$

$$\frac{\text{enthalpy of combustion per volume of C}_2\text{H}_2}{\text{enthalpy of combustion per volume of C}_4\text{H}_{10}} = \frac{\frac{-49.9 \text{ kJ}}{\text{g C}_2\text{H}_2} \times \frac{26.04 \text{ g C}_2\text{H}_2}{\text{mol C}_2\text{H}_2}}{\frac{-49.5 \text{ kJ}}{\text{g C}_4\text{H}_{10}} \times \frac{58.12 \text{ g C}_4\text{H}_{10}}{\text{mol C}_4\text{H}_{10}}} = 0.452$$

Almost twice the volume of acetylene is needed to furnish the same energy as a given volume of butane.

73. The molar volume of a gas at STP is 22.42 L (from Chapter 5).

$$4.19 \times 10^6 \text{ kJ} \times \frac{1 \text{ mol CH}_4}{891 \text{ kJ}} \times \frac{22.42 \text{ L CH}_4}{\text{mol CH}_4} = 1.05 \times 10^5 \text{ L CH}_4$$

74. Mass of H<sub>2</sub>O = 1.00 gal  $\times \frac{3.785 \text{ L}}{\text{gal}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1.00 \text{ g}}{\text{mL}} = 3790 \text{ g H}_2\text{O}$

$$\text{Energy required (theoretical)} = s \times m \times \Delta T = \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times 3790 \text{ g} \times 10.0 ^\circ\text{C} = 1.58 \times 10^5 \text{ J}$$

For an actual (80.0% efficient) process, more than this quantity of energy is needed since heat is always lost in any transfer of energy. The energy required is:

$$1.58 \times 10^5 \text{ J} \times \frac{100. \text{ J}}{80.0 \text{ J}} = 1.98 \times 10^5 \text{ J}$$

$$\text{Mass of C}_2\text{H}_2 = 1.98 \times 10^5 \text{ J} \times \frac{1 \text{ mol C}_2\text{H}_2}{1300. \times 10^3 \text{ J}} \times \frac{26.04 \text{ g C}_2\text{H}_2}{\text{mol C}_2\text{H}_2} = 3.97 \text{ g C}_2\text{H}_2$$

### Additional Exercises

75. a.  $2 \text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ SO}_3(\text{g})$  ( $w = -P\Delta V$ ); Since the volume of the piston apparatus decreased as reactants were converted to products,  $w$  is positive ( $w > 0$ ).
- b.  $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ ; Since the volume increased,  $w$  is negative ( $w < 0$ ).
- c.  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ NO}(\text{g})$ ; Since the volume did not change, no PV work is done ( $w = 0$ ).

In order to predict the sign of  $w$  for a reaction, compare the coefficients of all the product gases in the balanced equation to the coefficients of all the reactant gases. When a balanced reaction has more mol of product gases than mol of reactant gases (as in b), the reaction will expand in volume ( $\Delta V$  positive), and the system does work on the surroundings. When a balanced reaction has a decrease in the mol of gas from reactants to products (as in a), the reaction will contract in volume ( $\Delta V$  negative), and the surroundings will do compression work on the system. When there is no change in the mol of gas from reactants to products (as in c),  $\Delta V = 0$  and  $w = 0$ .

76.  $w = -P\Delta V$ ;  $\Delta n = \text{mol gaseous products} - \text{mol gaseous reactants}$ . Only gases can do PV work (we ignore solids and liquids). When a balanced reaction has more mol of product gases than mol of reactant gases ( $\Delta n$  positive), the reaction will expand in volume ( $\Delta V$  positive) and the system will do work on the surroundings. For example, in reaction c,  $\Delta n = 2 - 0 = 2 \text{ mol}$ , and this reaction would do expansion work against the surroundings. When a balanced reaction has a decrease in the mol of gas from reactants to products ( $\Delta n$  negative), the reaction will contract in volume ( $\Delta V$  negative) and the surroundings will do compression work on the system, e.g., reaction a where  $\Delta n = 0 - 1 = -1$ . When there is no change in the mol of gas from reactants to products,  $\Delta V = 0$  and

$w = 0$ , e.g., reaction b where  $\Delta n = 2 - 2 = 0$ .

