WORKED EXAMPLE 8.1 Calculating the Amount of *PV* Work

Calculate the work in kilojoules done during a reaction in which the volume expands from 12.0 L to 14.5 L against an external pressure of 5.0 atm.

Strategy

Expansion work done during a chemical reaction is calculated with the formula $w = -P\Delta V$, where P is the external pressure opposing the change in volume. In this instance, $P = 5.0$ atm and $\Delta V = (14.5 - 12.0)\ \text{L} = 2.5\ \text{L}$. Remember that an expanding system loses work energy, which thus has a negative sign.

Solution

$$w = -(5.0\ \text{atm})(2.5\ \text{L}) = -12.5\ \text{L}\cdot\text{atm}$$

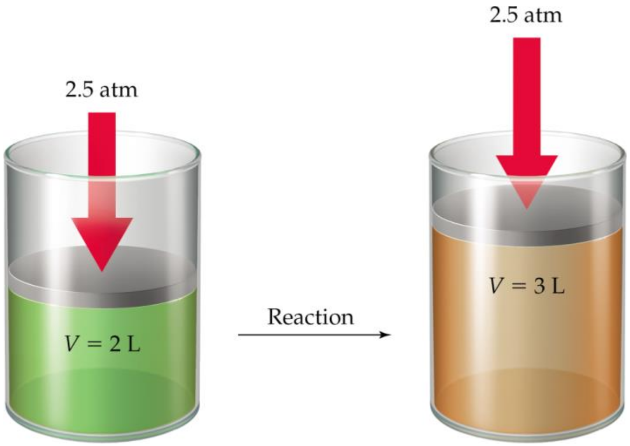
$$(-12.5\ \text{L}\cdot\text{atm})\left(101\ \frac{\text{J}}{\text{L}\cdot\text{atm}}\right) = -1.3 \times 10^{3}\ \text{J} = -1.3\ \text{kJ}$$

WORKED EXAMPLE 8.1 Calculating the Amount of *PV* Work

Continued

PROBLEM 8.2 Calculate the work in kilojoules done during a synthesis of ammonia in which the volume contracts from 8.6 L to 4.3 L at a constant external pressure of 44 atm. In which direction does the work energy flow? What is the sign of the energy change?

KEY CONCEPT PROBLEM 8.3 How much work is done in kilojoules, and in which direction, as a result of the following reaction?



WORKED EXAMPLE 8.2 Calculating ΔE for a Reaction

The reaction of nitrogen with hydrogen to make ammonia, has $\Delta H^\circ = -92.2\text{kJ}$:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \qquad \Delta H^\circ = -92.2\text{ kJ}$$

What is the value of ΔE in kilojoules if the reaction is carried out at a constant pressure of 40.0 atm and the volume change is −1.12 L?

Strategy

We are given an enthalpy change (ΔH), a volume change (ΔV), and a pressure (P), and we are asked to find an energy change (ΔE). Rearrange the equation $\Delta H = \Delta E + P\,\Delta V$ to the form $\Delta E = \Delta H - P\,\Delta V$, and substitute the appropriate values for ΔH, P, and ΔV:

Solution

$$\begin{aligned}
&\Delta E = \Delta H - P\Delta V\\
\text{where}\quad &\Delta H = -92.2\text{ kJ}\\
&P\Delta V = (40.0\text{ atm})(-1.12\text{ L}) = -44.8\text{ L}\cdot\text{atm}\\
&\qquad = (-44.8\text{ L}\cdot\text{atm})\left(101\,\frac{\text{J}}{\text{L}\cdot\text{atm}}\right) = -4520\text{ J} = -4.52\text{ kJ}\\
&\Delta E = (-92.2\text{ kJ}) - (-4.52\text{ kJ}) = -87.7\text{ kJ}
\end{aligned}$$

Note that ΔE is smaller (less negative) than ΔH for this reaction because the volume change is negative. The products have less volume than the reactants, so a contraction occurs and a small amount of PV work is gained by the system.

