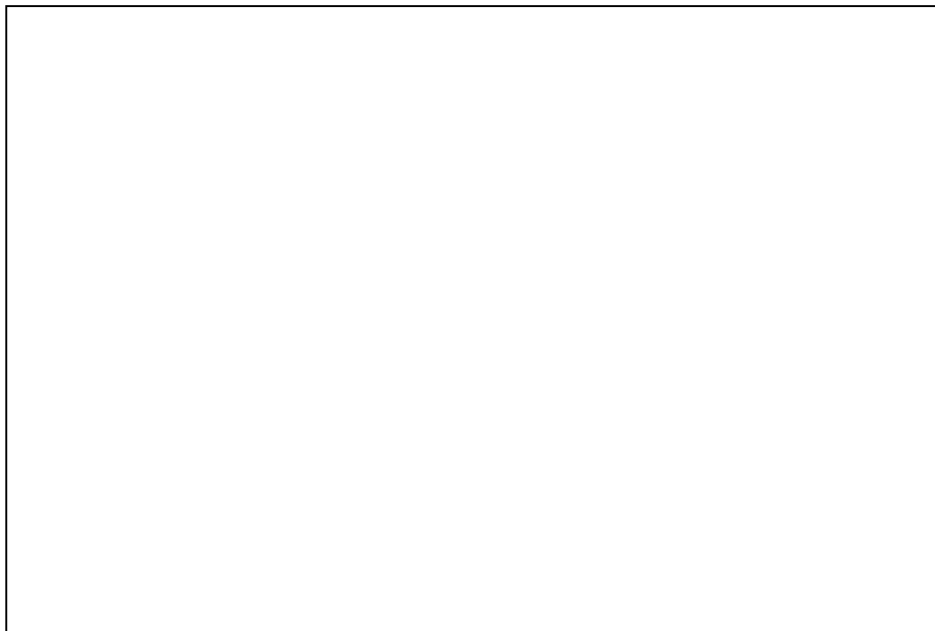


Chapter 5: Thermochemistry



Chapter 5

- 5.1 Energy
- 5.2 Enthalpy
- 5.3 Energy, Temperature Changes, and Changes of State
- 5.4 Enthalpy Changes and Chemical Reactions
- 5.5 Hess's Law
- 5.6 Standard Heats of Reaction

Chapter Goals

- Recognize different types of energy.
- Understand the principles of thermodynamics including heat and work.
- Define enthalpy and understand its relationship to chemical systems.
- Relate energy to temperature change.
- Relate energy to physical change.
- Relate energy to chemical change.

Chapter In Context

In this chapter we begin an exploration of thermochemistry, the study of the role that energy in the form of heat plays in chemical processes. We will investigate the energy changes that take place during phase changes and the chemical reactions you have studied in previous chapters and learn why some chemical reactions occur while others do not. In the chapter that follows, we will study energy changes at the molecular level and the consequences those energy changes have on the properties of atoms and elements.

- Environmental Studies/Industry:

A major portion of our economy is based on extracting potential energy from fossil fuels that have been built up over millions of years through photosynthesis, where plants chemically store energy obtained from sunlight. The energy is stored in the form of chemical compounds that are high in chemical potential energy. Chemicals that are high in chemical potential energy can be made to react to give off heat, and that heat energy can in turn be used to run an engine or heat a home. During all these processes energy is transformed from one form to another, but is never really removed or added to. That is, energy is constant: our economy is based on finding sources of one type of energy (chemically stored potential energy) and turning it into another kind of energy (heat, thermal energy).

5.1 Energy



OWL Opening Exploration
5.1 Types of Energy

Chemical reactions involve reactants undergoing chemical change to form new substances, products.

Reactants → Products

What is not apparent in the above equation is the role of energy in a reaction. For many reactions, energy, often in the form of heat, is absorbed—that is, it acts somewhat like a reactant. You might write an equation for those reactions that looks like this:

Energy + Reactants → Products

In other reactions, energy is produced—that is, it acts like a product:

Reactants → Products + Energy

In many reactions, such as the combustion of gasoline in a car or natural gas on a stovetop burner, energy is the most important product.

Energy is defined most simply as the ability to do work. **Work** is defined in many ways, the simplest definition being the force involved in moving an object some distance. From a chemist's point of view, energy is best viewed as the ability to cause change, and **thermochemistry** is the study of how energy in the form of heat is involved in chemical change.

