CHAPTER 6
THERMOCHEMISTRY

PROBLEM-SOLVING STRATEGIES AND TUTORIAL SOLUTIONS

TYPES OF PROBLEMS

Problem Type 1: The First Law of Thermodynamics.
- **(a)** Applying the First Law of Thermodynamics.
- **(b)** Calculating the work done in gas expansion.
- **(c)** Enthalpy and the First Law of Thermodynamics. Calculating the internal energy change of a gaseous reaction.

Problem Type 2: Thermochemical Equations.

Problem Type 3: Calculating Heat Absorbed or Released Using Specific Heat Data.

Problem Type 4: Calorimetry.
- **(a)** Constant-volume calorimetry.
- **(b)** Constant-pressure calorimetry.

Problem Type 5: Standard Enthalpy of Formation and Reaction.
- **(a)** Calculating the standard enthalpy of reaction.
- **(b)** Direct method of calculating the standard enthalpy of formation.
- **(c)** Indirect method of calculating the standard enthalpy of formation, Hess's law.

PROBLEM TYPE 1: THE FIRST LAW OF THERMODYNAMICS

A. Applying the First Law of Thermodynamics

The **First Law of Thermodynamics** states that energy can be converted from one form to another, but cannot be created or destroyed. Another way of stating the first law is that the energy of the universe is constant. The universe is composed of both the system and the surroundings.

$$\Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

where,

the subscripts "sys" and "surr" denote system and surroundings, respectively.

However, in chemistry, we are normally interested in the changes associated with the *system* (which may be a flask containing reactants and products), not with its surroundings. Therefore, a more useful form of the first law is

$$\Delta E = q + w \qquad \text{(6.1, text)}$$

where,

ΔE is the change in the internal energy of the system
q is the heat exchange between the system and surroundings
w is the work done on (or by) the system

Using the sign convention for thermochemical processes (see Section 6.3 of your text for discussion), q is positive for an endothermic process and negative for an exothermic process. For work, w is positive for work done *on* the system *by* the surroundings and negative for work done *by* the system *on* the surroundings. Try to understand the sign convention in this manner. If a *system* loses heat to the surroundings or does work on the surroundings, we expect its internal energy to decrease since both processes are energy depleting. Conversely, if heat is added to the *system* or if work is done on the *system*, then the internal energy of the system would increase.

EXAMPLE 6.1

A system does 975 kJ of work on its surroundings while at the same time it absorbs 625 kJ of heat. What is the change in energy, ΔE, for the system?

Strategy: The system does work on the surroundings, so what is the sign for w? Heat is absorbed by the gas from the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution: To calculate the energy change of the gas (ΔE), we need Equation (6.1) of the text. To solve this problem, you must make sure to get the sign convention correct. The system does work on the surroundings; this is an energy-depleting process.

$$w = \mathbf{-975\ kJ}$$

The system absorbs 625 kJ of heat. Therefore, the internal energy of the system would increase.

$$q = \mathbf{+625\ kJ}$$

Finally,

$$\Delta E = q + w = 625\text{ kJ} + (-975\text{ kJ}) = \mathbf{-350\ kJ}$$

PRACTICE EXERCISE

1. The surroundings do 455 kJ of work on the system while at the same time the system releases 253 kJ of heat. What is the change in energy, ΔE, for the system?

Text Problem: 6.18

B. Calculating the work done in gas expansion

A useful example of mechanical work is the expansion of a gas. Picture a gas-filled cylinder that is fitted with a weightless, frictionless, movable piston, at a certain temperature, pressure, and volume. As the gas expands, it pushes the piston upward against a constant, opposing, external atmospheric pressure, P. The gas (system) is doing work on the surroundings. The work can be calculated as follows:

$$w = -P\Delta V \qquad (6.3,\text{ text})$$

where,

P is the external pressure
ΔV is the change in volume ($V_f - V_i$)

Note: The minus sign in the equation takes care of the sign convention for w. For gas expansion, $\Delta V > 0$, so $-P\Delta V$ is a negative quantity. When a gas expands, it's doing work on the surroundings; the internal energy of the system decreases. For gas compression, $\Delta V < 0$, so $-P\Delta V$ is a positive quantity. When a gas is compressed, the surroundings are doing work on the system, increasing the internal energy.

EXAMPLE 6.2

A gas initially at a pressure of 10.0 atm and occupying a volume of 5.0 L is allowed to expand at constant temperature against a constant external pressure of 4.0 atm. After expansion, the gas occupies a volume of 12.5 L. Calculate the work done by the gas on the surroundings.

Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume [Equation (6.3) of the text].

$$w = -P\Delta V$$

What is the conversion factor between L·atm and J?

Solution: We are given the external pressure in the problem, but we must calculate ΔV.

$$\Delta V = V_f - V_i = 12.5\text{ L} - 5.0\text{ L} = \mathbf{7.5\text{ L}}$$

Substitute P and ΔV into Equation (6.3) of the text and solve for w.

$$w = -P\Delta V = -(4.0\text{ atm})(7.5\text{ L}) = \mathbf{-3.0 \times 10^1\text{ L·atm}}$$

It would be more convenient to express w in units of joules. The following conversion factor can be obtained from Appendix 1 of the text:

$$1\text{ L·atm} = 101.3\text{ J}$$

Thus, we can write:

$$w = (-3.0 \times 10^1 \cancel{\text{L·atm}}) \times \frac{101.3\text{ J}}{1 \cancel{\text{L·atm}}} = \mathbf{-3.0 \times 10^3\text{ J}}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

PRACTICE EXERCISE

2. Calculate the work done on the system when 6.0 L of a gas is compressed to 1.0 L by a constant external pressure of 2.0 atm.

Text Problem: 6.20

C. Enthalpy and the First Law of Thermodynamics—Calculating the internal energy change of a gaseous reaction

Let's return to the following form of the first law of thermodynamics.

$$\Delta E_{\text{sys}} = q + w$$

Under constant-pressure conditions we can write:

$$\Delta E = q_p + w$$

Recall that the heat evolved or absorbed (q) by a reaction carried out under constant-pressure conditions is equal to the enthalpy change of the system, ΔH.

Thus,

$$\Delta E = \Delta H + w$$

Also, we know that for gas expansion or compression under a constant external pressure, $w = -P\Delta V$. Substituting into the above equation, we have:

$$\Delta E = \Delta H - P\Delta V$$

Also, for an ideal gas at constant pressure,

$$P\Delta V = \Delta(nRT)$$

$$\Delta V = \frac{\Delta(nRT)}{P}$$

Substituting gives:

$$\Delta E = \Delta H - \Delta(nRT)$$

Finally, at constant temperature,

$$\Delta E = \Delta H - RT\Delta n \qquad (6.10, \text{text})$$

where Δn is defined as

$$\Delta n = \text{number of moles of product gases} - \text{number of moles of reactant gases}$$

EXAMPLE 6.3

Calculate the change in internal energy when 1 mole of H_2 and 1/2 mole of O_2 are converted to 1 mole of H_2O at 1 atm and 25°C.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H° = -286 \text{ kJ/mol}$$

Strategy: Calculate the total change in the number of moles of ***gas***. Note that the product is a liquid. Substitute the values of $\Delta H°$ and Δn into Equation (6.10) of the text.

Solution:

$$\Delta n = 0 \text{ mol} - (1 \text{ mol} + 1/2 \text{ mol}) = -1.5 \text{ mol}$$

Substitute the values for $\Delta H°$ and Δn into Equation (6.10).

$T = 25° + 273° = 298$ K

$$\Delta E° = \Delta H° - RT\Delta n$$

$$\Delta E° = -286 \text{ kJ/mol} - \left(8.314\frac{\cancel{J}}{\text{mol}\cdot\cancel{K}}\right)(298\cancel{K})(-1.5) \times \frac{1 \text{ kJ}}{1000\cancel{J}} = -\mathbf{282\ kJ/mol}$$

PRACTICE EXERCISE

3. Calculate the change in the internal energy when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume that water vapor is an ideal gas and that the volume of liquid water is negligible compared with that of steam at 100°C. [$\Delta H_{vap}(H_2O) = 40.67$ kJ/mol at 100°C].

Text Problem: 6.28

PROBLEM TYPE 2: THERMOCHEMICAL EQUATIONS

Equations showing both the mass and enthalpy relations are called **thermochemical equations**. The following guidelines are helpful in writing and interpreting thermochemical equations:

1. The stoichiometric coefficients always refer to the number of moles of each substance.
2. When an equation is reversed, the roles of reactants and products change. Consequently, the magnitude of ΔH for the equation remains the same, but its sign changes.
3. If both sides of a thermochemical equation are multiplied by a factor n, then ΔH must also be multiplied by the same factor.
4. When writing thermochemical equations, the physical states of all reactants and products must be specified, because they help determine the actual enthalpy changes.

See Section 6.4 of your text for further discussion.

EXAMPLE 6.4
Given the thermochemical equation

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H = -99 \text{ kJ/mol}$$

how much heat is evolved when (a) 1/2 mol of SO_2 reacts and (b) 3 mol of SO_2 reacts?

Strategy: The thermochemical equation shows that for every 1 mole of SO_2 reacted, 99 kJ of heat are given off (note the negative sign). We can write a conversion factor from this information.

$$\frac{-99 \text{ kJ}}{1 \text{ mol } SO_2}$$

Solution:

(a) If 1/2 mole of SO_2 reacts, that means that we are multiplying the equation by 1/2. Therefore, we must multiply ΔH by 1/2.

$$\textbf{heat evolved} = 0.5 \text{ mol } SO_2 \times \frac{99 \text{ kJ}}{1 \text{ mol } SO_2} = \mathbf{5.0 \times 10^1\ kJ}$$

(b) Following the same argument as in part (a):

$$\textbf{heat evolved} = 3(99 \text{ kJ}) = \mathbf{3.0 \times 10^2\ kJ}$$

Why isn't there a negative sign in our answer? The sign convention for an exothermic reaction (energy, as heat, is released by the system) is negative ($-\Delta H$). However, in the above example, we state that heat is evolved, so a negative sign is unnecessary.

Tip: Remember that the heat evolved or absorbed (q) by a reaction carried out under constant-pressure conditions is equal to the enthalpy change of the system, ΔH.

PRACTICE EXERCISE

4. Given the thermochemical equation

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g) \quad \Delta H = -99 \text{ kJ/mol}$$

how much heat is evolved when 75 g of SO_2 is combusted?

Text Problem: 6.26

PROBLEM TYPE 3: CALCULATING HEAT ABSORBED OR RELEASED USING SPECIFIC HEAT DATA

If the specific heat (s) and the amount of substance is known, then the change in the sample's temperature (Δt) will tell us the amount of heat (q) that has been absorbed or released in a particular process. The equation for calculating the heat change is given by:

$$q = ms\Delta t \qquad (6.12, \text{text})$$

or

$$q = C\Delta t$$

where m is the mass of the sample and Δt is the temperature change.

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

EXAMPLE 6.5

How much heat is absorbed by 80.0 g of iron (Fe) when its temperature is raised from 25°C to 500°C? The specific heat of iron is 0.444 J/g·°C.

Strategy: We know the mass, specific heat, and the change in temperature for iron. We can use Equation (6.12) of the text to solve this problem.