WORKED EXAMPLE 8.2 Calculating Δ*E* for a Reaction

Continued

PROBLEM 8.5 The reaction between hydrogen and oxygen to yield water vapor has $\Delta H^\circ = -484$ kJ:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H^\circ = -484\text{ kJ}$$

How much *PV* work is done, and what is the value of Δ*E* in kilojoules for the reaction of 0.50 mol of H_2 with 0.25 mol of O_2 at atmospheric pressure if the volume change is –5.6L?

PROBLEM 8.6 The explosion of 2.00 mol of solid trinitrotoluene (TNT, $C_7H_5N_3O_6$) with a volume of approximately 274 mL produces gases with a volume of 448 L at room temperature and 1.0 atm pressure. How much *PV* work in kilojoules is done during the explosion?

$$2\,C_7H_5N_3O_6(s) \longrightarrow 12\,CO(g) + 5\,H_2(g) + 3\,N_2(g) + 2\,C(s)$$

WORKED EXAMPLE 8.3 Calculating the Amount of Heat Released in a Reaction

How much heat in kilojoules is evolved when 5.00 g of aluminum reacts with a stoichiometric amount of FE_2O_3?

$$2\ \text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2\ \text{Fe}(s) + \text{Al}_2\text{O}_3(s) \qquad \Delta H^\circ = -852\ \text{kJ}$$

Strategy

According to the balanced equation, 852 kJ of heat is evolved from the reaction of 2 mol of Al. To find out how much heat is evolved from the reaction of 5.00 g of Al, we have to find out how many moles of aluminum are in 5.00 g.

Solution

The molar mass of Al is 26.98 g/mol, so 5.00 g of Al equals 0.185 mol:

$$5.00\ \text{g Al} \times \frac{1\ \text{mol Al}}{26.98\ \text{g Al}} = 0.185\ \text{mol Al}$$

Because 2 mol of Al releases 852 kJ of heat, 0.185 mol of Al releases 78.8 kJ of heat:

$$0.185\ \text{mol Al} \times \frac{852\ \text{kJ}}{2\ \text{mol Al}} = 78.8\ \text{kJ}$$

Ballpark Check

Since the molar mass of Al is about 27 g, 5 g of aluminum is roughly 0.2 mol, and the heat evolved is about 852/2 kJ/mol × 0.2 mol, or approximately 85 kJ.

WORKED EXAMPLE 8.3 Calculating the Amount of Heat Released in a Reaction

Continued

PROBLEM 8.7 How much heat in kilojoules is evolved or absorbed in each of the following reactions?

(a) Burning of 15.5 g of propane:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H^\circ = -2220 \text{ kJ}$$

(b) Reaction of 4.88 g of barium hydroxide octahydrate with ammonium chloride:

$$Ba(OH)_2 \cdot 8\,H_2O(s) + 2\,NH_4Cl(s) \longrightarrow BaCl_2(aq) + 2\,NH_3(aq) + 10\,H_2O(l) \qquad \Delta H^\circ = +80.3 \text{ kJ}$$

PROBLEM 8.8 Nitromethane (CH_3NO_2), sometimes used as a fuel in drag racers, burns according to the following equation:

$$4\,CH_3NO_2(l) + 7\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(g) + 4\,NO_2(g) \qquad \Delta H^\circ = -2441.6 \text{ kJ}$$

How much heat is released by burning 100.0 g of nitromethane?

WORKED EXAMPLE 8.4 Calculating a Specific Heat

What is the specific heat of silicon if it takes 192 J to raise the temperature of 45.0 g of Si by 6.0 ° C?

Strategy

To find a specific heat of a substance, calculate the amount of energy necessary to raise the temperature of 1 g of the substance by 1 ° C.