When  $\Delta V > 0$  ( $\Delta n > 0$ ), then  $w < 0$  and system does work on the surroundings (c and e).

When  $\Delta V < 0$  ( $\Delta n < 0$ ), then  $w > 0$  and the surroundings do work on the system (a and d).

When  $\Delta V = 0$  ( $\Delta n = 0$ ), then  $w = 0$  (b).

77.  $\Delta E_{\text{overall}} = \Delta E_{\text{step 1}} + \Delta E_{\text{step 2}}$ ; This is a cyclic process which means that the overall initial state and final state are the same. Since  $\Delta E$  is a state function,  $\Delta E_{\text{overall}} = 0$  and  $\Delta E_{\text{step 1}} = -\Delta E_{\text{step 2}}$ .

$$\Delta E_{\text{step 1}} = q + w = 45 \text{ J} + (-10. \text{ J}) = 35 \text{ J}$$

$$\Delta E_{\text{step 2}} = -\Delta E_{\text{step 1}} = -35 \text{ J} = q + w, \quad -35 \text{ J} = -60 \text{ J} + w, \quad w = 25 \text{ J}$$

78.  $w = -P\Delta V$ ; We need the final volume of the gas. Since  $T$  and  $n$  are constant,  $P_1 V_1 = P_2 V_2$ .

$$V_2 = \frac{V_1 P_1}{P_2} = \frac{10.0 \text{ L} (15.0 \text{ atm})}{2.00 \text{ atm}} = 75.0 \text{ L}$$

$$w = -P\Delta V = -2.00 \text{ atm} (75.0 \text{ L} - 10.0 \text{ L}) = -130. \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -13.2 \text{ kJ} = \text{work}$$

79. Heat loss by hot water = heat gain by cold water; Keeping all quantities positive to avoid sign errors:

$$\frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times m_{\text{hot}} \times (55.0^\circ\text{C} - 37.0^\circ\text{C}) = \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times 90.0 \text{ g} \times (37.0^\circ\text{C} - 22.0^\circ\text{C})$$

$$m_{\text{hot}} = \frac{90.0 \text{ g} \times 15.0^\circ\text{C}}{18.0^\circ\text{C}} = 75.0 \text{ g hot water needed}$$

80.  $2 \text{ K(s)} + 2 \text{ H}_2\text{O(l)} \rightarrow 2 \text{ KOH(aq)} + \text{H}_2\text{(g)}, \quad \Delta H^\circ = 2(-481 \text{ kJ}) - 2(-286 \text{ kJ}) = -390. \text{ kJ}$

$$5.00 \text{ g K} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} \times \frac{-390. \text{ kJ}}{2 \text{ mol K}} = -24.9 \text{ kJ of heat released upon reaction of 5.00 g of potassium.}$$

$$24,900 \text{ J} = \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times (1.00 \times 10^3 \text{ g}) \times \Delta T, \quad \Delta T = \frac{24,900}{4.18 \times 1.00 \times 10^3} = 5.96^\circ\text{C}$$

$$\text{Final temperature} = 24.0 + 5.96 = 30.0^\circ\text{C}$$

81.  $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)} \quad \Delta H = -56 \text{ kJ}$

$$0.2000 \text{ L} \times \frac{0.400 \text{ mol HCl}}{\text{L}} = 8.00 \times 10^{-2} \text{ mol HCl}$$

$$0.1500 \text{ L} \times \frac{0.500 \text{ mol NaOH}}{\text{L}} = 7.50 \times 10^{-2} \text{ mol NaOH}$$



Since the balanced reaction requires a 1:1 mol ratio between HCl and NaOH, and since fewer mol of NaOH are actually present as compared to HCl, then NaOH is the limiting reagent.