Kinetic and Potential Energy

Energy takes many forms such as mechanical, electrical, or gravitational. These are categorized into two broad classes: **kinetic energy**, energy associated with motion, and **potential energy**, energy associated with position.

Most of the events we see around us involve *conversion* of energy from one form to another. Consider the use of a small photocell to run a fan (Figure 5.1).

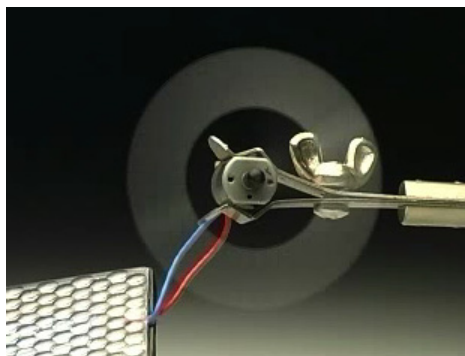


Figure 5.1 A photoelectric cell drives this small fan.

In this example, light (radiant energy) is absorbed by the photocell, which converts it into an electric current. That electric current is then used to drive the fan. The energy conversions occurring are therefore:

radiant (kinetic and potential) → electrical (kinetic and potential) → mechanical (kinetic)

Measuring Energy: Energy Units

Energy is measured in different units. For example, heating fuel is typically measured in British Thermal Units, BTUs, and food energy content is measured in Calories. Energy

Calculating Kinetic and Potential Energy

Kinetic energy is calculated from the equation

$$KE = \frac{1}{2} mv^2$$

m = mass

v = velocity

Potential energy calculations depend on the forces that exist between particles. Because different types of particles experience different types of forces, it is not possible to use a single equation to calculate potential energy.

Chapter Goals Revisited

- Recognize different types of energy.
Use and interconvert energy units.

associated with most chemical processes is reported in terms of joules (J) and kilojoules (kJ), or calories (cal) and kilocalories (kcal). The food energy unit, Calorie, is equal to 1 kcal.

One joule is equal to the energy needed to accelerate a 1 kg object by $1 \text{ m}^2/\text{s}^2$. One calorie is the energy needed to raise the temperature of one gram of pure water by one degree Celsius. Table 5.2 shows conversion factors for joules, calories, BTU, and kilowatt-hours, the energy unit used in measuring electrical energy.

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

Table 5.2 Energy unit conversion factors

	J	kJ	cal	kcal	kWh	BTU
1 J =	1	0.001	0.2390	2.390×10^{-4}	2.778×10^{-7}	9.479×10^{-4}
1 kJ =	1000	1	239.0	0.2390	2.778×10^{-4}	0.9479
1 cal =	4.184	4.184×10^{-3}	1	0.001	1.162×10^{-6}	3.968×10^{-3}
1 kcal =	4184	4.184	1000	1	1.162×10^{-3}	3.968
1 kWh =	3.6×10^6	3.6×10^3	8.604×10^5	860.4	1	3143
1 BTU =	1055	1.055	252	0.252	2.93×10^{-4}	1

EXAMPLE PROBLEM: Energy Unit Conversion

A barrel contains 42 gallons of oil. This is the equivalent of 4.50×10^{10} J of energy. How many kilowatt-hours of electrical energy does this barrel represent?

SOLUTION:

The conversion factor table tells us that $1 \text{ J} = 2.778 \times 10^{-7} \text{ kWh}$ of energy. The conversion is therefore,

$$450 \times 10^{10} \text{ J} \left(\frac{2.778 \times 10^{-7} \text{ kWh}}{1 \text{ J}} \right) = 1250 \text{ kWh}$$



OWL Example Problem
5.2: Energy Unit Conversion (Tutor)
5.3: Energy Unit Conversion

Principles of Thermodynamics

Thermochemistry is part of the field of **thermodynamics**, the study of the relationships between heat, energy and work and the conversion of one into the other. When considering chemical events, it is useful to define the **system**, the item or reaction of interest and separate that from the **surroundings**, everything else. An **isolated system** is one in which neither matter nor energy can be passed to or from the surroundings. A **closed system** is one in which energy but not matter can be passed to or from the surroundings. In almost all cases in chemistry, the system of interest is closed and the **internal energy**, the energy of the system, changes when energy in the form of heat (q) is added or lost and work (w) is done by or on the system. While the total internal energy of a system cannot be measured directly, the **change in internal energy**, ΔE_{system} , is calculated from the following equation:

$$\Delta E_{\text{system}} = q + w \quad (5.x)$$

q = energy in the form of heat exchanged between system and surroundings

w = work done by or on the system

The **first law of thermodynamics** states that the total energy for an isolated system is constant. That is, the combined amount of energy and matter in an isolated system is constant. Energy is neither created nor destroyed during chemical or physical changes, but it is instead transformed from one form to another. In other words, energy is conserved during a chemical or physical change, or

$$\Delta E_{\text{universe}} = 0 \quad (5.x)$$

Chapter Goals Revisited

- Understand the principles of thermodynamics including heat and work. **Define system and surroundings for a physical or chemical event.**