Solution

$$\text{Specific heat of Si} = \frac{192\ \text{J}}{(45.0\ \text{g})(6.0\ ^\circ\text{C})} = 0.71\ \text{J}/(\text{g}\cdot{}^\circ\text{C})$$

WORKED EXAMPLE 8.5 Calculating Δ*H* in a Calorimetry Experiment

Aqueous silver ion reacts with aqueous chloride ion to yield a white precipitate of solid silver chloride:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

When 10.0 mL of 1.00 M$AgNO_3$ solution is added to 10.0 mL of 1.00 M NaCl solution at 25.0 ° C in a calorimeter, a white precipitate of AgCl forms and the temperature of the aqueous mixture increases to 32.6 ° C. Assuming that the specific heat of the aqueous mixture is 4.18 J/(g • ° C), that the density of the mixture is 1.00 g/mL, and that the calorimeter itself absorbs a negligible amount of heat, calculate Δ*H* in kilojoules for the reaction.

Strategy

Because the temperature rises during the reaction, heat must be liberated and Δ*H* must be negative. The amount of heat evolved during the reaction is equal to the amount of heat absorbed by the mixture:

$$\text{Heat evolved} = \text{Specific heat} \times \text{Mass of mixture} \times \text{Temperature change}$$

Calculating the heat evolved on a per-mole basis then gives the enthalpy change Δ*H*.

Solution

$$\text{Specific heat} = 4.18\ \text{J/(g}\cdot{}^\circ\text{C)}$$

$$\text{Mass} = (20.0\ \text{mL})\left(1.00\ \frac{\text{g}}{\text{mL}}\right) = 20.0\ \text{g}$$

$$\text{Temperature change} = 32.6\ {}^\circ\text{C} - 25.0\ {}^\circ\text{C} = 7.6\ {}^\circ\text{C}$$

$$\text{Heat evolved} = \left(4.18\ \frac{\text{J}}{\text{g}\cdot{}^\circ\text{C}}\right)(20.0\ \text{g})(7.6\ {}^\circ\text{C}) = 6.4 \times 10^2\ \text{J}$$

According to the balanced equation, the number of moles of AgCl produced equals the number of moles of Ag^+ (or $C1^-$) reacted:

$$\text{Moles of } Ag^+ = (10.0\ \text{mL})\left(\frac{1.00\ \text{mol } Ag^+}{1000\ \text{mL}}\right) = 1.00 \times 10^{-2}\ \text{mol } Ag^+$$

$$\text{Moles of AgCl} = 1.00 \times 10^{-2}\ \text{mol AgCl}$$

$$\text{Heat evolved per mole of AgCl} = \frac{6.4 \times 10^2\ \text{J}}{1.00 \times 10^{-2}\ \text{mol AgCl}} = 64\ \text{kJ/mol AgCl}$$

Therefore, Δ*H* = –64 KJ (negative because heat is released)

WORKED EXAMPLE 8.5 Calculating Δ*H* in a Calorimetry Experiment

Continued

PROBLEM 8.9 Assuming that Coca-Cola has the same specific heat as water [4.18 J/(g · °C)], calculate the amount of heat in kilojoules transferred when one can (about 350 g) is cooled from 25 °C to 3 °C.

PROBLEM 8.10 What is the specific heat of lead if it takes 97.2 J to raise the temperature of a 75.0 g block by 10.0 °C?

PROBLEM 8.11 When 25.0 mL of 1.0 MH_2SO_4 is added to 50.0 mL of 1.0 M NaOH at 25.0 °C in a calorimeter, the temperature of the aqueous solution increases to 33.9 °C. Assuming that the specific heat of the solution is 4.18 J/(g · °C), that its density is 1.00 g/mL, and that the calorimeter itself absorbs a negligible amount of heat, calculate ΔH in kilojoules for the reaction.

$$H_2SO_4(aq) + 2\,NaOH(aq) \longrightarrow 2\,H_2O(l) + Na_2SO_4(aq)$$

WORKED EXAMPLE 8.6 Using Hess's Law to Calculate ΔH°

Methane, the main constituent of natural gas, burns in oxygen to yield carbon dioxide and water:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$