$$\text{Heat released} = 7.50 \times 10^{-2} \text{ mol NaOH} \times \frac{-56 \text{ kJ}}{\text{mol NaOH}} = -4.2 \text{ kJ heat released}$$

82. The specific heat of water is  $4.18 \text{ J/g}\cdot^{\circ}\text{C}$ , which is equal to  $4.18 \text{ kJ/kg}\cdot^{\circ}\text{C}$ .

$$\text{We have } 1.00 \text{ kg of H}_2\text{O, so: } 1.00 \text{ kg} \times \frac{4.18 \text{ kJ}}{\text{kg}\cdot^{\circ}\text{C}} = 4.18 \text{ kJ}/^{\circ}\text{C}$$

This is the portion of the heat capacity that can be attributed to  $\text{H}_2\text{O}$ .

$$\text{Total heat capacity} = C_{\text{cal}} + C_{\text{H}_2\text{O}}, \quad C_{\text{cal}} = 10.84 - 4.18 = 6.66 \text{ kJ}/^{\circ}\text{C}$$

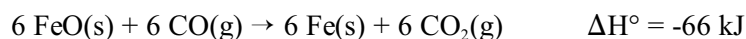
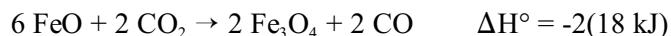
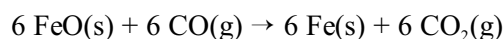
83. Heat released =  $1.056 \text{ g} \times 26.42 \text{ kJ/g} = 27.90 \text{ kJ}$  = Heat gain by water and calorimeter

$$\text{Heat gain} = 27.90 \text{ kJ} = \frac{4.18 \text{ kJ}}{\text{kg}\cdot^{\circ}\text{C}} \times 0.987 \text{ kg} \times \Delta T + \frac{6.66 \text{ kJ}}{^{\circ}\text{C}} \times \Delta T$$

$$27.90 = (4.13 + 6.66) \Delta T = 10.79 \Delta T, \quad \Delta T = 2.586^{\circ}\text{C}$$

$$2.586^{\circ}\text{C} = T_f - 23.32^{\circ}\text{C}, \quad T_f = 25.91^{\circ}\text{C}$$

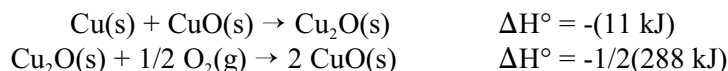
84. To avoid fractions, let's first calculate  $\Delta H$  for the reaction:



$$\text{So for: } \text{FeO(s)} + \text{CO(g)} \rightarrow \text{Fe(s)} + \text{CO}_2\text{(g)} \quad \Delta H^{\circ} = \frac{-66 \text{ kJ}}{6} = -11 \text{ kJ}$$

85. a.  $\Delta H^{\circ} = 3 \text{ mol } (227 \text{ kJ/mol}) - 1 \text{ mol } (49 \text{ kJ/mol}) = 632 \text{ kJ}$
- b. Since  $3 \text{ C}_2\text{H}_2\text{(g)}$  is higher in energy than  $\text{C}_6\text{H}_6\text{(l)}$ , acetylene will release more energy per gram when burned in air.

86.  $\text{Cu(s)} + 1/2 \text{ O}_2\text{(g)} \rightarrow \text{CuO(s)} \quad \Delta H^{\circ} = \Delta H_{\text{f,CuO(s)}}^{\circ}$