Solution: Substitute the known values into Equation (6.12).

$$q = m_{\mathrm{Fe}} s_{\mathrm{Fe}} \Delta t$$

$$q = (80.0\,\cancel{\mathrm{g}})(0.444\ \mathrm{J}/\cancel{\mathrm{g}\cdot{}^\circ\mathrm{C}})(500-25)\cancel{{}^\circ\mathrm{C}} = \mathbf{1.69 \times 10^4\ J}$$

PRACTICE EXERCISE

5. A piece of iron initially at a temperature of 25°C absorbs 10.0 kJ of heat. If its mass is 50.0 g, calculate the final temperature of the piece of iron. The specific heat of iron is 0.444 J/g·°C.

Text Problems: 6.34, **6.36**

PROBLEM TYPE 4: CALORIMETRY

A. Constant-volume calorimetry

For a discussion of constant-volume calorimetry, see Section 6.5 of your text. Heat of combustion is usually measured in a constant-volume calorimeter. The heat released during combustion is absorbed by the calorimeter. Because no heat enters or leaves the system throughout the process, we can write:

$$q_{\mathrm{system}} = 0 = q_{\mathrm{cal}} + q_{\mathrm{rxn}}$$

or,

$$q_{\mathrm{rxn}} = -q_{\mathrm{cal}}$$

The heat absorbed by the calorimeter can be calculated using the heat capacity of the bomb calorimeter and the temperature rise.

$$q_{\mathrm{cal}} = C_{\mathrm{cal}} \Delta t$$

> **Note:** The negative sign for q_{rxn} indicates that heat was released during the combustion. You should expect this, because all combustion processes are exothermic. Thermal energy is transferred from the system to the surroundings.

EXAMPLE 6.6

0.500 g of ethanol [$CH_3CH_2OH(l)$] was burned in a bomb calorimeter. The temperature of the water rose 1.60°C. The heat capacity of the calorimeter plus water was 9.06 kJ/°C.

(a) Write a balanced equation for the combustion of ethanol.

(b) Calculate the molar heat of combustion of ethanol.

(a) Recall that a **combustion reaction** is typically a vigorous and exothermic reaction that takes place between certain substances and oxygen. If the reactant contains only C, H, and/or O, then the products are CO_2 and H_2O. Therefore, the balanced equation for the combustion of ethanol is:

$$CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

(b)

Strategy: Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter? What is the heat generated by the combustion of 0.500 g ethanol? What is the conversion factor between grams and moles of ethanol?

Solution: The heat absorbed by the calorimeter and water is equal to the product of the heat capacity and the temperature change. From Equation (6.16) of the text, assuming no heat is lost to the surroundings, we write

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$
$$q_{\text{cal}} = (9.06\ \text{kJ/°C})(1.60\text{°C}) = 14.5\ \text{kJ}$$

Because $q_{\text{sys}} = 0 = q_{\text{cal}} + q_{\text{rxn}}$, $q_{\text{rxn}} = -q_{\text{cal}}$. The heat change of the reaction is −14.5 kJ. This is the heat released by the combustion of 0.500 g of ethanol; therefore, we can write the conversion factor as

$$\frac{-14.5\ \text{kJ}}{0.500\ \text{g ethanol}}$$

From the molar mass of ethanol and the above conversion factor, the heat of combustion of 1 mole of ethanol can be calculated.

$$\mathcal{M}_{\text{ethanol}} = 2(12.01\ \text{g}) + 6(1.008\ \text{g}) + 16.00\ \text{g} = 46.07\ \text{g}$$

$$\textbf{Molar heat of combustion} = \frac{-14.5\ \text{kJ}}{0.500\ \cancel{\text{g}}\ \text{ethanol}} \times \frac{46.07\ \cancel{\text{g}}\ \text{ethanol}}{1\ \text{mol ethanol}} = \mathbf{-1.34 \times 10^3\ kJ/mol\ ethanol}$$

PRACTICE EXERCISE

6. The combustion of benzoic acid is often used as a standard source of heat for calibrating combustion bomb calorimeters. The heat of combustion of benzoic acid has been accurately determined to be 26.42 kJ/g. When 0.8000 g of benzoic acid was burned in a calorimeter containing water, a temperature rise of 4.08°C was observed. What is the heat capacity of the bomb calorimeter plus water?

Text Problem: 6.102

B. Constant-pressure calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter that is used to determine the heat changes for noncombustion reactions. The reactions usually occur in solution. Because the measurements are carried out under constant atmospheric pressure conditions, the heat change for the process (q_{rxn}) is equal to the enthalpy change (ΔH).

The heat released during reaction is absorbed both by the solution in the calorimeter. We ignore the small heat capacity of the calorimeter in our calculations. Because no heat enters or leaves the system throughout the process, we can write:

$$q_{\text{system}} = 0 = q_{\text{soln}} + q_{\text{rxn}}$$

or,

$$q_{\text{soln}} = -q_{\text{rxn}}$$

The heat absorbed by the solution can be calculated using the equation

$$q_{\text{soln}} = m_{\text{soln}}s_{\text{soln}}\Delta t$$

EXAMPLE 6.7

The heat of neutralization for the following reaction is –56.2 kJ/mol.

$$\mathrm{NaOH}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

1.00×10^2 mL of 1.50 *M* HCl is mixed with 1.00×10^2 mL of 1.50 *M* NaOH in a constant-pressure calorimeter. The initial temperature of the HCl and NaOH solutions is the same, 23.2°C. Calculate the final temperature of the mixed solution. Assume that the density and specific heat of the mixed solution is the same as for water (1.00 g/mL and 4.184 J/g·°C, respectively).

Strategy: The neutralization reaction is exothermic. 56.2 kJ of heat are released when 1 mole of H^+ reacts with 1 mole of OH^-. Assuming no heat is lost to the surroundings, we can equate the heat lost by the reaction to the heat gained by the combined solution. How do we calculate the heat released during the reaction? Are we reacting 1 mole of H^+ with 1 mole of OH^-? How do we calculate the heat absorbed by the combined solution?

Solution: Assuming no heat is lost to the surroundings, we can write:

$$q_{\text{soln}} + q_{\text{rxn}} = 0$$

or

$$q_{\text{soln}} = -q_{\text{rxn}}$$

First, let's set up how we would calculate the heat gained by the solution,

$$q_{\text{soln}} = m_{\text{soln}} s_{\text{soln}} \Delta t$$

where m and s are the mass and specific heat of the solution and $\Delta t = t_f - t_i$.

We assume that the specific heat of the solution is the same as the specific heat of water, and we assume that the density of the solution is the same as the density of water (1.00 g/mL). Since the density is 1.00 g/mL, the mass of 200 mL of solution (100 mL + 100 mL) is 200 g.

Substituting into the equation above, the heat gained by the solution can be represented as:

$$q_{\text{soln}} = (2.00 \times 10^2\ \text{g})(4.184\ \text{J/g·°C})(t_f - 23.2°\text{C})$$

Next, let's calculate q_{rxn}, the heat released when 100 mL of 1.50 *M* HCl are mixed with 100 mL of 1.50 *M* NaOH. There is exactly enough NaOH to neutralize all the HCl. Note that 1 mole HCl ≏ 1 mole NaOH. The number of moles of HCl is:

$$(1.00 \times 10^2\ \cancel{\text{mL}}) \times \frac{1.50\ \text{mol HCl}}{1000\ \cancel{\text{mL}}} = 0.150\ \text{mol HCl}$$

The amount of heat released when 1 mole of H^+ is reacted is given in the problem (–56.2 kJ/mol). The amount of heat liberated when 0.150 mole of H^+ is reacted is:

$$q_{\text{rxn}} = 0.150\ \cancel{\text{mol}} \times \frac{-56.2 \times 10^3\ \text{J}}{1\ \cancel{\text{mol}}} = -8.43 \times 10^3\ \text{J}$$

Finally, knowing that the heat lost by the reaction equals the heat gained by the solution, we can solve for the final temperature of the mixed solution.

$$q_{\text{soln}} = -q_{\text{rxn}}$$

$$(2.00 \times 10^2\ \text{g})(4.184\ \text{J/g·°C})(t_f - 23.2°\text{C}) = -(-8.43 \times 10^3\ \text{J})$$

$$(8.37 \times 10^2)t_f - (1.94 \times 10^4) = 8.43 \times 10^3\ \text{J}$$

$$t_f = \mathbf{33.2°C}$$

PRACTICE EXERCISE

7. A 10.4 g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 75.0 g of water at 23.5°C. The final temperature of the system was found to be 25.7°C. Calculate the specific heat of the metal, then use Table 6.2 of the text to predict the identity of the metal.

Text Problem: 6.38

PROBLEM TYPE 5: STANDARD ENTHALPY OF FORMATION AND REACTION

The **standard enthalpy of formation** (ΔH_f°) is defined as the heat change that results when one mole of a compound is formed from its elements at a pressure of 1 atm. The standard enthalpy of formation of any element in its most stable form is zero.

A. Calculating the standard enthalpy of reaction

From standard enthalpies of formation, we can calculate the **standard enthalpy of reaction, ΔH_{rxn}°**.

Consider the hypothetical reaction

$$aA + bB \longrightarrow cC + dD$$

where *a*, *b*, *c*, and *d* are stoichiometric coefficients.

The standard enthalpy of reaction is given by

$$\Delta H_{rxn}^\circ = [c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)]$$

Note that in calculations, the stoichiometric coefficients are just numbers without units.

The equation can be written in the general form:

$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) \qquad (6.18, \text{text})$$

where *m* and *n* denote the stoichiometric coefficients for the reactants and products, and Σ (sigma) means "the sum of".

EXAMPLE 6.8
A reaction used for rocket engines is

$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(l)$$

What is the standard enthalpy of reaction in kilojoules? The standard enthalpies of formation are ΔH_f° [$N_2H_4(l)$] = 95.1 kJ/mol, ΔH_f° [$H_2O_2(l)$] = −187.8 kJ/mol, and ΔH_f° [$H_2O(l)$] = −285.8 kJ/mol.

Strategy: The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation, ΔH_f°, of the species.

Solution: We use the ΔH_f° values in Appendix 3 and Equation (6.18) of the text.

$$\Delta H_{rxn}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

$$\Delta H_{rxn}^\circ = \Delta H_f^\circ[N_2(g)] + 4\Delta H_f^\circ[H_2O(l)] - \{\Delta H_f^\circ[N_2H_4(l)] + 2\Delta H_f^\circ[H_2O_2(l)]\}$$

Remember, the standard enthalpy of formation of any element in its most stable form is zero. Therefore, $\Delta H_f^\circ [N_2(g)] = 0$.

$$\Delta H_{rxn}^\circ = [0 + 4(-285.8 \text{ kJ/mol})] - [95.1 \text{ kJ/mol} + 2(-187.8 \text{ kJ/mol})] = \mathbf{-862.7\ kJ/mol}$$

PRACTICE EXERCISE

8. The combustion of methane, the main component of natural gas, occurs according to the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_{rxn}^\circ = -890 \text{ kJ/mol}$$

Use standard enthalpies of formation for CO_2 and H_2O to determine the standard enthalpy of formation of methane.

Text Problems: 6.52, 6.54, 6.56, 6.60

B. Direct method of calculating the standard enthalpy of formation

This method of measuring ΔH_f° applies to compounds that can be readily synthesized from their elements. The best way to describe this direct method is to look at an example.

EXAMPLE 6.9

The combustion of sulfur occurs according to the following thermochemical equation:

$$\mathbf{S(rhombic) + O_2(\mathit{g}) \longrightarrow SO_2(\mathit{g}) \qquad \Delta \mathit{H}_{rxn}^\circ = -296\ kJ/mol}$$

What is the enthalpy of formation of SO_2?

Strategy: What is the ΔH_f° value for an element in its standard state?