As shown in Figure 5.x, sign convention is important in thermodynamics because it indicates what is happening to the internal energy of the system. When energy in the form of heat is transferred from the surroundings to the system, q is positive, and when heat is transferred from the system to the surroundings, q is negative. Similarly, when work is done by the surroundings on the system, w is positive, and it is negative when work is done by the system on the surroundings.

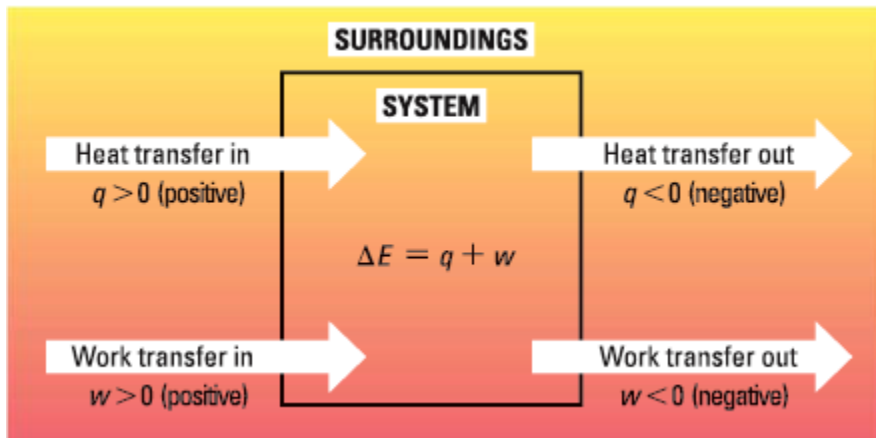


Figure 5.x Sign conventions for q and w .

Sign conventions in thermodynamics

$+q$ and $+w$

- energy is added to system
- internal energy of system increases

$-q$ and $-w$

- energy is removed from system
- internal energy of system decreases

Chapter Goals Revisited

- Understand the principles of thermodynamics including heat and work. **Calculate internal energy change for a system.**

EXAMPLE PROBLEM: First Law Calculations

A gas is compressed and during this process the surroundings does 128 J of work on the gas. At the same time, the gas loses 270 J of energy to the surroundings as heat. What is the change in the internal energy of the gas?

SOLUTION:

According to the first law of thermodynamics, $\Delta E_{\text{system}} = q + w$. During the process described here, the gas loses heat to the surroundings (q is negative) while work is done on the gas by the surroundings (w is positive).

$$q = -270 \text{ J}$$

$$w = 128 \text{ J}$$

$$\Delta E_{\text{system}} = q + w = (-270 \text{ J}) + (128 \text{ J}) = -142 \text{ J}$$



OWL Example Problem
5.4: First Law Calculations

5.2 Enthalpy



OWL Opening Exploration
5.X

Enthalpy, H , is defined as the sum of the internal energy of a system plus the product of pressure and volume.

$$H = E + PV \quad (5.x)$$

In most chemical systems under study, reactions are performed under conditions of constant pressure. Under these conditions, the **change in enthalpy, ΔH** , is equal to the heat exchanged under constant pressure. Note that, like the internal energy of a system, enthalpy cannot be measured directly and it is not possible to know the amount of enthalpy present in a chemical sample. However, enthalpy change and therefore *relative* enthalpy, can be measured.

Do Bonds Contain Energy?

No, they do not. However, energy can be transferred when bonds are formed or are broken.

- Energy is always required to break bonds.
- Energy is always given off when bonds are formed.

Enthalpy is a measure of the total heat content of a system, and is related to both chemical potential energy and the degree to which electrons are attracted to nuclei in molecules. When electrons are strongly attracted to nuclei, there are strong bonds between atoms, molecules are relatively stable, and enthalpy is low. In contrast, when electrons are only weakly attracted to nuclei, there are weak bonds between atoms, molecules are relatively unstable, and enthalpy is high.