87. a.  $\text{C}_2\text{H}_4\text{(g)} + \text{O}_3\text{(g)} \rightarrow \text{CH}_3\text{CHO(g)} + \text{O}_2\text{(g)}, \quad \Delta H^\circ = -166 \text{ kJ} - [143 \text{ kJ} + 52 \text{ kJ}] = -361 \text{ kJ}$   
 b.  $\text{O}_3\text{(g)} + \text{NO(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}, \quad \Delta H^\circ = 34 \text{ kJ} - [90. \text{ kJ} + 143 \text{ kJ}] = -199 \text{ kJ}$   
 c.  $\text{SO}_3\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)}, \quad \Delta H^\circ = -909 \text{ kJ} - [-396 \text{ kJ} + (-286 \text{ kJ})] = -227 \text{ kJ}$   
 d.  $2 \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)}, \quad \Delta H^\circ = 2(34) \text{ kJ} - 2(90.) \text{ kJ} = -112 \text{ kJ}$

### Challenge Problems

88. Only when there is a volume change can PV work be done. In pathway 1 (steps 1 + 2), only the first step does PV work (step 2 has a constant volume of 30.0 L). In pathway 2 (steps 3 + 4), only step 4 does PV work (step 3 has a constant volume of 10.0 L).

$$\text{Pathway 1: } w = -P\Delta V = -2.00 \text{ atm} (30.0 \text{ L} - 10.0 \text{ L}) = -40.0 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -4.05 \times 10^3 \text{ J}$$

$$\text{Pathway 2: } w = -P\Delta V = -1.00 \text{ atm} (30.0 \text{ L} - 10.0 \text{ L}) = -20.0 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -2.03 \times 10^3 \text{ J}$$

Note: The sign is (-) because the system is doing work on the surroundings (an expansion).

We get a different value of work for the two pathways which both have the same initial and final states. Since  $w$  depends on the pathway, work cannot be a state function.

89. a.  $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)} + 12 \text{O}_2\text{(g)} \rightarrow 12 \text{CO}_2\text{(g)} + 11 \text{H}_2\text{O(l)}$   
 b. A bomb calorimeter is at constant volume, so heat released =  $q_v = \Delta E$ :

$$\Delta E = \frac{-24.00 \text{ kJ}}{1.46 \text{ g}} \times \frac{342.30 \text{ g}}{\text{mol}} = -5630 \text{ kJ/mol C}_{12}\text{H}_{22}\text{O}_{11}$$

- c. Since  $PV = nRT$ , then  $P\Delta V = RT\Delta n$  where  $\Delta n = \text{mol gaseous products} - \text{mol gaseous reactants}$ .

$$\Delta H = \Delta E + P\Delta V = \Delta E + RT\Delta n$$

For this reaction,  $\Delta n = 12 - 12 = 0$ , so  $\Delta H = \Delta E = -5630 \text{ kJ/mol}$ .

90. Energy needed =  $\frac{20. \times 10^3 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{\text{hr}} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.30 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{5640 \text{ kJ}}{\text{mol}} = 3.3 \times 10^5 \text{ kJ/hr}$

$$\text{Energy from sun} = 1.0 \text{ kW/m}^2 = 1000 \text{ W/m}^2 = \frac{1000 \text{ J}}{\text{s m}^2} = \frac{1.0 \text{ kJ}}{\text{s m}^2}$$

$$10,000 \text{ m}^2 \times \frac{1.0 \text{ kJ}}{\text{s m}^2} \times \frac{60 \text{ s}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} = 3.6 \times 10^7 \text{ kJ/hr}$$

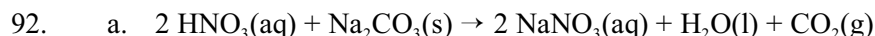
$$\% \text{ efficiency} = \frac{\text{Energy used per hour}}{\text{Total energy per hour}} \times 100 = \frac{3.3 \times 10^5 \text{ kJ}}{3.6 \times 10^7 \text{ kJ}} \times 100 = 0.92\%$$

91. Energy used in 8.0 hours = 40. kWh =  $\frac{40. \text{ kJ h}}{\text{s}} \times \frac{3600 \text{ s}}{\text{h}} = 1.4 \times 10^5 \text{ kJ}$

$$\text{Energy from the sun in 8.0 hours} = \frac{1.0 \text{ kJ}}{\text{s m}^2} \times \frac{60 \text{ s}}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} \times 8.0 \text{ h} = 2.9 \times 10^4 \text{ kJ/m}^2$$