Solution: Knowing that the standard enthalpy of formation of any element in its most stable form is zero, and using Equation (6.18) of the text, we write:

$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants})$$

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ(SO_2)] - [\Delta H_f^\circ(S) + \Delta H_f^\circ(O_2)]$$

$$-296 \text{ kJ/mol} = [\Delta H_f^\circ(SO_2) - [0 + 0]$$

$$\mathbf{\Delta \mathit{H}_f^\circ(SO_2) = -296\ kJ/mol\ SO_2}$$

Note: You should recognize that this chemical equation as written meets the definition of a *formation* reaction. Thus, ΔH_{rxn}° *is* ΔH_f° of $SO_2(g)$.

PRACTICE EXERCISE

9. Hydrogen iodide (HI) can be produced according to the following equation:

$$H_2(g) + I_2(s) \longrightarrow 2HI(g) \qquad \Delta H_{rxn}^\circ = 51.8 \text{ kJ/mol}$$

What is the enthalpy of formation (ΔH_f°) of HI?

Text Problem: 6.50

C. Indirect method of calculating the standard enthalpy of formation, Hess's law

Many compounds cannot be directly synthesized from their elements. In these cases, ΔH_f° can be determined by an indirect approach using **Hess's law**. Hess's law states that when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. This means that if we can break down the reaction of interest into a series of reactions for which $\Delta H_{\text{rxn}}^\circ$ can be measured, we can calculate $\Delta H_{\text{rxn}}^\circ$ for the overall reaction. Let's look at an example.

EXAMPLE 6.10

From the following heats of combustion with fluorine, calculate the enthalpy of formation of methane, CH_4.

$$\begin{array}{lll} \text{(a)} & CH_4(g) + 4F_2(g) \longrightarrow CF_4(g) + 4HF(g) & \Delta H_{\text{rxn}}^\circ = -1942 \text{ kJ/mol} \\ \text{(b)} & \text{C(graphite)} + 2F_2(g) \longrightarrow CF_4(g) & \Delta H_{\text{rxn}}^\circ = -933 \text{ kJ/mol} \\ \text{(c)} & H_2(g) + F_2(g) \longrightarrow 2HF(g) & \Delta H_{\text{rxn}}^\circ = -542 \text{ kJ/mol} \end{array}$$

Strategy: Our goal is to calculate the enthalpy change for the formation of CH_4 from its elements C and H_2. This reaction does not occur directly, however, so we must use an indirect route using the information given in the three equations, which we will call equations (a), (b), and (c).

Solution: The enthalpy of formation of methane can be determined from the following equation.

$$\text{C(graphite)} + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H_{\text{rxn}}^\circ = ?$$

First, we need one mole of C(graphite) as a reactant. Equation (b) has C(graphite) on the reactant side so let's keep that equation as written. Next, we need two moles of H_2 as a reactant. Equation (c) has 1 mole of H_2 as a reactant, so let's multiply this equation by 2.

$$\text{(d)} \quad 2H_2(g) + 2F_2(g) \longrightarrow 4HF(g) \qquad \Delta H_{\text{rxn}}^\circ = 2(-542 \text{ kJ/mol}) = -1084 \text{ kJ/mol}$$

Last, we need one mole of CH_4 as a product. Equation (a) has one mole of CH_4 as a reactant, so we need to reverse the equation.

$$\text{(e)} \quad CF_4(g) + 4HF(g) \longrightarrow CH_4(g) + 4F_2(g) \qquad \Delta H_{\text{rxn}}^\circ = +1942 \text{ kJ/mol}$$

Note: $\Delta H_{\text{rxn}}^\circ$ changed sign when reversing the direction of the reaction.

Adding Equations (b), (d), and (e) together, we have:

$$\begin{array}{lll} \text{(b)} & \text{C(graphite)} + \cancel{2F_2}(g) \longrightarrow \cancel{CF_4}(g) & \Delta H_{\text{rxn}}^\circ = -933 \text{ kJ/mol} \\ \text{(d)} & 2H_2(g) + \cancel{2F_2}(g) \longrightarrow \cancel{4HF}(g) & \Delta H_{\text{rxn}}^\circ = -1084 \text{ kJ/mol} \\ \text{(e)} & \cancel{CF_4}(g) + \cancel{4HF}(g) \longrightarrow CH_4(g) + \cancel{4F_2}(g) & \Delta H_{\text{rxn}}^\circ = +1942 \text{ kJ/mol} \\ \hline & \text{C(graphite)} + 2H_2(g) \longrightarrow CH_4(g) & \Delta H_{\text{rxn}}^\circ = -75 \text{ kJ/mol} \end{array}$$

Since the above equation represents the synthesis of CH_4 from its elements, the $\Delta H_{\text{rxn}}^\circ$ calculated is the ΔH_f° of methane.

$$\Delta H_{\text{rxn}}^\circ = \mathbf{\Delta H_f^\circ(CH_4) = -75 \text{ kJ/mol}}$$

PRACTICE EXERCISE

10. From the following enthalpies of reaction, calculate the enthalpy of combustion of methane (CH_4) with F_2:

$$CH_4(g) + 4F_2(g) \longrightarrow CF_4(g) + 4HF(g) \qquad \Delta H^\circ_{\text{rxn}} = ?$$

$$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\circ_{\text{rxn}} = -75\ \text{kJ/mol}$$

$$C(\text{graphite}) + 2F_2(g) \longrightarrow CF_4(g) \qquad \Delta H^\circ_{\text{rxn}} = -933\ \text{kJ/mol}$$

$$H_2(g) + F_2(g) \longrightarrow 2HF(g) \qquad \Delta H^\circ_{\text{rxn}} = -542\ \text{kJ/mol}$$

Text Problems: 6.62, 6.64

ANSWERS TO PRACTICE EXERCISES

1. $\Delta E = 202$ kJ

2. $w = 1.0 \times 10^3$ J

3. $\Delta E = 37.57$ kJ

4. heat evolved $= 1.2 \times 10^2$ kJ

5. 475°C

6. $C_{\text{cal}} = 5.18$ kJ/°C

7. $s_{\text{metal}} = 0.906$ J/g°C. The metal is probably aluminum.

8. $\Delta H^\circ_f(CH_4) = -75.1$ kJ/mol

9. $\Delta H^\circ_f(HI) = 25.9$ kJ/mol

10. $\Delta H^\circ_{\text{rxn}} = -1942$ kJ/mol

SOLUTIONS TO SELECTED TEXT PROBLEMS

6.16 (a) Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0)(89.3 - 26.7)\text{mL}$$

$$\mathbf{w = 0}$$

(b) The external, opposing pressure is 1.5 atm, so

$$w = -P\Delta V = -(1.5\text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = -94\ \cancel{\text{mL}}\cdot\text{atm} \times \frac{0.001\text{ L}}{1\ \cancel{\text{mL}}} = -0.094\text{ L}\cdot\text{atm}$$

To convert the answer to joules, we write:

$$w = -0.094\ \cancel{\text{L}\cdot\text{atm}} \times \frac{101.3\text{ J}}{1\ \cancel{\text{L}\cdot\text{atm}}} = \mathbf{-9.5\ J}$$

(c) The external, opposing pressure is 2.8 atm, so

$$w = -P\Delta V = -(2.8\text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = (-1.8 \times 10^2\ \cancel{\text{mL}}\cdot\text{atm}) \times \frac{0.001\text{ L}}{1\ \cancel{\text{mL}}} = -0.18\text{ L}\cdot\text{atm}$$

To convert the answer to joules, we write:

$$w = -0.18\ \cancel{\text{L}\cdot\text{atm}} \times \frac{101.3\text{ J}}{1\ \cancel{\text{L}\cdot\text{atm}}} = \mathbf{-18\ J}$$

6.18 Applying the First Law of Thermodynamics, Problem Type 1A.

Strategy: Compression is work done on the gas, so what is the sign for w? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution: To calculate the energy change of the gas (ΔE), we need Equation (6.1) of the text. Work of compression is positive and because heat is given off by the gas, q is negative. Therefore, we have:

$$\Delta E = q + w = -26\text{ kJ} + 74\text{ kJ} = \mathbf{48\ kJ}$$

As a result, the energy of the gas increases by 48 kJ.

6.20 Calculating the work done in gas expansion, Problem Type 1B.

Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

$$w = -P\Delta V$$

We assume that the volume of liquid water is zero compared to that of steam. How do we calculate the volume of the steam? What is the conversion factor between L·atm and J?

Solution: First, we need to calculate the volume that the water vapor will occupy (V_f).

Using the ideal gas equation:

$$V_{H_2O} = \frac{n_{H_2O}RT}{P} = \frac{(1\ \cancel{mol})\left(0.0821\frac{L\cdot \cancel{atm}}{\cancel{mol}\cdot \cancel{K}}\right)(373\ \cancel{K})}{(1.0\ \cancel{atm})} = 31\ L$$

It is given that the volume occupied by liquid water is negligible. Therefore,

$$\Delta V = V_f - V_i = 31\ L - 0\ L = 31\ L$$

Now, we substitute P and ΔV into Equation (6.3) of the text to solve for w.

$$w = -P\Delta V = -(1.0\ atm)(31\ L) = -31\ L\cdot atm$$

The problems asks for the work done in units of joules. The following conversion factor can be obtained from Appendix 2 of the text.

$$1\ L\cdot atm = 101.3\ J$$

Thus, we can write:

$$w = -31\ \cancel{L}\cdot\cancel{atm} \times \frac{101.3\ J}{1\ \cancel{L}\cdot\cancel{atm}} = \mathbf{-3.1 \times 10^3\ J}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

6.26 Thermochemical Equations, Problem Type 2.

Strategy: The thermochemical equation shows that for every 2 moles of NO_2 produced, 114.6 kJ of heat are given off (note the negative sign). We can write a conversion factor from this information.

$$\frac{-114.6\ kJ}{2\ mol\ NO_2}$$

How many moles of NO_2 are in 1.26×10^4 g of NO_2? What conversion factor is needed to convert between grams and moles?

Solution: We need to first calculate the number of moles of NO_2 in 1.26×10^4 g of the compound. Then, we can convert to the number of kilojoules produced from the exothermic reaction. The sequence of conversions is:

grams of NO_2 → moles of NO_2 → kilojoules of heat generated

Therefore, the heat given off is:

$$(1.26 \times 10^4\ \cancel{g}\ NO_2) \times \frac{1\ \cancel{mol}\ NO_2}{46.01\ \cancel{g}\ NO_2} \times \frac{-114.6\ kJ}{2\ \cancel{mol}\ NO_2} = \mathbf{-1.57 \times 10^4\ kJ}$$

6.28 We initially have 6 moles of gas (3 moles of chlorine and 3 moles of hydrogen). Since our product is 6 moles of hydrogen chloride, there is no change in the number of moles of gas. Therefore there is no volume change; $\Delta V = 0$.

$$w = -P\Delta V = -(1\ atm)(0\ L) = 0$$

$$\Delta E° = \Delta H° - P\Delta V$$

$-P\Delta V = 0$, so

$$\Delta E = \Delta H$$

$$\Delta H = 3\Delta H°_{\text{rxn}} = 3(-184.6\text{ kJ/mol}) = -553.8\text{ kJ/mol}$$

We need to multiply $\Delta H°_{\text{rxn}}$ by three, because the question involves the formation of 6 moles of HCl; whereas, the equation as written only produces 2 moles of HCl.

$$\boldsymbol{\Delta E° = \Delta H° = -553.8\text{ kJ/mol}}$$

6.34 $q = m_{\text{Cu}}s_{\text{Cu}}\Delta t = (6.22 \times 10^3\text{ g})(0.385\text{ J/g}\cdot°\text{C})(324.3°\text{C} - 20.5°\text{C}) = 7.28 \times 10^5\text{ J} = \mathbf{728\text{ kJ}}$

6.36 Calculating Heat Absorbed Using Specific Heat Data, Problem Type 3.

Strategy: We know the masses of gold and iron as well as the initial temperatures of each. We can look up the specific heats of gold and iron in Table 6.2 of the text. Assuming no heat is lost to the surroundings, we can equate the heat lost by the iron sheet to the heat gained by the gold sheet. With this information, we can solve for the final temperature of the combined metals.