Use the following information to calculate ΔH° in kilojoules for the combustion of methane:

$$\begin{array}{ll}
CH_4(g) + O_2(g) \longrightarrow CH_2O(g) + H_2O(g) & \Delta H^\circ = -275.6\text{ kJ} \\
CH_2O(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g) & \Delta H^\circ = -526.7\text{ kJ} \\
H_2O(l) \longrightarrow H_2O(g) & \Delta H^\circ = 44.0\text{ kJ}
\end{array}$$

Strategy

It often takes some trial and error, but the idea is to combine the individual reactions so that their sum is the desired reaction. The important points are that:

- All the reactants [$CH_4(g)$ and $O_2(g)$] must appear on the left.
- All the products [$CO_2(g)$ and $H_2O(l)$] must appear on the right.
- All intermediate products [$CH_2O(g)$ and $H_2O(g)$] must occur on *both* the left and the right so that they cancel.
- A reaction written in the reverse of the direction given [$H_2O(g) \rightarrow H_2O(l)$] must have the sign of its ΔH° reversed (Section 8.6).
- If a reaction is multiplied by a coefficient [$H_2O(g) \rightarrow H_2O(l)$ is multiplied by 2], then ΔH° for the reaction must be multiplied by the same coefficient.

Solution

$$\begin{array}{lr}
CH_4(g) + O_2(g) \longrightarrow \cancel{CH_2O(g)} + \cancel{H_2O(g)} & \Delta H^\circ = -275.6\text{ kJ} \\
\cancel{CH_2O(g)} + O_2(g) \longrightarrow CO_2(g) + \cancel{H_2O(g)} & \Delta H^\circ = -526.7\text{ kJ} \\
2\,[\cancel{H_2O(g)} \longrightarrow H_2O(l)] & 2\,[\Delta H^\circ = -44.0\text{ kJ}] = -88.0\text{ kJ} \\
\hline
CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) & \Delta H^\circ = -890.3\text{ kJ}
\end{array}$$

WORKED EXAMPLE 8.7 Using Hess's Law to Calculate $\Delta H°$

Water gas is the name for the mixture of CO and H_2 prepared by the reaction of steam with carbon at 1000 °C:

$$\underbrace{C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)}_{\text{“Water gas”}}$$

The hydrogen is then purified and used as a starting material for preparing ammonia. Use the following information to calculate $\Delta H°$ in kilojoules for the water-gas reaction:

$$\begin{array}{ll}
C(s) + O_2(g) \longrightarrow CO_2(g) & \Delta H° = -393.5\ \text{kJ} \\
2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) & \Delta H° = -566.0\ \text{kJ} \\
2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) & \Delta H° = -483.6\ \text{kJ}
\end{array}$$

Strategy

As in Worked Example 8.6, the idea is to find a combination of the individual reactions whose sum is the desired reaction. In this instance, it's necessary to reverse the second and third steps and to multiply both by 1/2 to make the overall equation balance. In so doing, the signs of the enthalpy changes for those steps must be changed and multiplied by 1/2. (Alternatively, we could multiply the first step by 2 and then divide the final result by 2.) Note that $CO_2(g)$ and $O_2(g)$ cancel because they appear on both the right and left sides of equations.

Solution

$$\begin{array}{lrr}
C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} & \Delta H° = & -393.5\ \text{kJ} \\
1/2\,[2\,\cancel{CO_2(g)} \longrightarrow 2\,CO(g) + \cancel{O_2(g)}] & 1/2\,[\Delta H° = 566.0\ \text{kJ}] = & 283.0\ \text{kJ} \\
1/2\,[2\,H_2O(g) \longrightarrow 2\,H_2(g) + \cancel{O_2(g)}] & 1/2\,[\Delta H° = 483.6\ \text{kJ}] = & 241.8\ \text{kJ} \\
\hline
C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) & \Delta H° = & 131.3\ \text{kJ}
\end{array}$$

The water-gas reaction is endothermic by 131.3 kJ.