The sign of ΔH indicates the direction of energy transfer (Figure 5.x). In an **exothermic** reaction, heat is transferred from the system to the surroundings. The enthalpy change for an exothermic reaction has a negative value ($\Delta H < 0$). During exothermic reactions, weakly bonded molecules are converted to strongly bonded molecules, chemical potential energy is converted into heat, and the temperature of the surroundings increases. In an **endothermic** reaction, heat is transferred from the surroundings to the system. The enthalpy change for an endothermic reaction has a positive value ($\Delta H > 0$). During endothermic reactions, strongly bonded molecules are converted to weakly bonded molecules, heat is converted into chemical potential energy, and the temperature of the surroundings decreases.

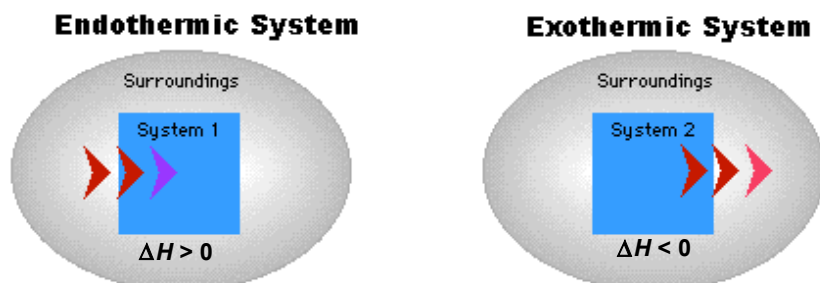


Figure 5.x Enthalpy sign conventions

Representing Energy Change

Chemists often think of chemical and physical changes in terms of the associated enthalpy changes and visualize these changes in an *enthalpy diagram*. In these diagrams, the horizontal axis indicates the different states of a system undergoing change or the reactants and products in a reaction. The vertical axis shows the relative enthalpy of each state, which is indicated using a horizontal line. Enthalpy increases as you move up the vertical axis, so higher that line occurs on the y-axis, the higher the enthalpy for a given species. Figure 5.YY shows simple enthalpy diagrams for endothermic and exothermic chemical reactions.

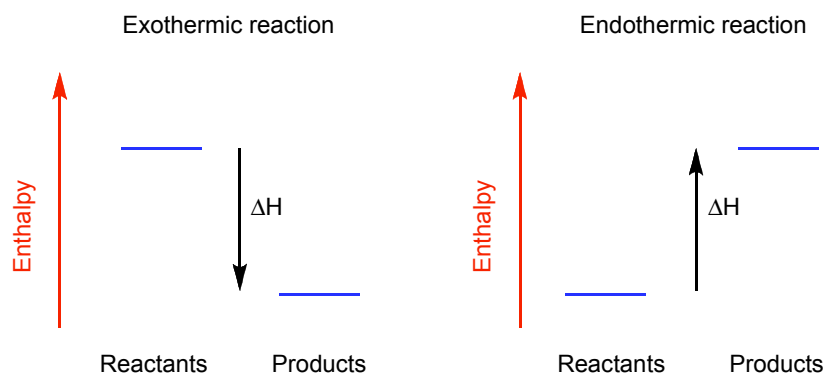


Figure 5.YY Enthalpy diagrams

The enthalpy change for the reaction, ΔH , is the difference between the enthalpies of the different states or the reactants and products. In the exothermic enthalpy diagram in Figure 5.YY, the products of the reaction are at lower enthalpy than the reactants, so ΔH

Chapter Goals Revisited

- Define enthalpy and understand its relationship to chemical systems.
Define endothermic and exothermic processes.

Chapter Goals Revisited

- Define enthalpy and understand its relationship to chemical systems.
Use energy diagrams to represent endothermic and exothermic processes.

for the reaction is negative. The reaction is exothermic, the reaction releases heat, and the chemical bonding in the products is stronger than that in the reactants

5.3 Energy, Temperature Changes and Changes of State



OWL Opening Exploration

5.6 Temperature Change from Heat Transfer: Simulation

5.7 Heat Transfer and Thermal Equilibrium: Simulation

When an object is heated, three things can happen: it can get warmer, it can undergo a phase change, and it can undergo a chemical change. In this section, we explore the first two possibilities while the remainder of the chapter explores the third.