Only 13% of the sunlight is converted into electricity:

$$0.13 \times (2.9 \times 10^4 \text{ kJ/m}^2) \times \text{Area} = 1.4 \times 10^5 \text{ kJ}, \quad \text{Area} = 37 \text{ m}^2$$



$$\Delta H^\circ = [2(-467 \text{ kJ}) + (-286 \text{ kJ}) + (-393.5 \text{ kJ})] - [2(-207 \text{ kJ}) + (-1131 \text{ kJ})] = -69 \text{ kJ}$$

$$2.0 \times 10^4 \text{ gallons} \times \frac{4 \text{ qt}}{\text{gal}} \times \frac{946 \text{ mL}}{\text{qt}} \times \frac{1.42 \text{ g}}{\text{mL}} = 1.1 \times 10^8 \text{ g of concentrated nitric acid solution}$$

$$1.1 \times 10^8 \text{ g solution} \times \frac{70.0 \text{ g HNO}_3}{100.0 \text{ g solution}} = 7.7 \times 10^7 \text{ g HNO}_3$$

$$7.7 \times 10^7 \text{ g HNO}_3 \times \frac{1 \text{ mol}}{63.02 \text{ g}} \times \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol HNO}_3} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 6.5 \times 10^7 \text{ g Na}_2\text{CO}_3$$

There are  $(7.7 \times 10^7 / 63.02)$  mol of  $\text{HNO}_3$  from the previous calculation. There are 69 kJ of heat evolved for every two moles of nitric acid neutralized. Combining these two results:

$$7.7 \times 10^7 \text{ g HNO}_3 \times \frac{1 \text{ mol HNO}_3}{63.02 \text{ g HNO}_3} \times \frac{-69 \text{ kJ}}{2 \text{ mol HNO}_3} = -4.2 \times 10^7 \text{ kJ}$$

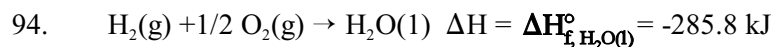
b. They feared the heat generated by the neutralization reaction would vaporize the unreacted nitric acid, causing widespread airborne contamination.

93.  $400 \text{ kcal} \times \frac{4.18 \text{ kJ}}{\text{kcal}} = 1.67 \times 10^3 \text{ kJ} \approx 2 \times 10^3 \text{ kJ}$

$$\text{PE} = m g z = \left( 180 \text{ lb} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} \right) \times \frac{9.80 \text{ m}}{\text{s}^2} \times \left( 8 \text{ in} \times \frac{2.54 \text{ cm}}{\text{in}} \times \frac{1 \text{ m}}{100 \text{ cm}} \right) = 160 \text{ J} \approx 200 \text{ J}$$

200 J of energy are needed to climb one step. The total number of steps to climb are:

$$2 \times 10^6 \text{ J} \times \frac{1 \text{ step}}{200 \text{ J}} = 1 \times 10^4 \text{ steps}$$



$w = -P\Delta V$ ; Since  $PV = nRT$ , then at constant T and P,  $P\Delta V = RT\Delta n$  where  $\Delta n = \text{mol gaseous products} - \text{mol gaseous reactants}$ .

For:  $2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$ ,  $\Delta H = -2(-285.8 \text{ kJ}) = 571.6 \text{ kJ}$  and  $\Delta n = 3 - 0 = 3$

$$\Delta H = \Delta E + P\Delta V = \Delta E + RT\Delta n, \quad \Delta E = \Delta H - RT\Delta n = 571.6 \times 10^3 \text{ J} - 8.3145 \text{ J/mol}\cdot\text{K} (298 \text{ K})(3 \text{ mol})$$

$$\Delta E = 5.716 \times 10^5 \text{ J} - 7430 \text{ J} = 5.642 \times 10^5 \text{ J} = 564.2 \text{ kJ}$$