WORKED EXAMPLE 8.7 Using Hess's Law to Calculate ΔH°

Continued

PROBLEM 8.12 The industrial degreasing solvent methylene chloride (CH_2Cl_2) is prepared from methane by reaction with chlorine:

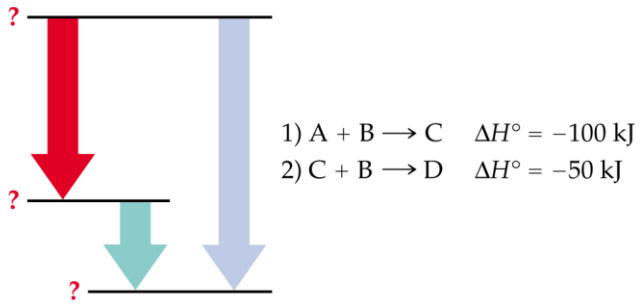
$$CH_4(g) + 2\,Cl_2(g) \longrightarrow CH_2Cl_2(g) + 2\,HCl(g)$$

Use the following data to calculate ΔH° in kilojoules for the reaction:

$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g) \qquad \Delta H^\circ = -98.3\text{ kJ}$$

$$CH_3Cl(g) + Cl_2(g) \longrightarrow CH_2Cl_2(g) + HCl(g) \qquad \Delta H^\circ = -104\text{ kJ}$$

KEY CONCEPT PROBLEM 8.13 The reaction of A with B to give D proceeds in two steps and can be represented by the following Hess's law diagram:



1) $A + B \longrightarrow C \quad \Delta H^\circ = -100\text{ kJ}$
2) $C + B \longrightarrow D \quad \Delta H^\circ = -50\text{ kJ}$

(a) What are the equation and ΔH° for the net reaction?
(b) Which arrow on the diagram corresponds to which step? Which arrow corresponds to the net reaction?
(c) The diagram shows three energy levels. The energies of which substances are represented by each?

KEY CONCEPT PROBLEM 8.14 Draw a Hess's law diagram similar to that in Problem 8.13 depicting the energy changes for the reaction in Problem 8.12.

WORKED EXAMPLE 8.8 Using Standard Heats of Formation to Calculate $\Delta H°$

Calculate $\Delta H°$ in kilojoules for the synthesis of lime (CaO) from limestone ($CaCO_3$), an important step in the manufacture of cement.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \begin{aligned} \Delta H°_f[CaCO_3(s)] &= -1207.6 \text{ kJ/mol} \\ \Delta H°_f[CaO(s)] &= -634.9 \text{ kJ/mol} \\ \Delta H°_f[CO_2(g)] &= -393.5 \text{ kJ/mol} \end{aligned}$$

Strategy

Subtract the heat of formation of the reactant from the sum of the heats of formation of the products.

Solution

$$\begin{aligned} \Delta H° &= [\Delta H°_f(CaO) + \Delta H°_f(CO_2)] - [\Delta H°_f(CaCO_3)] \\ &= (1 \text{ mol})(-634.9 \text{ kJ/mol}) + (1 \text{ mol})(-393.5 \text{ kJ/mol}) - (1 \text{ mol})(-1207.6 \text{ kJ/mol}) \\ &= 179.2 \text{ kJ} \end{aligned}$$

The reaction is endothermic by 179.2 kJ.

WORKED EXAMPLE 8.9 Using Standard Heats of Formation to Calculate $\Delta H°$

Oxyacetylene welding torches burn acetylene gas, $C_2H_2(g)$. Use the information in Table 8.2 to calculate $\Delta H°$ in kilojoules for the combustion reaction of acetylene to yield CO_2 and $H_2O(g)$.

Strategy and Solution

Write the balanced equation, look up the appropriate heats of formation for each reactant and product in Table 8.2, and then carry out the calculation, making sure to multiply each $\Delta H°_f$ by the coefficient given in the balanced equation. Remember also that $\Delta H°_f(O_2) = 0$ kj/mol.

