Chapter 6

Thermochemistry

Concept Check 6.1

A solar-powered water pump has photovoltaic cells on protruding top panels. These cells collect energy from sunlight, storing it momentarily in a battery, which later runs an electric motor that pumps water up to a storage tank on a hill. What energy conversions are involved in using sunlight to pump water into the storage tank?

Solution

The photovoltaic cells collect the sun's energy, converting it to electric energy. This electric energy is stored in the battery as chemical energy, which is later changed back to electric energy that runs a motor. As the motor rotates, it changes the electric energy to kinetic energy (energy of motion) of the motor, then of the water, which in turn is changed to potential energy (energy of position) of water as the water moves upward in the gravitation field of earth.

Concept Check 6.2

Natural gas consists primarily of methane, CH_4. It is used in a process called steam reforming to prepare a gaseous mixture of carbon monoxide and hydrogen for industrial use.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g);\ \Delta H = 206 \text{ kJ}$$

The reverse reaction, the reaction of carbon monoxide and hydrogen, has been explored as a way to prepare methane (synthetic natural gas). Which of the following are exothermic? Of these, which one is the most exothermic?

a. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

b. $2CH_4(g) + 2H_2O(g) \rightarrow 2CO(g) + 6H_2(g)$

c. $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$

d. $2CO(g) + 6H_2(g) \rightarrow 2CH_4(g) + 2H_2O(g)$

Solution

a. This reaction is the one shown in the problem, and it has a positive ΔH, so the reaction is endothermic.
b. This reaction is simply twice a., so it is also endothermic.
c. This reaction is the reverse of a., so it is exothermic.
d. This reaction is simply twice that of c., so it is more exothermic than c.

Thus, d. is the most exothermic reaction.

Concept Check 6.3

The heat of fusion (also called heat of melting), ΔH_{fus}, of ice is the enthalpy change for

$H_2O(s) \rightarrow H_2O(l)$; ΔH_{fus}.

Similarly, the heat of vaporization, ΔH_{vap}, of liquid water is the enthalpy change for

$H_2O(l) \rightarrow H_2O(g)$; ΔH_{vap}.

How is the heat of sublimation, ΔH_{sub}, the enthalpy change for the reaction

$H_2O(s) \rightarrow H_2O(g)$; ΔH_{sub}

related to ΔH_{fus} and ΔH_{vap}?

Solution

You can think of the sublimation of ice as taking place in two stages. First, the solid melts to liquid, then the liquid vaporizes. The first process has an enthalpy ΔH_{fus}. The second process has an enthalpy ΔH_{vap}. Therefore, the total enthalpy, which is the enthalpy of sublimation, is the sum of these two enthalpies:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Conceptual Problem 6.25

A small car is traveling at twice the speed of a larger car, which has twice the mass of the smaller car. Which car has the greater kinetic energy? (Or do they both have the same kinetic energy?)

Solution

Kinetic energy is proportional to mass and to speed squared. Compare the kinetic energy of the smaller car with that of the larger car (with twice the mass), assuming both are traveling at the same speed. The larger car would have twice the kinetic energy of the smaller car. Or, we could say that the smaller car has only half the kinetic energy of the larger car. Now suppose the speed of the smaller car is increased by a factor of two (so it is now moving at twice its original speed). Its kinetic energy is increased by a factor of four. Therefore, the smaller car now has one-half times four times, or twice, the kinetic energy of the larger car. The smaller car has the greater kinetic energy.

Conceptual Problem 6.26

The equation for the combustion of butane, C_4H_{10}, is

$C_4H_{10}(g) + (13/2)O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

Which one of the following generates the least heat? Why?

a. Burning one mole of butane.
b. Reacting one mole of oxygen with excess butane.
c. Producing one mole of carbon dioxide by burning butane.
d. Producing one mole of water by burning butane.

Solution

The equation says that 1 mol of butane reacts with (13/2) mol of oxygen to yield 4 mol carbon dioxide and 5 mol water. The reaction yields a certain amount of heat, which you can symbolize as *q*. So a. yields heat *q*. On the other hand, b. is only 1 mol oxygen, not (13/2) mol. So, b. yields heat equal to (2/13) *q*. This result might be easier to see by first looking at c. Note that the one mole of carbon dioxide stated in c. is only ¼ that given in the equation. This means that c. yields ¼ *q* (just the inverse of the coefficient in the equation). Similarly, d. yields (1/5) *q*. Therefore, b. yields the least heat.

Conceptual Problem 6.27

A 250g sample of water at 20.0 degrees Celsius is placed in a freezer that is held at a constant temperature of –20.0 degrees Celsius. Considering the water as the "system," answer the following questions

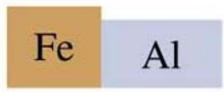
a. What is the sign of q_{sys} for the water after it is placed in the freezer?
b. After a few hours, what will be the state of the water?
c. How will the initial enthalpy for the water compare with the final enthalpy of the water after it has spent several hours in the freezer?
d. What will the temperature of the water be after several hours in the freezer?