Solution: Treating the calorimeter as an isolated system (no heat lost to the surroundings), we can write:

$$q_{\text{Au}} + q_{\text{Fe}} = 0$$

or

$$q_{\text{Au}} = -q_{\text{Fe}}$$

The heat gained by the gold sheet is given by:

$$q_{\text{Au}} = m_{\text{Au}}s_{\text{Au}}\Delta t = (10.0\text{ g})(0.129\text{ J/g}\cdot°\text{C})(t_f - 18.0)°\text{C}$$

where m and s are the mass and specific heat, and $\Delta t = t_{\text{final}} - t_{\text{initial}}$.

The heat lost by the iron sheet is given by:

$$q_{\text{Fe}} = m_{\text{Fe}}s_{\text{Fe}}\Delta t = (20.0\text{ g})(0.444\text{ J/g}\cdot°\text{C})(t_f - 55.6)°\text{C}$$

Substituting into the equation derived above, we can solve for t_f.

$$q_{\text{Au}} = -q_{\text{Fe}}$$

$$(10.0\text{ g})(0.129\text{ J/g}\cdot°\text{C})(t_f - 18.0)°\text{C} = -(20.0\text{ g})(0.444\text{ J/g}\cdot°\text{C})(t_f - 55.6)°\text{C}$$

$$1.29\, t_f - 23.2 = -8.88\, t_f + 494$$

$$10.2\, t_f = 517$$

$$t_f = \mathbf{50.7°C}$$

Check: Must the final temperature be between the two starting values?

6.38 Constant-pressure calorimetry, Problem Type 4B.

Strategy: The neutralization reaction is exothermic. 56.2 kJ of heat are released when 1 mole of H^+ reacts with 1 mole of OH^-. Assuming no heat is lost to the surroundings, we can equate the heat lost by the reaction to the heat gained by the combined solution. How do we calculate the heat released during the reaction? Are we reacting 1 mole of H^+ with 1 mole of OH^-? How do we calculate the heat absorbed by the combined solution?

Solution: Assuming no heat is lost to the surroundings, we can write:

$$q_{soln} + q_{rxn} = 0$$

or

$$q_{soln} = -q_{rxn}$$

First, let's set up how we would calculate the heat gained by the solution,

$$q_{soln} = m_{soln}s_{soln}\Delta t$$

where m and s are the mass and specific heat of the solution and $\Delta t = t_f - t_i$.

We assume that the specific heat of the solution is the same as the specific heat of water, and we assume that the density of the solution is the same as the density of water (1.00 g/mL). Since the density is 1.00 g/mL, the mass of 400 mL of solution (200 mL + 200 mL) is 400 g.

Substituting into the equation above, the heat gained by the solution can be represented as:

$$q_{soln} = (4.00 \times 10^2\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(t_f - 20.48^\circ\text{C})$$

Next, let's calculate q_{rxn}, the heat released when 200 mL of 0.862 M HCl are mixed with 200 mL of 0.431 M $Ba(OH)_2$. The equation for the neutralization is:

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(l) + BaCl_2(aq)$$

There is exactly enough $Ba(OH)_2$ to neutralize all the HCl. Note that 2 mole HCl $\simeq$ 1 mole $Ba(OH)_2$, and that the concentration of HCl is double the concentration of $Ba(OH)_2$. The number of moles of HCl is:

$$(2.00 \times 10^2\ \cancel{\text{mL}}) \times \frac{0.862\ \text{mol HCl}}{1000\ \cancel{\text{mL}}} = 0.172\ \text{mol HCl}$$

The amount of heat released when 1 mole of H^+ is reacted is given in the problem (−56.2 kJ/mol). The amount of heat liberated when 0.172 mole of H^+ is reacted is:

$$q_{rxn} = 0.172\ \cancel{\text{mol}} \times \frac{-56.2 \times 10^3\ \text{J}}{1\ \cancel{\text{mol}}} = -9.67 \times 10^3\ \text{J}$$

Finally, knowing that the heat lost by the reaction equals the heat gained by the solution, we can solve for the final temperature of the mixed solution.

$$q_{soln} = -q_{rxn}$$

$$(4.00 \times 10^2\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(t_f - 20.48^\circ\text{C}) = -(-9.67 \times 10^3\ \text{J})$$

$$(1.67 \times 10^3)t_f - (3.43 \times 10^4) = 9.67 \times 10^3\ \text{J}$$

$$t_f = \mathbf{26.3^\circ C}$$

6.46 The standard enthalpy of formation of any element in its most stable form is zero. Therefore, since $\Delta H_f^\circ(O_2) = 0$, $\mathbf{O_2}$ is the more stable form of the element oxygen at this temperature.

6.48 **(a)** $Br_2(l)$ is the most stable form of bromine at 25°C; therefore, $\Delta H_f^\circ[Br_2(l)] = 0$. Since $Br_2(g)$ is less stable than $Br_2(l)$, $\Delta H_f^\circ[Br_2(g)] > 0$.

(b) $I_2(s)$ is the most stable form of iodine at 25°C; therefore, $\Delta H_f^\circ[I_2(s)] = 0$. Since $I_2(g)$ is less stable than $I_2(s)$, $\Delta H_f^\circ[I_2(g)] > 0$.

6.50 Direct method of calculating the standard enthalpy of formation, Problem Type 5B.

Strategy: What is the reaction for the formation of Ag_2O from its elements? What is the ΔH_f° value for an element in its standard state?

Solution: The balanced equation showing the formation of $Ag_2O(s)$ from its elements is:

$$2Ag(s) + \frac{1}{2}O_2(g) \longrightarrow Ag_2O(s)$$

Knowing that the standard enthalpy of formation of any element in its most stable form is zero, and using Equation (6.18) of the text, we write:

$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants})$$

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ(Ag_2O)] - [2\Delta H_f^\circ(Ag) + \tfrac{1}{2}\Delta H_f^\circ(O_2)]$$

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ(Ag_2O)] - [0 + 0]$$

$$\boldsymbol{\Delta H_f^\circ(Ag_2O) = \Delta H_{rxn}^\circ}$$

In a similar manner, you should be able to show that $\boldsymbol{\Delta H_f^\circ(CaCl_2) = \Delta H_{rxn}^\circ}$ for the reaction

$$Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$$

6.52 Calculating the standard enthalpy of reaction, Problem Type 5A.

Strategy: The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation, ΔH_f°, of the species.

Solution: We use the ΔH_f° values in Appendix 3 and Equation (6.18) of the text.

$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants})$$

(a) $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

$$\Delta H_{rxn}^\circ = \Delta H_f^\circ(H^+) + \Delta H_f^\circ(Cl^-) - \Delta H_f^\circ(HCl)$$

$$-74.9\text{ kJ/mol} = 0 + \Delta H_f^\circ(Cl^-) - (1)(-92.3\text{ kJ/mol})$$

$$\boldsymbol{\Delta H_f^\circ(Cl^-) = -167.2\text{ kJ/mol}}$$

(b) The neutralization reaction is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

and,

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f[H_2O(l)] - [\Delta H^\circ_f(H^+) + \Delta H^\circ_f(OH^-)]$$

$\Delta H^\circ_f[H_2O(l)] = -285.8$ kJ/mol (See Appendix 3 of the text.)

$$\boldsymbol{\Delta H^\circ_{rxn}} = (1)(-285.8 \text{ kJ/mol}) - [(1)(0 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})] = \mathbf{-56.2\ kJ/mol}$$

6.54 **(a)** $\Delta H^\circ = [2\Delta H^\circ_f(CO_2) + 2\Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(C_2H_4) + 3\Delta H^\circ_f(O_2)]]$

$\Delta H^\circ = [(2)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})] - [(1)(52.3 \text{ kJ/mol}) + (3)(0)]$

$\boldsymbol{\Delta H^\circ} = \mathbf{-1411\ kJ/mol}$

(b) $\Delta H^\circ = [2\Delta H^\circ_f(H_2O) + 2\Delta H^\circ_f(SO_2)] - [2\Delta H^\circ_f(H_2S) + 3\Delta H^\circ_f(O_2)]$

$\Delta H^\circ = [(2)(-285.8 \text{ kJ/mol}) + (2)(-296.1 \text{ kJ/mol})] - [(2)(-20.15 \text{ kJ/mol}) + (3)(0)]$

$\boldsymbol{\Delta H^\circ} = \mathbf{-1124\ kJ/mol}$

6.56 $\Delta H^\circ_{rxn} = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})$

The reaction is:

$$H_2(g) \longrightarrow H(g) + H(g)$$

and,

$$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(H) + \Delta H^\circ_f(H)] - \Delta H^\circ_f(H_2)$$

$\Delta H^\circ_f(H_2) = 0$

$$\Delta H^\circ_{rxn} = 436.4 \text{ kJ/mol} = 2\Delta H^\circ_f(H) - (1)(0)$$

$$\boldsymbol{\Delta H^\circ_f(H)} = \frac{436.4 \text{ kJ/mol}}{2} = \mathbf{218.2\ kJ/mol}$$

6.58 Using the ΔH°_f values in Appendix 3 and Equation (6.18) of the text, we write

$\Delta H^\circ_{rxn} = [5\Delta H^\circ_f(B_2O_3) + 9\Delta H^\circ_f(H_2O)] - [2\Delta H^\circ_f(B_5H_9) + 12\Delta H^\circ_f(O_2)]$

$\Delta H^\circ = [(5)(-1263.6 \text{ kJ/mol}) + (9)(-285.8 \text{ kJ/mol})] - [(2)(73.2 \text{ kJ/mol}) + (12)(0 \text{ kJ/mol})]$

$\boldsymbol{\Delta H^\circ} = -9036.6$ kJ/mol

Looking at the balanced equation, this is the amount of heat released for every 2 moles of B_5H_9 reacted. We can use the following ratio

$$\frac{-9036.6 \text{ kJ}}{2 \text{ mol } B_5H_9}$$

to convert to kJ/g B_5H_9. The molar mass of B_5H_9 is 63.12 g, so

$$\text{heat released per gram } B_5H_9 = \frac{-9036.6 \text{ kJ}}{2 \cancel{\text{mol}}\ B_5H_9} \times \frac{1 \cancel{\text{mol}}\ B_5H_9}{63.12 \text{ g } B_5H_9} = \mathbf{-71.58\ kJ/g\ B_5H_9}$$

6.60 $\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_{\text{f}}(\text{products}) - \sum m\Delta H^\circ_{\text{f}}(\text{reactants})$

The balanced equation for the reaction is:

$$\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$$

$$\Delta H^\circ_{\text{rxn}} = [\Delta H^\circ_{\text{f}}(\text{CaO}) + \Delta H^\circ_{\text{f}}(\text{CO}_2)] - \Delta H^\circ_{\text{f}}(\text{CaCO}_3)$$

$$\Delta H^\circ_{\text{rxn}} = [(1)(-635.6\text{ kJ/mol}) + (1)(-393.5\text{ kJ/mol})] - (1)(-1206.9\text{ kJ/mol}) = 177.8\text{ kJ/mol}$$

The enthalpy change calculated above is the enthalpy change if 1 mole of CO_2 is produced. The problem asks for the enthalpy change if 66.8 g of CO_2 are produced. We need to use the molar mass of CO_2 as a conversion factor.

$$\Delta H^\circ = 66.8\,\cancel{\text{g}}\,\text{CO}_2 \times \frac{1\,\cancel{\text{mol}}\,\text{CO}_2}{44.01\,\cancel{\text{g}}\,\text{CO}_2} \times \frac{177.8\text{ kJ}}{1\,\cancel{\text{mol}}\,\text{CO}_2} = \mathbf{2.70 \times 10^2\ kJ}$$

6.62 Indirect method of calculating the standard enthalpy of formation, Hess's law. Problem Type 5C.

Strategy: Our goal is to calculate the enthalpy change for the formation of C_2H_6 from is elements C and H_2. This reaction does not occur directly, however, so we must use an indirect route using the information given in the three equations, which we will call equations (a), (b), and (c).