Heat Transfer and Temperature Changes

When an object gains thermal kinetic energy, its constituent atoms and molecules move more rapidly and its temperature increases. There are three factors that control the magnitude of a temperature change for an object: the amount of heat energy added to the object, the mass of the object, and the material the object is made of. Consider lighting a match and using it to heat a large glass of water. Heat is transferred from the burning match to the water, but the temperature of the water does not increase very much. Now consider using a lit match to heat the tip of a needle. In this case, the needle becomes quite hot. A similar amount of heat energy is added to each object, but the needle gets hotter because it has a smaller mass than the water and is made of metal, which has a lower specific heat capacity than the water. **Specific heat capacity** is the amount of energy needed to raise the temperature of 1 g of a substance by 1 °C (equation 5.x).

$$c, \text{ specific heat capacity (J/g}\cdot\text{°C)} = \frac{q, \text{ heat energy absorbed (J)}}{m, \text{ mass (g)} \cdot \Delta T, \text{ change in temperature (°C)}} \quad (5.x)$$

Some specific heat capacity values are given in Table 5.Y.

Table 5.Y

Specific Heat Capacity Values of Common Substances		
Substance	Name	Specific Heat (J/g K)
Al(s)	aluminum	0.897
Fe(s)	iron	0.449
Cu(s)	copper	0.385
Au(s)	gold	0.129
NH ₃ (g)	ammonia	4.70
C ₂ H ₅ OH(l)	ethanol	2.44
H ₂ O(l)	water (liquid)	4.184
H ₂ O(s)	water (ice)	2.06
	wood	1.8
	concrete	0.9
	glass	0.8
	granite	0.8
O ₂ (g)	oxygen	0.917
N ₂ (g)	nitrogen	1.04

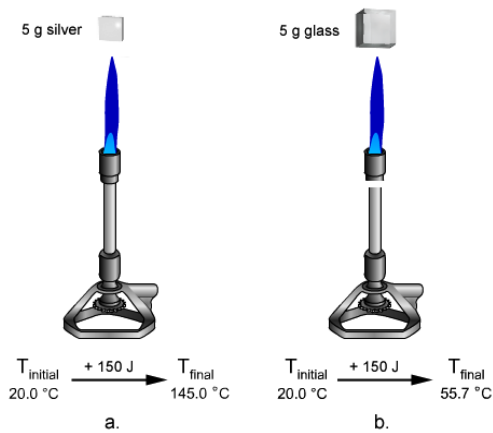
Specific heat capacity values are reported in units of J/g·°C or J/g·K. The values do not change with the different units because a one-degree increment is the same on both temperature scales. Notice in Table 5.Y that some materials, such as metals, have low specific heat capacity, which means it takes relatively little energy to cause a large temperature increase. Other materials, such as water, have high specific heat capacities so it takes much more energy to effect the same increase in temperature. For example, the same amount of heat energy will raise the temperature of a 1-g sample of gold over 30 times more than it would a 1-g sample of water.

Chapter Goals Revisited

- Relate energy to temperature change.
Use specific heat capacity to relate energy, mass, and change in temperature.

Determining Specific Heat Capacity

The value of the specific heat capacity can be determined if the energy, mass, and temperature change are all known for the sample. Consider the experiment shown in Figure 5.YY. In this experiment, 5-g samples of silver and of glass are heated and 150 J of heat energy is added to each sample.



Chapter Goals Revisited

- Relate energy to temperature change. **Use specific heat capacity in calculations.**

Figure 5. YY Addition of 150 J of heat energy to 5 g of (a) silver and (b) glass.

The temperature change of the silver sample is much greater than that of the glass sample. This indicates that silver has a smaller specific heat capacity.

EXAMPLE PROBLEM: Determining Specific Heat Capacity

Using the data in Figure 5.YY, determine the specific heat capacity of silver.

SOLUTION:

Use Equation 5.x to calculate the specific heat capacity of silver.

$$q = \text{heat energy transferred} = 150\text{ J}$$

$$m = 5.0\text{ g}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 145.0\text{ }^{\circ}\text{C} - 20.0\text{ }^{\circ}\text{C} = 125.0\text{ }^{\circ}\text{C}$$

$$c_{\text{Ag}} = \frac{q}{m \cdot \Delta T} = \frac{150\text{ J}}{(5\text{ g})(125\text{ }^{\circ}\text{C})} = 0.24\text{ J/g}\cdot^{\circ}\text{C}$$



OWL Example Problems
5.8 *Determining Specific Heat Capacity*

Using Specific Heat Capacity

Calculating the amount of energy associated with temperature changes and predicting the magnitude of temperature changes are essential skills in working with energy and chemical systems. Two examples of how these calculations are performed are shown below.