Solution

a. After the water is placed into the freezer, it will lose heat to the freezer, so q_{sys} is negative.
b. The water will have turned to ice.
c. The initial enthalpy (of the water) is higher than the final enthalpy (of the ice).
d. After several hours, the temperature of the water will be -20°C.

Conceptual Problem 6.28

A 20.0 g block of iron at 50.0 degrees Celsius and a 20.0 g block of aluminum at 45 degrees Celsius are placed in contact with each other.

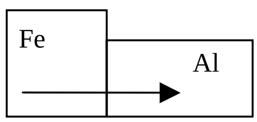


Assume that heat is only transferred between the two blocks.

a. Draw an arrow indicating the heat flow between the blocks.
b. What is the sign of q_{sys} for the aluminum when the blocks first come into contact?
c. What will you observe when q_{sys} for the iron is zero?
d. Estimate the temperature of the Al and Fe blocks when q_{sys} of the iron equals the q_{sys} of the aluminum.

Solution

a. Heat will flow from the iron block to the aluminum block.



b. The aluminum block will be absorbing heat, so q_{sys} will be positive.
c. The temperatures of the aluminum block and the iron block will both be the same.
d. The heat gained by the aluminum will equal the heat lost by the iron. Each heat term will be equal to mass x sp ht x ΔT. This gives

$$(20.0\ g)(0.901\ J/g°C)(T_f - 45.0°C) = (20.0\ g)(0.449\ J/g°C)(50.0°C - T_f)$$

You can cancel the mass and the units from both sides to give a simplified expression

$$(0.901)(T_f - 45.0°C) = (0.449)(50.0°C - T_f)$$

This can be simplified to give 1.350 T_f = 62.995, or T_f = 46.$\underline{6}$6 = 46.7°C.

Conceptual Problem 6.29

What is the enthalpy change for the preparation of one mol of liquid water from the elements, given the following equations?

$$H_2(g) + (1/2)O_2(g) \rightarrow H_2O(g);\ \Delta H_f$$
$$H_2O(l) \rightarrow H_2O(g);\ \Delta H_{vap}$$

Solution

You can imagine this process taking place in two steps: first, the preparation of water vapor from the elements, and second, the change of the vapor to liquid. Here are the equations:

$H_2(g) + ½O_2(g) \rightarrow H_2O(g);\ \Delta H_f$

$H_2O(g) \rightarrow H_2O(l);\ -\Delta H_{vap}$

The last equation is the reverse of the vaporization of water, so the enthalpy of the step is the negative of the enthalpy of vaporization. The enthalpy change for the preparation of one mole of liquid water, Δ*H*, is the sum of the enthalpy changes for these two steps:

$$\Delta H = \Delta H_f + (-\Delta H_{vap}) = \Delta H_f - \Delta H_{vap}$$

Conceptual Problem 6.30

A block of aluminum and a block of iron, both having the same mass, are removed from a freezer and placed outside on a warm day. When the same quantity of heat has flowed into each block, which block will be warmer? Assume that neither block has yet reached the outside temperature. (See Table 6.1 for the specific heats of the metals.)

Solution

The expression for the heat is q = s x m x Δt. For the same amount of heat and mass, the product s x Δt must be constant. The metal with the smaller specific heat will have the larger Δt. Since the specific heat for aluminum (0.901 J/g°C) is larger than for iron (0.449 J/g°C), the block of iron will have the larger Δt and be warmer.

Conceptual Problem 6.31

You have two samples of different metals, metal A and metal B, each having the same mass. You heat both metals to 95 degrees Celsius and then place each one into separate beakers containing the same quantity of water at 25 degrees Celsius.

a. You measure the temperatures of the water in the two beakers when each metal has cooled by 10 degrees Celsius and find that the temperature of the water with metal A is higher than the temperature of the water with metal B. Which metal has the greater specific heat? Explain.

b. After waiting a period of time, the temperature of the water in each beaker rises to a mazimum value. In which beaker does the water rise to the higher value, the one with metal A or the one with metal B? Explain.

Solution

a. The heat lost by the metal is equal to the heat gained by the water. Since $q = s \times m \times \Delta t$, the heat gained by the water is directly proportional to Δt. Since Δt is larger for metal A, it lost more heat. Now, each metal has the same mass and Δt, so the specific heat is directly proportional to q. Since q is larger for A, the specific heat is larger for A.

b. The metal with the higher specific heat will have absorbed more heat to reach the starting temperature of 95°C; therefore, it will release more heat to the water causing the water to reach a higher temperature. The beaker with metal A will rise to the higher temperature.

Conceptual Problem 6.32

A soluble salt, MX_2, is added to water in a beaker. The equation for the dissolving of the salt is:

$$MX_2(s) \rightarrow M^{2+}(aq) + 2X^{-}(aq); \Delta H > 0$$

a. Immediately after the salt dissolves, is the solution warmer or colder?
b. Indicate the direction of heat flow, in or out of the beaker, while the salt dissolves.
c. After the salt dissolves and the water returns to room temperature, what is the value of q for the system?

Solution

a. Since ΔH is positive, the reaction is endothermic, and the solution will be colder.
b. While the salt dissolves, heat will flow into the beaker to raise the temperature of the water back to the initial temperature.
c. After the water returns to room temperature, q for the system will be zero.