The balanced equation is

$$2\,C_2H_2(g) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 2\,H_2O(g)$$

The necessary heats of formation are

$$\Delta H°_f[C_2H_2(g)] = 227.4\text{ kJ/mol} \qquad \Delta H°_f[H_2O(g)] = -241.8\text{ kJ/mol}$$
$$\Delta H°_f[CO_2(g)] = -393.5\text{ kJ/mol}$$

The standard enthalpy change for the reaction is

$$\begin{aligned}\Delta H° &= [4\,\Delta H°_f(CO_2) + 2\,\Delta H°_f(H_2O)] - [2\,\Delta H°_f(C_2H_2)] \\ &= (4\text{ mol})(-393.5\text{ kJ/mol}) + (2\text{ mol})(-241.8\text{ kJ/mol}) - (2\text{ mol})(227.4\text{ kJ/mol}) \\ &= -2512.4\text{ kJ}\end{aligned}$$

PROBLEM 8.15 Use the information in Table 8.2 to calculate $\Delta H°$ in kilojoules for the reaction of ammonia with O_2 to yield nitric oxide (NO) and $H_2O(g)$, a step in the Ostwald process for the commercial production of nitric acid.

PROBLEM 8.16 Use the information in Table 8.2 to calculate $\Delta H°$ in kilojoules for the photosynthesis of glucose ($C_6H_{12}O_6$) and O_2 from CO_2, and liquid H_2O, a reaction carried out by all green plants.

WORKED EXAMPLE 8.10 Using Bond Dissociation Energies to Calculate Δ*H*°

Use the data in Table 5.1 (page 139) to find an approximate ΔH° in kilojoules for the industrial synthesis of chloroform by reaction of methane with $C1_2$.

$$CH_4(g) + 3\,Cl_2(g) \longrightarrow CHCl_3(g) + 3\,HCl(g)$$

Strategy

Identify all the bonds in the reactants and products, and look up the appropriate bond dissociation energies in Table 5.1. Then subtract the sum of the bond dissociation energies in the products from the sum of the bond dissociation energies in the reactants to find the enthalpy change for the reaction.

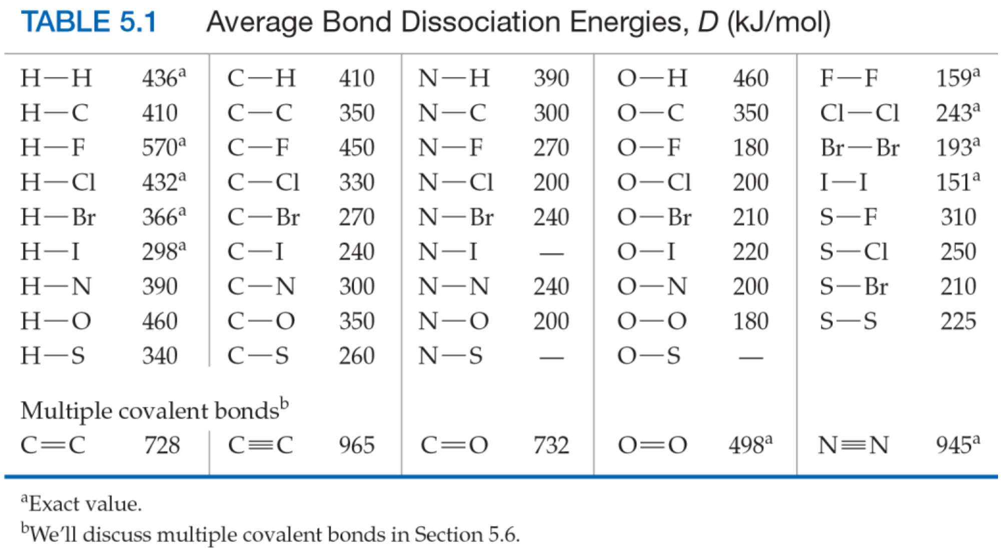


TABLE 5.1 Average Bond Dissociation Energies, *D* (kJ/mol)

H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		
Multiple covalent bonds[b]									
C═C	728	C≡C	965	C═O	732	O═O	498[a]	N≡N	945[a]

[a] Exact value.