Solution: Here is the equation for the formation of C_2H_6 from its elements.

$$2\text{C(graphite)} + 3\text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g) \qquad \Delta H^\circ_{\text{rxn}} = ?$$

Looking at this reaction, we need two moles of graphite as a reactant. So, we multiply Equation (a) by two to obtain:

$$\text{(d)}\quad 2\text{C(graphite)} + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) \qquad \Delta H^\circ_{\text{rxn}} = 2(-393.5\text{ kJ/mol}) = -787.0\text{ kJ/mol}$$

Next, we need three moles of H_2 as a reactant. So, we multiply Equation (b) by three to obtain:

$$\text{(e)}\quad 3\text{H}_2(g) + \tfrac{3}{2}\text{O}_2(g) \longrightarrow 3\text{H}_2\text{O}(l) \qquad \Delta H^\circ_{\text{rxn}} = 3(-285.8\text{ kJ/mol}) = -857.4\text{ kJ/mol}$$

Last, we need one mole of C_2H_6 as a product. Equation (c) has two moles of C_2H_6 as a reactant, so we need to reverse the equation and divide it by 2.

$$\text{(f)}\quad 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_6(g) + \tfrac{7}{2}\text{O}_2(g) \qquad \Delta H^\circ_{\text{rxn}} = \tfrac{1}{2}(3119.6\text{ kJ/mol}) = 1559.8\text{ kJ/mol}$$

Adding Equations (d), (e), and (f) together, we have:

Reaction	ΔH° (kJ/mol)
(d) $2\text{C(graphite)} + 2\cancel{\text{O}_2}(g) \longrightarrow 2\cancel{\text{CO}_2}(g)$	−787.0
(e) $3\text{H}_2(g) + \tfrac{3}{2}\cancel{\text{O}_2}(g) \longrightarrow 3\cancel{\text{H}_2\text{O}}(l)$	−857.4
(f) $2\cancel{\text{CO}_2}(g) + 3\cancel{\text{H}_2\text{O}}(l) \longrightarrow \text{C}_2\text{H}_6(g) + \tfrac{7}{2}\cancel{\text{O}_2}(g)$	1559.8
$\mathbf{2C(graphite) + 3H_2(g) \longrightarrow C_2H_6(g)}$	$\mathbf{\Delta H^\circ = -84.6\ kJ/mol}$

6.64 The second and third equations can be combined to give the first equation.

$$\begin{array}{ll}
2\text{Al}(s) + \tfrac{3}{2}\cancel{\text{O}_2}(g) \longrightarrow \text{Al}_2\text{O}_3(s) & \Delta H^\circ = -1669.8 \text{ kJ/mol} \\
\text{Fe}_2\text{O}_3(s) \longrightarrow 2\text{Fe}(s) + \tfrac{3}{2}\cancel{\text{O}_2}(g) & \Delta H^\circ = 822.2 \text{ kJ/mol} \\
\hline
2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2\text{Fe}(s) + \text{Al}_2\text{O}_3(s) & \boldsymbol{\Delta H^\circ = -847.6 \textbf{ kJ/mol}}
\end{array}$$

6.72 Rearrange the equations as necessary so they can be added to yield the desired equation.

$$\begin{array}{ll}
2\text{B} \longrightarrow \cancel{\text{A}} & -\Delta H_1 \\
\cancel{\text{A}} \longrightarrow \text{C} & \Delta H_2 \\
\hline
2\text{B} \longrightarrow \text{C} & \boldsymbol{\Delta H^\circ = \Delta H_2 - \Delta H_1}
\end{array}$$

6.74 **(a)** $\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_{\text{f}}(\text{products}) - \sum m\Delta H^\circ_{\text{f}}(\text{reactants})$

$$\Delta H^\circ_{\text{rxn}} = [4\Delta H^\circ_{\text{f}}(\text{NH}_3) + \Delta H^\circ_{\text{f}}(\text{N}_2)] - 3\Delta H^\circ_{\text{f}}(\text{N}_2\text{H}_4)$$

$$\boldsymbol{\Delta H^\circ_{\text{rxn}}} = [(4)(-46.3 \text{ kJ/mol}) + (0)] - (3)(50.42 \text{ kJ/mol}) = \mathbf{-336.5 \textbf{ kJ/mol}}$$

(b) The balanced equations are:

(1) $\text{N}_2\text{H}_4(l) + \text{O}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$

(2) $4\text{NH}_3(g) + 3\text{O}_2(g) \longrightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O}(l)$

The standard enthalpy change for equation (1) is:

$$\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_{\text{f}}(\text{N}_2) + 2\Delta H^\circ_{\text{f}}[\text{H}_2\text{O}(l)] - \{\Delta H^\circ_{\text{f}}[\text{N}_2\text{H}_4(l)] + \Delta H^\circ_{\text{f}}(\text{O}_2)\}$$

$$\Delta H^\circ_{\text{rxn}} = [(1)(0) + (2)(-285.8 \text{ kJ/mol})] - [(1)(50.42 \text{ kJ/mol}) + (1)(0)] = -622.0 \text{ kJ/mol}$$

The standard enthalpy change for equation (2) is:

$$\Delta H^\circ_{\text{rxn}} = [2\Delta H^\circ_{\text{f}}(\text{N}_2) + 6\Delta H^\circ_{\text{f}}(\text{H}_2\text{O})] - [4\Delta H^\circ_{\text{f}}(\text{NH}_3) + 3\Delta H^\circ_{\text{f}}(\text{O}_2)]$$

$$\Delta H^\circ_{\text{rxn}} = [(2)(0) + (6)(-285.8 \text{ kJ/mol})] - [(4)(-46.3 \text{ kJ/mol}) + (3)(0)] = -1529.6 \text{ kJ/mol}$$

We can now calculate the enthalpy change per kilogram of each substance. $\Delta H^\circ_{\text{rxn}}$ above is in units of kJ/mol. We need to convert to kJ/kg.

$$\text{N}_2\text{H}_4(l)\text{:}\quad \boldsymbol{\Delta H^\circ_{\text{rxn}}} = \frac{-622.0 \text{ kJ}}{1 \cancel{\text{mol}} \text{ N}_2\text{H}_4} \times \frac{1 \cancel{\text{mol}} \text{ N}_2\text{H}_4}{32.05 \cancel{\text{g}} \text{ N}_2\text{H}_4} \times \frac{1000 \cancel{\text{g}}}{1 \text{ kg}} = \mathbf{-1.941 \times 10^4 \textbf{ kJ/kg N}_2\textbf{H}_4}$$

$$\text{NH}_3(g)\text{:}\quad \boldsymbol{\Delta H^\circ_{\text{rxn}}} = \frac{-1529.6 \text{ kJ}}{4 \cancel{\text{mol}} \text{ NH}_3} \times \frac{1 \cancel{\text{mol}} \text{ NH}_3}{17.03 \cancel{\text{g}} \text{ NH}_3} \times \frac{1000 \cancel{\text{g}}}{1 \text{ kg}} = \mathbf{-2.245 \times 10^4 \textbf{ kJ/kg NH}_3}$$

Since **ammonia, NH_3,** releases more energy per kilogram of substance, it would be a better fuel.

6.76 The reaction is, $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$. First, let's calculate $\Delta H°$ for this reaction using ΔH_f° values in Appendix 3.

$$\Delta H^\circ_{rxn} = 2\Delta H_f^\circ(NaCl) - [2\Delta H_f^\circ(Na) + \Delta H_f^\circ(Cl_2)]$$

$$\Delta H^\circ_{rxn} = 2(-411.0 \text{ kJ/mol}) - [2(0) + 0] = -822.0 \text{ kJ/mol}$$

This is the amount of heat released when 1 mole of Cl_2 reacts (see balanced equation). We are not reacting 1 mole of Cl_2, however. From the volume and density of Cl_2, we can calculate grams of Cl_2. Then, using the molar mass of Cl_2 as a conversion factor, we can calculate moles of Cl_2. Combining these two calculations into one step, we find moles of Cl_2 to be:

$$2.00 \cancel{L}\,Cl_2 \times \frac{1.88 \cancel{g}\,Cl_2}{1 \cancel{L}\,Cl_2} \times \frac{1 \text{ mol } Cl_2}{70.90 \cancel{g}\,Cl_2} = 0.0530 \text{ mol } Cl_2$$

Finally, we can use the ΔH°_{rxn} calculated above to find the amount of heat released when 0.0530 mole of Cl_2 reacts.

$$0.0530 \cancel{mol}\,Cl_2 \times \frac{-822.0 \text{ kJ}}{1 \cancel{mol}\,Cl_2} = \mathbf{-43.6 \text{ kJ}}$$

6.78 The initial and final states of this system are identical. Since enthalpy is a state function, its value depends only upon the state of the system. The enthalpy change is **zero**.

6.80 $H(g) + Br(g) \longrightarrow HBr(g) \qquad \Delta H^\circ_{rxn} = ?$

Rearrange the equations as necessary so they can be added to yield the desired equation.

$$\begin{array}{ll}
H(g) \longrightarrow \frac{1}{2}\cancel{H_2}(g) & \Delta H^\circ_{rxn} = \frac{1}{2}(-436.4 \text{ kJ/mol}) = -218.2 \text{ kJ/mol} \\
Br(g) \longrightarrow \frac{1}{2}\cancel{Br_2}(g) & \Delta H^\circ_{rxn} = \frac{1}{2}(-192.5 \text{ kJ/mol}) = -96.25 \text{ kJ/mol} \\
\frac{1}{2}\cancel{H_2}(g) + \frac{1}{2}\cancel{Br_2}(g) \longrightarrow HBr(g) & \Delta H^\circ_{rxn} = \frac{1}{2}(-72.4 \text{ kJ/mol}) = -36.2 \text{ kJ/mol} \\
\hline
H(g) + Br(g) \longrightarrow HBr(g) & \mathbf{\Delta H^\circ = -350.7 \text{ kJ/mol}}
\end{array}$$

6.82 $q_{system} = 0 = q_{metal} + q_{water} + q_{calorimeter}$

$q_{metal} + q_{water} + q_{calorimeter} = 0$

$m_{metal}s_{metal}(t_{final} - t_{initial}) + m_{water}s_{water}(t_{final} - t_{initial}) + C_{calorimeter}(t_{final} - t_{initial}) = 0$

All the needed values are given in the problem. All you need to do is plug in the values and solve for s_{metal}.

$$(44.0 \text{ g})(s_{metal})(28.4 - 99.0)^\circ\text{C} + (80.0 \text{ g})(4.184 \text{ J/g}\cdot^\circ\text{C})(28.4 - 24.0)^\circ\text{C} + (12.4 \text{ J/}^\circ\text{C})(28.4 - 24.0)^\circ\text{C} = 0$$

$$(-3.11 \times 10^3)s_{metal} \text{ (g}\cdot^\circ\text{C)} = -1.53 \times 10^3 \text{ J}$$

$$s_{metal} = \mathbf{0.492 \text{ J/g}\cdot^\circ\text{C}}$$

6.84 A good starting point would be to calculate the standard enthalpy for both reactions.

Calculate the standard enthalpy for the reaction: $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

This reaction corresponds to the standard enthalpy of formation of CO, so we use the value of −110.5 kJ/mol (see Appendix 3 of the text).