[b] We'll discuss multiple covalent bonds in Section 5.6.

WORKED EXAMPLE 8.10 Using Bond Dissociation Energies to Calculate $\Delta H°$

Continued

Solution

The reactants have four C — H bonds and three C1 — C1 bonds; the products have one C — H bond, three C — C1 bonds, and three H — C1 bonds. The bond dissociation energies from Table 5.1 are:

$\text{C—H} \quad D = 410\ \text{kJ/mol} \qquad \text{Cl—Cl} \quad D = 243\ \text{kJ/mol}$

$\text{C—Cl} \quad D = 330\ \text{kJ/mol} \qquad \text{H—Cl} \quad D = 432\ \text{kJ/mol}$

Subtracting the product bond dissociation energies from the reactant bond dissociation energies gives the enthalpy change for the reaction:

$$\begin{aligned}\Delta H° &= [3\,D_{\text{Cl—Cl}} + 4\,D_{\text{C—H}}] - [D_{\text{C—H}} + 3\,D_{\text{H—Cl}} + 3\,D_{\text{C—Cl}}]\\ &= [(3\ \text{mol})(243\ \text{kJ/mol}) + (4\ \text{mol})(410\ \text{kJ/mol})] - [(1\ \text{mol})(410\ \text{kJ/mol})\\ &\qquad + (3\ \text{mol})(432\ \text{kJ/mol}) + (3\ \text{mol})(330\ \text{kJ/mol})]\\ &= -327\ \text{kJ}\end{aligned}$$

The reaction is exothermic by approximately 330 kJ.

PROBLEM 8.17 Use the data in Table 5.1 (page 139) to calculate an approximate $\Delta H°$ in kilojoules for the industrial synthesis of ethyl alcohol from ethylene: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$.

PROBLEM 8.18 Use the data in Table 5.1 to calculate an approximate $\Delta H°$ in kilojoules for the synthesis of hydrazine from ammonia: $2\ NH_3(g) + Cl_2(g) \rightarrow N_2H_4(g) + 2\ HCl(g)$.

WORKED EXAMPLE 8.11 Predicting the Sign of ΔS for a Reaction

Predict whether $\Delta S°$ is likely to be positive or negative for each of the following reactions:

(a) $H_2C{=}CH_2(g) + Br_2(g) \rightarrow BrCH_2CH_2Br(l)$
(b) $2\,C_2H_6(g) + 7\,O_2(g) \rightarrow 4\,CO_2(g) + 6\,H_2O(g)$

Strategy

Look at each reaction, and try to decide whether molecular randomness increases or decreases. Reactions that increase the number of gaseous molecules generally have a positive ΔS, while reactions that decrease the number of gaseous molecules have a negative ΔS.

Solution

(a) The amount of molecular randomness in the system decreases when 2 mol of gaseous reactants combine to give 1 mol of liquid product, so the reaction has a negative $\Delta S°$.

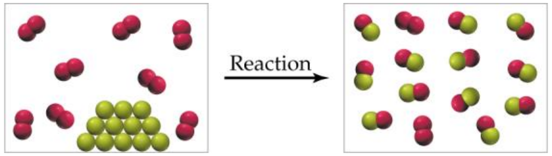
(b) The amount of molecular randomness in the system increases when 9 mol of gaseous reactants give 10 mol of gaseous products, so the reaction has a positive $\Delta S°$.

PROBLEM 8.20 Ethane, C_2H_6, can be prepared by the reaction of acetylene (C_2H_2) with hydrogen:

$$C_2H_2(g) + 2\,H_2(g) \longrightarrow C_2H_6(g)$$

Is $\Delta S°$ for the reaction likely to be positive or negative? Explain.

KEY CONCEPT PROBLEM 8.21 Is the reaction represented in the following drawing likely to have a positive or a negative value of S° ? Explain.