Calculate the standard enthalpy for the reaction: $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

$$\Delta H^\circ_{\text{rxn}} = [\Delta H^\circ_f(\text{CO}) + \Delta H^\circ_f(\text{H}_2)] - [\Delta H^\circ_f(\text{C}) + \Delta H^\circ_f(\text{H}_2\text{O})]$$

$$\Delta H^\circ_{\text{rxn}} = [(1)(-110.5\text{ kJ/mol}) + (1)(0)] - [(1)(0) + (1)(-241.8\text{ kJ/mol})] = 131.3\text{ kJ/mol}$$

The first reaction, which is exothermic, can be used to promote the second reaction, which is endothermic. Thus, the two gases are produced alternately.

6.86 First, calculate the energy produced by 1 mole of octane, C_8H_{18}.

$$C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$$

$$\Delta H^\circ_{\text{rxn}} = 8\Delta H^\circ_f(\text{CO}_2) + 9\Delta H^\circ_f[\text{H}_2\text{O}(l)] - [\Delta H^\circ_f(\text{C}_8\text{H}_{18}) + \tfrac{25}{2}\Delta H^\circ_f(\text{O}_2)]$$

$$\Delta H^\circ_{\text{rxn}} = [(8)(-393.5\text{ kJ/mol}) + (9)(-285.8\text{ kJ/mol})] - [(1)(-249.9\text{ kJ/mol}) + (\tfrac{25}{2})(0)]$$
$$= -5470\text{ kJ/mol}$$

The problem asks for the energy produced by the combustion of 1 gallon of octane. $\Delta H^\circ_{\text{rxn}}$ above has units of kJ/mol octane. We need to convert from kJ/mol octane to kJ/gallon octane. The heat of combustion for 1 gallon of octane is:

$$\Delta H^\circ = \frac{-5470\text{ kJ}}{1\ \cancel{\text{mol}}\text{ octane}} \times \frac{1\ \cancel{\text{mol}}\text{ octane}}{114.2\ \cancel{\text{g}}\text{ octane}} \times \frac{2660\ \cancel{\text{g}}}{1\text{ gal}} = -1.274 \times 10^5\text{ kJ/gal}$$

The combustion of hydrogen corresponds to the standard heat of formation of water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

Thus, $\Delta H^\circ_{\text{rxn}}$ is the same as ΔH°_f for $H_2O(l)$, which has a value of −285.8 kJ/mol. The number of moles of hydrogen required to produce 1.274×10^5 kJ of heat is:

$$n_{\text{H}_2} = (1.274 \times 10^5\ \cancel{\text{kJ}}) \times \frac{1\text{ mol H}_2}{285.8\ \cancel{\text{kJ}}} = 445.8\text{ mol H}_2$$

Finally, use the ideal gas law to calculate the volume of gas corresponding to 445.8 moles of H_2 at 25°C and 1 atm.

$$V_{\text{H}_2} = \frac{n_{\text{H}_2}RT}{P} = \frac{(445.8\ \cancel{\text{mol}})\left(0.0821\frac{\text{L}\cdot\cancel{\text{atm}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}}\right)(298\ \cancel{\text{K}})}{(1\ \cancel{\text{atm}})} = \mathbf{1.09 \times 10^4\ L}$$

That is, the volume of hydrogen that is energy-equivalent to 1 gallon of gasoline is over **10,000 liters** at 1 atm and 25°C!

6.88 The combustion reaction is: $C_2H_6(l) + \tfrac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

The heat released during the combustion of 1 mole of ethane is:

$$\Delta H^\circ_{\text{rxn}} = [2\Delta H^\circ_f(\text{CO}_2) + 3\Delta H^\circ_f(\text{H}_2\text{O})] - [\Delta H^\circ_f(\text{C}_2\text{H}_6) + \tfrac{7}{2}\Delta H^\circ_f(\text{O}_2)]$$

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= [(2)(-393.5\text{ kJ/mol}) + (3)(-285.8\text{ kJ/mol})] - [(1)(-84.7\text{ kJ/mol} + (\tfrac{7}{2})(0)]\\ &= -1560\text{ kJ/mol}\end{aligned}$$

The heat required to raise the temperature of the water to 98°C is:

$$q = m_{H_2O}s_{H_2O}\Delta t = (855\,\cancel{g})(4.184\text{ J}/\cancel{g}\cdot\cancel{^\circ C})(98.0-25.0)\cancel{^\circ C} = 2.61\times10^5\text{ J} = 261\text{ kJ}$$

The combustion of 1 mole of ethane produces 1560 kJ; the number of moles required to produce 261 kJ is:

$$261\,\cancel{\text{kJ}}\times\frac{1\text{ mol ethane}}{1560\,\cancel{\text{kJ}}} = 0.167\text{ mol ethane}$$

The volume of ethane is:

$$V_{\textbf{ethane}} = \frac{nRT}{P} = \frac{(0.167\,\cancel{\text{mol}})\left(0.0821\dfrac{\text{L}\cdot\cancel{\text{atm}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}}\right)(296\,\cancel{\text{K}})}{\left(752\,\cancel{\text{mmHg}}\times\dfrac{1\,\cancel{\text{atm}}}{760\,\cancel{\text{mmHg}}}\right)} = \mathbf{4.10\ L}$$

6.90 The heat gained by the liquid nitrogen must be equal to the heat lost by the water.

$$q_{N_2} = -q_{H_2O}$$

If we can calculate the heat lost by the water, we can calculate the heat gained by 60.0 g of the nitrogen.

$$\text{Heat lost by the water} = q_{H_2O} = m_{H_2O}s_{H_2O}\Delta t$$

$$q_{H_2O} = (2.00\times10^2\,\cancel{g})(4.184\text{ J}/\cancel{g}\cdot\cancel{^\circ C})(41.0-55.3)\cancel{^\circ C} = -1.20\times10^4\text{ J}$$

The heat gained by 60.0 g nitrogen is the opposite sign of the heat lost by the water.

$$q_{N_2} = -q_{H_2O}$$

$$q_{N_2} = 1.20\times10^4\text{ J}$$

The problem asks for the molar heat of vaporization of liquid nitrogen. Above, we calculated the amount of heat necessary to vaporize 60.0 g of liquid nitrogen. We need to convert from J/60.0 g N_2 to J/mol N_2.

$$\Delta H_{\textbf{vap}} = \frac{1.20\times10^4\text{ J}}{60.0\,\cancel{g\,N_2}}\times\frac{28.02\,\cancel{g\,N_2}}{1\text{ mol }N_2} = \mathbf{5.60\times10^3\ J/mol} = \mathbf{5.60\ kJ/mol}$$

6.92 Recall that the standard enthalpy of formation (ΔH°_f) is defined as the heat change that results when 1 mole of a compound is formed from its elements at a pressure of 1 atm. Only in choice **(a)** does $\Delta H^\circ_{\text{rxn}} = \Delta H^\circ_f$. In choice (b), C(diamond) is *not* the most stable form of elemental carbon under standard conditions; C(graphite) is the most stable form.

6.94 **(a)** No work is done by a gas expanding in a vacuum, because the pressure exerted on the gas is zero.

(b) $w = -P\Delta V$

$$w = -(0.20\text{ atm})(0.50-0.050)\text{L} = -0.090\text{ L}\cdot\text{atm}$$

Converting to units of joules:

$$w = -0.090\,\cancel{\text{L}\cdot\text{atm}} \times \frac{101.3\ \text{J}}{\cancel{\text{L}\cdot\text{atm}}} = \mathbf{-9.1\ J}$$

(c) The gas will expand until the pressure is the same as the applied pressure of 0.20 atm. We can calculate its final volume using the ideal gas equation.

$$V = \frac{nRT}{P} = \frac{(0.020\ \cancel{\text{mol}})\left(0.0821\frac{\text{L}\cdot\cancel{\text{atm}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}}\right)(273+20)\cancel{\text{K}}}{0.20\ \cancel{\text{atm}}} = \mathbf{2.4\ L}$$

The amount of work done is:

$$w = -P\Delta V = (0.20\ \text{atm})(2.4 - 0.050)\text{L} = -0.47\ \text{L}\cdot\text{atm}$$

Converting to units of joules:

$$w = -0.47\,\cancel{\text{L}\cdot\text{atm}} \times \frac{101.3\ \text{J}}{\cancel{\text{L}\cdot\text{atm}}} = \mathbf{-48\ J}$$

6.96 **(a)** The more closely packed, the greater the mass of food. Heat capacity depends on both the mass and specific heat.

$$C = ms$$

The heat capacity of the food is greater than the heat capacity of air; hence, the cold in the freezer will be retained longer.

(b) Tea and coffee are mostly water; whereas, soup might contain vegetables and meat. Water has a higher heat capacity than the other ingredients in soup; therefore, coffee and tea retain heat longer than soup.

6.98 $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$. This equation represents twice the standard enthalpy of formation of Fe_2O_3. From Appendix 3, the standard enthalpy of formation of $\text{Fe}_2\text{O}_3 = -822.2$ kJ/mol. So, $\Delta H°$ for the given reaction is:

$$\Delta H°_{\text{rxn}} = (2)(-822.2\ \text{kJ/mol}) = -1644\ \text{kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when four moles of Fe react. But, we are reacting 250 g of Fe, not 4 moles. We can convert from grams of Fe to moles of Fe, then use $\Delta H°$ as a conversion factor to convert to kJ.

$$250\,\cancel{\text{g}}\,\text{Fe} \times \frac{1\ \cancel{\text{mol}}\ \text{Fe}}{55.85\,\cancel{\text{g}}\,\text{Fe}} \times \frac{-1644\ \text{kJ}}{4\ \cancel{\text{mol}}\ \text{Fe}} = \mathbf{-1.84 \times 10^3\ kJ}$$

6.100 The heat required to raise the temperature of 1 liter of water by 1°C is:

$$4.184\frac{\text{J}}{\cancel{\text{g}}\cdot\cancel{°\text{C}}} \times \frac{1\,\cancel{\text{g}}}{1\,\cancel{\text{mL}}} \times \frac{1000\,\cancel{\text{mL}}}{1\ \text{L}} \times 1\cancel{°\text{C}} = 4184\ \text{J/L}$$

Next, convert the volume of the Pacific Ocean to liters.

$$(7.2 \times 10^8\ \cancel{\text{km}^3}) \times \left(\frac{1000\,\cancel{\text{m}}}{1\,\cancel{\text{km}}}\right)^3 \times \left(\frac{100\,\cancel{\text{cm}}}{1\,\cancel{\text{m}}}\right)^3 \times \frac{1\ \text{L}}{1000\,\cancel{\text{cm}^3}} = 7.2 \times 10^{20}\ \text{L}$$

The amount of heat needed to raise the temperature of 7.2×10^{20} L of water is:

$$(7.2 \times 10^{20}\,\cancel{\text{L}}) \times \frac{4184\ \text{J}}{1\,\cancel{\text{L}}} = 3.0 \times 10^{24}\ \text{J}$$

Finally, we can calculate the number of atomic bombs needed to produce this much heat.

$$(3.0 \times 10^{24}\,\cancel{\text{J}}) \times \frac{1\ \text{atomic bomb}}{1.0 \times 10^{15}\,\cancel{\text{J}}} = \mathbf{3.0 \times 10^{9}\ \textbf{atomic bombs}} = \textbf{3.0 billion atomic bombs}$$

6.102 Constant-volume calorimetry, Problem Type 4A.

Strategy: The heat released during the reaction is absorbed by both the water and the calorimeter. How do we calculate the heat absorbed by the water? How do we calculate the heat absorbed by the calorimeter? How much heat is released when 1.9862 g of benzoic acid are reacted? The problem gives the amount of heat that is released when 1 mole of benzoic acid is reacted (−3226.7 kJ/mol).

Solution: The heat of the reaction (combustion) is absorbed by both the water and the calorimeter.

$$q_{\text{rxn}} = -(q_{\text{water}} + q_{\text{cal}})$$

If we can calculate both q_{water} and q_{rxn}, then we can calculate q_{cal}. First, let's calculate the heat absorbed by the water.

$$q_{\text{water}} = m_{\text{water}}s_{\text{water}}\Delta t$$
$$q_{\text{water}} = (2000\,\cancel{\text{g}})(4.184\ \text{J}/\cancel{\text{g}}\cdot\cancel{^\circ\text{C}})(25.67 - 21.84)\cancel{^\circ\text{C}} = 3.20 \times 10^{4}\ \text{J} = 32.0\ \text{kJ}$$

Next, let's calculate the heat released (q_{rxn}) when 1.9862 g of benzoic acid are burned. ΔH_{rxn} is given in units of kJ/mol. Let's convert to q_{rxn} in kJ.

$$q_{\text{rxn}} = 1.9862\,\cancel{\text{g}}\ \text{benzoic acid} \times \frac{1\ \cancel{\text{mol}}\ \text{benzoic acid}}{122.1\,\cancel{\text{g}}\ \text{benzoic acid}} \times \frac{-3226.7\ \text{kJ}}{1\ \cancel{\text{mol}}\ \text{benzoic acid}} = -52.49\ \text{kJ}$$

And,

$$q_{\text{cal}} = -q_{\text{rxn}} - q_{\text{water}}$$

$$q_{\text{cal}} = 52.49\ \text{kJ} - 32.0\ \text{kJ} = 20.5\ \text{kJ}$$

To calculate the heat capacity of the bomb calorimeter, we can use the following equation:

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta t} = \frac{20.5\ \text{kJ}}{(25.67 - 21.84)^\circ\text{C}} = \mathbf{5.35\ kJ/^\circ C}$$

6.104 First, let's calculate the standard enthalpy of reaction.

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_{\text{f}}(\text{CaSO}_4) - [2\Delta H^\circ_{\text{f}}(\text{CaO}) + 2\Delta H^\circ_{\text{f}}(\text{SO}_2) + \Delta H^\circ_{\text{f}}(\text{O}_2)]\\ &= (2)(-1432.7\ \text{kJ/mol}) - [(2)(-635.6\ \text{kJ/mol}) + (2)(-296.1\ \text{kJ/mol}) + 0]\\ &= -1002\ \text{kJ/mol}\end{aligned}$$

This is the enthalpy change for every 2 moles of SO_2 that are removed. The problem asks to calculate the enthalpy change for this process if 6.6×10^{5} g of SO_2 are removed.

$$(6.6 \times 10^5\ \cancel{g}\,SO_2) \times \frac{1\ \cancel{mol}\ SO_2}{64.07\ \cancel{g}\ SO_2} \times \frac{-1002\ kJ}{2\ \cancel{mol}\ SO_2} = \mathbf{-5.2 \times 10^6\ kJ}$$

6.106 First, we need to calculate the volume of the balloon.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(8\ m)^3 = (2.1 \times 10^3\ \cancel{m^3}) \times \frac{1000\ L}{1\ \cancel{m^3}} = 2.1 \times 10^6\ L$$

(a) We can calculate the mass of He in the balloon using the ideal gas equation.

$$n_{He} = \frac{PV}{RT} = \frac{\left(98.7\ \cancel{kPa} \times \frac{1\ \cancel{atm}}{1.01325 \times 10^2\ \cancel{kPa}}\right)(2.1 \times 10^6\ \cancel{L})}{\left(0.0821 \frac{\cancel{L} \cdot \cancel{atm}}{mol \cdot \cancel{K}}\right)(273 + 18)\cancel{K}} = 8.6 \times 10^4\ mol\ He$$

$$\textbf{mass He} = (8.6 \times 10^4\ \cancel{mol}\ He) \times \frac{4.003\ g\ He}{1\ \cancel{mol}\ He} = \mathbf{3.4 \times 10^5\ g\ He}$$

(b) Work done $= -P\Delta V$

$$= -\left(98.7\ \cancel{kPa} \times \frac{1\ atm}{1.01325 \times 10^2\ \cancel{kPa}}\right)(2.1 \times 10^6\ L)$$

$$= (-2.0 \times 10^6\ \cancel{L \cdot atm}) \times \frac{101.3\ J}{1\ \cancel{L \cdot atm}}$$

Work done $= \mathbf{-2.0 \times 10^8\ J}$

6.108 **(a)** The heat needed to raise the temperature of the water from 3°C to 37°C can be calculated using the equation:

$$q = ms\Delta t$$

First, we need to calculate the mass of the water.

$$4\ \text{gl}\cancel{\text{ass}}\text{es of water} \times \frac{2.5 \times 10^2\ \cancel{mL}}{1\ \cancel{glass}} \times \frac{1\ g\ water}{1\ \cancel{mL}\ water} = 1.0 \times 10^3\ g\ water$$

The heat needed to raise the temperature of 1.0×10^3 g of water is:

$$q = ms\Delta t = (1.0 \times 10^3\ \cancel{g})(4.184\ J/\cancel{g \cdot °C})(37 - 3)\cancel{°C} = 1.4 \times 10^5\ J = \mathbf{1.4 \times 10^2\ kJ}$$

(b) We need to calculate both the heat needed to melt the snow and also the heat needed to heat liquid water form 0°C to 37°C (normal body temperature).

The heat needed to melt the snow is: .

$$(8.0 \times 10^2\ \cancel{g}) \times \frac{1\ \cancel{mol}}{18.02\ \cancel{g}} \times \frac{6.01\ kJ}{1\ \cancel{mol}} = 2.7 \times 10^2\ kJ$$

The heat needed to raise the temperature of the water from 0°C to 37°C is:

$$q = ms\Delta t = (8.0 \times 10^2\ \cancel{g})(4.184\ J/\cancel{g \cdot °C})(37 - 0)\cancel{°C} = 1.2 \times 10^5\ J = 1.2 \times 10^2\ kJ$$

The total heat lost by your body is:

$$(2.7 \times 10^2 \text{ kJ}) + (1.2 \times 10^2 \text{ kJ}) = \mathbf{3.9 \times 10^2\ kJ}$$

6.110 **(a)** $\Delta H° = \Delta H_f°(\text{F}^-) + \Delta H_f°(\text{H}_2\text{O}) - [\Delta H_f°(\text{HF}) + \Delta H_f°(\text{OH}^-)]$

$\Delta H° = [(1)(-329.1 \text{ kJ/mol}) + (1)(-285.8 \text{ kJ/mol})] - [(1)(-320.1 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})]$

$\mathbf{\Delta H° = -65.2\ kJ/mol}$

(b) We can add the equation given in part (a) to that given in part (b) to end up with the equation we are interested in.

$$\begin{array}{ll} \text{HF}(aq) + \cancel{\text{OH}^-}(aq) \longrightarrow \text{F}^-(aq) + \cancel{\text{H}_2\text{O}}(l) & \Delta H° = -65.2 \text{ kJ/mol} \\ \cancel{\text{H}_2\text{O}}(l) \longrightarrow \text{H}^+(aq) + \cancel{\text{OH}^-}(aq) & \Delta H° = +56.2 \text{ kJ/mol} \\ \hline \mathbf{HF}(aq) \longrightarrow \mathbf{H^+}(aq) + \mathbf{F^-}(aq) & \mathbf{\Delta H° = -9.0\ kJ/mol} \end{array}$$

6.112 The equation we are interested in is the formation of CO from its elements.

$$\text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g) \qquad \Delta H° = ?$$

Try to add the given equations together to end up with the equation above.

$$\begin{array}{ll} \text{C(graphite)} + \text{O}_2(g) \longrightarrow \cancel{\text{CO}_2}(g) & \Delta H° = -393.5 \text{ kJ/mol} \\ \cancel{\text{CO}_2}(g) \longrightarrow \text{CO}(g) + \tfrac{1}{2}\cancel{\text{O}_2}(g) & \Delta H° = +283.0 \text{ kJ/mol} \\ \hline \mathbf{C(graphite)} + \tfrac{1}{2}\mathbf{O_2}(g) \longrightarrow \mathbf{CO}(g) & \mathbf{\Delta H° = -110.5\ kJ/mol} \end{array}$$

We cannot obtain $\Delta H_f°$ for CO directly, because burning graphite in oxygen will form both CO and CO_2.

6.114 **(a)** mass = 0.0010 kg

Potential energy = mgh

$= (0.0010 \text{ kg})(9.8 \text{ m/s}^2)(51 \text{ m})$

Potential energy = 0.50 J

(b) Kinetic energy $= \frac{1}{2}mu^2 = 0.50 \text{ J}$

$$\frac{1}{2}(0.0010 \text{ kg})u^2 = 0.50 \text{ J}$$

$$u^2 = 1.0 \times 10^3 \text{ m}^2/\text{s}^2$$

$$\mathbf{u = 32\ m/s}$$

(c) $q = ms\Delta t$

$0.50\cancel{\text{J}} = (1.0\cancel{\text{g}})(4.184\cancel{\text{J}}/\cancel{\text{g}}°\text{C})\Delta t$

$\mathbf{\Delta t = 0.12°C}$

6.116 The reaction we are interested in is the formation of ethanol from its elements.

$$2\text{C(graphite)} + \tfrac{1}{2}\text{O}_2(g) + 3\text{H}_2(g) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l)$$

Along with the reaction for the combustion of ethanol, we can add other reactions together to end up with the above reaction.

Reversing the reaction representing the combustion of ethanol gives:

$$2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \qquad \Delta H^\circ = +1367.4\ \text{kJ/mol}$$

We need to add equations to add C (graphite) and remove H_2O from the reactants side of the equation. We write:

$$\begin{array}{ll}
2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) & \Delta H^\circ = +1367.4\ \text{kJ/mol} \\
2\text{C(graphite)} + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) & \Delta H^\circ = 2(-393.5\ \text{kJ/mol}) \\
3\text{H}_2(g) + \tfrac{3}{2}\text{O}_2(g) \longrightarrow 3\text{H}_2\text{O}(l) & \Delta H^\circ = 3(-285.8\ \text{kJ/mol}) \\
\hline
\mathbf{2C(graphite)} + \tfrac{1}{2}\mathbf{O_2}(g) + \mathbf{3H_2}(g) \longrightarrow \mathbf{C_2H_5OH}(l) & \boldsymbol{\Delta H_f^\circ = -277.0}\ \textbf{kJ/mol}
\end{array}$$

6.118 Heat gained by ice = Heat lost by the soft drink

$$m_{\text{ice}} \times 334\ \text{J/g} = -m_{\text{sd}}s_{\text{sd}}\Delta t$$

$$m_{\text{ice}} \times 334\ \text{J/g} = -(361\ \text{g})(4.184\ \text{J/g}\cdot{}^\circ\text{C})(0 - 23)^\circ\text{C}$$

$$m_{\text{ice}} = \mathbf{104\ g}$$

6.120 From Chapter 5, we saw that the kinetic energy (or internal energy) of 1 mole of a gas is $\frac{3}{2}RT$. For 1 mole of an ideal gas, $PV = RT$. We can write:

$$\text{internal energy} = \frac{3}{2}RT = \frac{3}{2}PV$$

$$= \frac{3}{2}(1.2 \times 10^5\ \text{Pa})(5.5 \times 10^3\ \text{m}^3)$$

$$= 9.9 \times 10^8\ \text{Pa}\cdot\text{m}^3$$

$$1\ \text{Pa}\cdot\text{m}^3 = 1\ \frac{\text{N}}{\text{m}^2}\text{m}^3 = 1\ \text{N}\cdot\text{m} = 1\ \text{J}$$

Therefore, the internal energy is $\mathbf{9.9 \times 10^8\ J}$.