WORKED EXAMPLE 8.12 Using the Free-Energy Equation to Calculate Equilibrium Temperature

Lime (CaO) is produced by heating limestone ($CaCO_3$) to drive off CO_2 gas, a reaction used to make Portland cement. Is the reaction spontaneous under standard conditions at 25 ° C? Calculate the temperature at which the reaction becomes spontaneous.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H^\circ = 179.2\text{ kJ};\ \Delta S^\circ = 160.0\text{ J/K}$$

Strategy

The spontaneity of the reaction at a given temperature can be found by determining whether ΔG is positive or negative at that temperature. The changeover point between spontaneous and nonspontaneous can be found by setting $\Delta G = 0$ and solving for T.

Solution

At 25 ° C (298 K), we have

$$\Delta G = \Delta H - T\Delta S = 179.2\text{ kJ} - (298\text{ K})(0.1600\text{ kJ/K}) = +131.5\text{ kJ}$$

Because ΔG is positive at this temperature, the reaction is nonspontaneous.

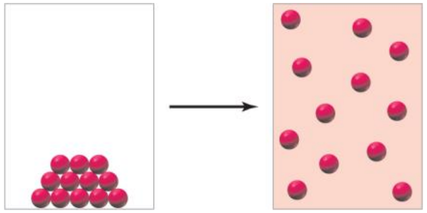
The changeover point between spontaneous and nonspontaneous is approximately

$$T = \frac{\Delta H}{\Delta S} = \frac{179.2\text{ kJ}}{0.1600\text{ kJ/K}} = 1120\text{ K}$$

The reaction becomes spontaneous above approximately 1120 K (847 ° C).

WORKED KEY CONCEPT EXAMPLE 8.13 Predicting the Signs of Δ*H*, Δ*S*, and Δ*G* for a Reaction

What are the signs of Δ*H*, Δ*S*, and Δ*G* for the following nonspontaneous transformation?



Strategy

First, decide what kind of process the drawing represents. Then decide whether the process increases or decreases the entropy of the system and whether it is exothermic or endothermic.

Solution

The drawing shows ordered particles in a solid subliming to give a gas. Formation of a gas from a solid increases molecular randomness, so Δ*S* is positive. Furthermore, because we're told that the process is nonspontaneous, Δ*G* is also positive. Because the process is favored by Δ*S* (positive) yet still nonspontaneous, Δ*H* must be unfavorable (positive). This makes sense, because conversion of a solid to a liquid or gas requires energy and is always endothermic.

PROBLEM 8.22 Which of the following reactions are spontaneous under standard conditions at 25 ° C? Which are nonspontaneous?

(a) $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq) \quad \Delta G^\circ = -55.7\ \text{kJ}$

(b) $2\ C(s) + 2\ H2(g) \rightarrow C_2H_4(g) \quad \Delta G^\circ = 68.1\ \text{kJ}$

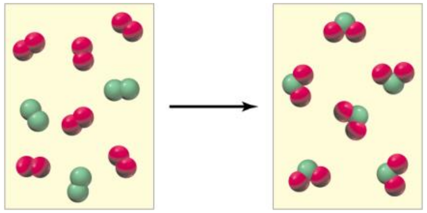
WORKED KEY CONCEPT EXAMPLE 8.13 Predicting the Signs of ΔH, ΔS, and ΔG for a Reaction

Continued

PROBLEM 8.23 Is the Haber process for the industrial synthesis of ammonia spontaneous or nonspontaneous under standard conditions at 25 ° C? At what temperature (° C) does the changeover occur?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \qquad \Delta H^\circ = -92.2\ \text{kJ};\ \Delta S^\circ = -199\ \text{J/K}$$

KEY CONCEPT PROBLEM 8.24 The following reaction is exothermic:



(a) Write a balanced equation for the reaction.
(b) What are the signs of ΔH and ΔS for the reaction?
(c) Is the reaction likely to be spontaneous at low temperatures only, at high temperatures only, or at all temperatures? Explain.