The final temperature of the copper metal can be calculated. (10 tons = 9.07×10^6 g)

$$q = m_{\text{Cu}}s_{\text{Cu}}\Delta t$$

$$9.9 \times 10^8\ \text{J} = (9.07 \times 10^6\ \text{g})(0.385\ \text{J/g}^\circ\text{C})(t_f - 21^\circ\text{C})$$

$$(3.49 \times 10^6)t_f = 1.06 \times 10^9$$

$$t_f = \mathbf{304^\circ C}$$

6.122 **(a)** $CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$

(b) The reaction for the combustion of acetylene is:

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

We can calculate the enthalpy change for this reaction from standard enthalpy of formation values given in Appendix 3 of the text.

$$\Delta H^\circ_{\text{rxn}} = [4\Delta H^\circ_f(CO_2) + 2\Delta H^\circ_f(H_2O)] - [2\Delta H^\circ_f(C_2H_2) + 5\Delta H^\circ_f(O_2)]$$

$$\Delta H^\circ_{\text{rxn}} = [(4)(-393.5\text{ kJ/mol}) + (2)(-285.8\text{ kJ/mol})] - [(2)(226.6\text{ kJ/mol}) + (5)(0)]$$

$$\Delta H^\circ_{\text{rxn}} = -2599\text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when two moles of C_2H_2 are reacted. The problem asks for the amount of heat that can be obtained starting with 74.6 g of CaC_2. From this amount of CaC_2, we can calculate the moles of C_2H_2 produced.

$$74.6\,\cancel{g}\,CaC_2 \times \frac{1\,\cancel{mol}\,CaC_2}{64.10\,\cancel{g}\,CaC_2} \times \frac{1\text{ mol }C_2H_2}{1\,\cancel{mol}\,CaC_2} = 1.16\text{ mol }C_2H_2$$

Now, we can use the $\Delta H^\circ_{\text{rxn}}$ calculated above as a conversion factor to determine the amount of heat obtained when 1.16 moles of C_2H_2 are burned.

$$1.16\,\cancel{mol}\,C_2H_2 \times \frac{2599\text{ kJ}}{2\,\cancel{mol}\,C_2H_2} = \mathbf{1.51 \times 10^3\text{ kJ}}$$

6.124 When 1.034 g of naphthalene are burned, 41.56 kJ of heat are evolved. Let's convert this to the amount of heat evolved on a molar basis. The molar mass of naphthalene is 128.2 g/mol.

$$q = \frac{-41.56\text{ kJ}}{1.034\,\cancel{g}\,C_{10}H_8} \times \frac{128.2\,\cancel{g}\,C_{10}H_8}{1\text{ mol }C_{10}H_8} = -5153\text{ kJ/mol}$$

q has a negative sign because this is an exothermic reaction.

This reaction is run at constant volume ($\Delta V = 0$); therefore, no work will result from the change.

$$w = -P\Delta V = 0$$

From Equation (6.4) of the text, it follows that the change in energy is equal to the heat change.

$$\mathbf{\Delta E} = q + w = q_V = \mathbf{-5153\text{ kJ/mol}}$$

To calculate ΔH, we rearrange Equation (6.10) of the text.

$$\Delta E = \Delta H - RT\Delta n$$

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

To calculate ΔH, Δn must be determined, which is the difference in moles of *gas* products and moles of *gas* reactants. Looking at the balanced equation for the combustion of naphthalene:

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

$$\Delta n = 10 - 12 = -2$$

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

$$\Delta H = -5153 \text{ kJ/mol} + (8.314\,\cancel{\text{J}}/\text{mol}\cdot\cancel{\text{K}})(298\,\cancel{\text{K}})(-2) \times \frac{1 \text{ kJ}}{1000\,\cancel{\text{J}}}$$

$$\mathbf{\Delta H = -5158 \text{ kJ/mol}}$$

Is ΔH equal to q_p in this case?

6.126 We know that $\Delta E = q + w$. $\Delta H = q$, and $w = -P\Delta V = -RT\Delta n$. Using thermodynamic data in Appendix 3 of the text, we can calculate ΔH.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l),\ \Delta H = 2(-285.8 \text{ kJ/mol}) = -571.6 \text{ kJ/mol}$$

Next, we calculate w. The change in moles of gas (Δn) equals -3.

$$w = -P\Delta V = -RT\Delta n$$

$$w = -(8.314 \text{ J/mol}\cdot\cancel{\text{K}})(298\,\cancel{\text{K}})(-3) = +7.43 \times 10^3 \text{ J/mol} = 7.43 \text{ kJ/mol}$$

$$\Delta E = q + w$$

$$\Delta E = -571.6 \text{ kJ/mol} + 7.43 \text{ kJ/mol} = \mathbf{-564.2 \text{ kJ/mol}}$$

Can you explain why ΔE is smaller (in magnitude) than ΔH?

6.128 First, we calculate ΔH for the combustion of 1 mole of glucose using data in Appendix 3 of the text. We can then calculate the heat produced in the calorimeter. Using the heat produced along with ΔH for the combustion of 1 mole of glucose will allow us to calculate the mass of glucose in the sample. Finally, the mass % of glucose in the sample can be calculated.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H^\circ_{\text{rxn}} = (6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (1)(-1274.5 \text{ kJ/mol}) = -2801.3 \text{ kJ/mol}$$

The heat produced in the calorimeter is:

$$(3.134\,\cancel{^\circ\text{C}})(19.65 \text{ kJ}/\cancel{^\circ\text{C}}) = 61.58 \text{ kJ}$$

Let x equal the mass of glucose in the sample:

$$x\,\cancel{\text{g}}\text{ glucose} \times \frac{1\,\cancel{\text{mol}}\text{ glucose}}{180.2\,\cancel{\text{g}}\text{ glucose}} \times \frac{2801.3 \text{ kJ}}{1\,\cancel{\text{mol}}\text{ glucose}} = 61.58 \text{ kJ}$$

$$x = 3.961 \text{ g}$$

$$\%\text{ glucose} = \frac{3.961 \text{ g}}{4.117 \text{ g}} \times 100\% = \mathbf{96.21\%}$$

6.130 **(a)** From the mass of CO_2 produced, we can calculate the moles of carbon in the compound. From the mass of H_2O produced, we can calculate the moles of hydrogen in the compound.

$$1.419\,\cancel{\text{g}}\,\text{CO}_2 \times \frac{1\ \cancel{\text{mol}}\ \text{CO}_2}{44.01\ \cancel{\text{g}}\ \text{CO}_2} \times \frac{1\ \text{mol C}}{1\ \cancel{\text{mol}}\ \text{CO}_2} = 0.03224\ \text{mol C}$$

$$0.290\,\cancel{\text{g}}\,\text{H}_2\text{O} \times \frac{1\ \cancel{\text{mol}}\ \text{H}_2\text{O}}{18.02\ \cancel{\text{g}}\ \text{H}_2\text{O}} \times \frac{2\ \text{mol H}}{1\ \cancel{\text{mol}}\ \text{H}_2\text{O}} = 0.03219\ \text{mol H}$$

The mole ratio between C and H is 1:1, so the empirical formula is **CH**.

(b) The empirical molar mass of CH is 13.02 g/mol.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{76\ \text{g}}{13.02\ \text{g}} = 5.8 \approx 6$$

Therefore, the molecular formula is C_6H_6, and the hydrocarbon is benzene. The combustion reaction is:

$$2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$$

17.55 kJ of heat is released when 0.4196 g of the hydrocarbon undergoes combustion. We can now calculate the enthalpy of combustion ($\Delta H^\circ_{\text{rxn}}$) for the above reaction in units of kJ/mol. Then, from the enthalpy of combustion, we can calculate the enthalpy of formation of C_6H_6.

$$\frac{-17.55\ \text{kJ}}{0.4196\ \text{g C}_6\text{H}_6} \times \frac{78.11\ \text{g C}_6\text{H}_6}{1\ \text{mol C}_6\text{H}_6} \times 2\ \text{mol C}_6\text{H}_6 = -6534\ \text{kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = (12)\Delta H^\circ_{\text{f}}(\text{CO}_2) + (6)\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}) - (2)\Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_6)$$

$$-6534\ \text{kJ/mol} = (12)(-393.5\ \text{kJ/mol}) + (6)(-285.8\ \text{kJ/mol}) - (2)\Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_6)$$

$$\Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_6) = \mathbf{49\ kJ/mol}$$

6.132 Begin by using Equation (6.20) of the text, $\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}}$, where U is the lattice energy.

(1) $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$ $\Delta H_{\text{hydr}} = (4.0 - 788)\ \text{kJ/mol} = -784.0\ \text{kJ/mol}$

(2) $\text{Na}^+(g) + \text{I}^-(g) \rightarrow \text{Na}^+(aq) + \text{I}^-(aq)$ $\Delta H_{\text{hydr}} = (-5.1 - 686)\ \text{kJ/mol} = -691.1\ \text{kJ/mol}$

(3) $\text{K}^+(g) + \text{Cl}^-(g) \rightarrow \text{K}^+(aq) + \text{Cl}^-(aq)$ $\Delta H_{\text{hydr}} = (17.2 - 699)\ \text{kJ/mol} = -681.8\ \text{kJ/mol}$

Adding together equation (2) and (3) and then subtracting equation (1) gives the equation for the hydration of KI.

$$\begin{array}{lll}
(2) & \cancel{\text{Na}^+}(g) + \text{I}^-(g) \rightarrow \cancel{\text{Na}^+}(aq) + \text{I}^-(aq) & \Delta H = -691.1\ \text{kJ/mol} \\
(3) & \text{K}^+(g) + \cancel{\text{Cl}^-}(g) \rightarrow \text{K}^+(aq) + \cancel{\text{Cl}^-}(aq) & \Delta H = -681.8\ \text{kJ/mol} \\
(1) & \cancel{\text{Na}^+}(aq) + \cancel{\text{Cl}^-}(aq) \rightarrow \cancel{\text{Na}^+}(g) + \cancel{\text{Cl}^-}(g) & \Delta H = +784.0\ \text{kJ/mol} \\
\hline
 & \text{K}^+(g) + \text{I}^-(g) \rightarrow \text{K}^+(aq) + \text{I}^-(aq) & \Delta H = -588.9\ \text{kJ/mol}
\end{array}$$

We combine this last result with the given value of the lattice energy to arrive at the heat of solution of KI.

$$\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}} = (632\ \text{kJ/mol} - 588.9\ \text{kJ/mol}) = \mathbf{43\ kJ/mol}$$