EXAMPLE PROBLEM: Using Specific Heat Capacity

- (a) Determine the amount of heat energy is associated with heating a 154-gram iron bar from 20.0 °C to 485 °C.
 (b) Calculate the final temperature reached when 324 J of heat is added to a 24.5-g iron bar initially at 20.0 °C.

SOLUTION:

- (a) Use Equation 5.x to calculate the amount of heat transferred to the iron bar.

$$c_{\text{Fe}} = 0.449 \text{ J/g}\cdot^{\circ}\text{C}$$

$$m = 154 \text{ g}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 485 \text{ }^{\circ}\text{C} - 20.0 \text{ }^{\circ}\text{C} = 465 \text{ }^{\circ}\text{C}$$

$$q = m \cdot c_{\text{Fe}} \cdot \Delta T = (154 \text{ g})(0.449 \text{ J/g}\cdot^{\circ}\text{C})(465 \text{ }^{\circ}\text{C}) = 3.21 \times 10^4 \text{ J}$$

- (b) Use Equation 5.x to calculate the change in temperature of the iron bar.

$$c_{\text{Fe}} = 0.449 \text{ J/g}\cdot^{\circ}\text{C}$$

$$m = 24.5 \text{ g}$$

$$q = 324 \text{ J}$$

$$\Delta T = \frac{q}{m \cdot c_{\text{Fe}}} = \frac{324 \text{ J}}{(24.5 \text{ g})(0.449 \text{ J/g}\cdot^{\circ}\text{C})} = 29.5 \text{ }^{\circ}\text{C}$$

The temperature of the iron bar therefore increases from 20.0 °C to 49.5 °C.



OWL Example Problems

5.9 Using Specific Heat Capacity: Tutor

5.10 Using Specific Heat Capacity

Heat Transfer Between Substances: Thermal Equilibrium and Temperature Changes

When objects at different temperatures come into contact, the hotter object transfers thermal energy to the cooler object. This causes the hotter object to cool, and the cooler object to warm. This process occurs until the two objects reach the same temperature, a state of *thermal equilibrium*. At any point in the heat transfer, the quantity of heat energy lost by the hotter object ($-q_{\text{lost}}$) is equal to that gained by the cooler object ($+q_{\text{gained}}$). That is, $q_{\text{lost}} + q_{\text{gained}} = 0$.

Consider a heated iron bar plunged into water. If we define iron as the system and the water as the surroundings, the process is exothermic as heat energy is lost by the system (iron) to the surroundings (water). Figure 5.x illustrates the energetic changes that take place in the system and surroundings.

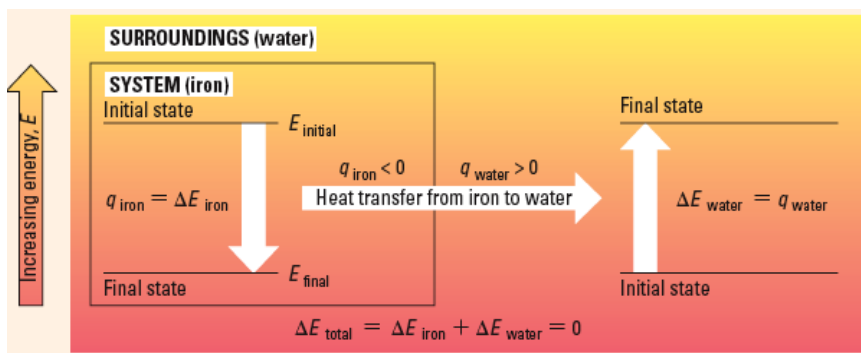


Figure 5.x Energy changes when heated iron bar plunged into water

When two objects with different initial temperatures are brought into contact, they reach the same temperature at thermal equilibrium. The final temperature is calculated by recognizing that magnitude of energy transferred for each is the same, as shown in the following example.

EXAMPLE PROBLEM: Predicting Thermal Equilibrium Temperatures

A 12.00-g block of copper at 12.0 °C is immersed in a 5.00-g pool of ethanol with a temperature of 68.0 °C. When thermal equilibrium is reached, what is the temperature of the copper and ethanol?

SOLUTION:

Because the magnitude of energy lost by the ethanol is equal to the energy gained by the copper, $q_{\text{Cu}} + q_{\text{ethanol}} = 0$.

Use equation 5.x to calculate the energy lost and gained upon reaching thermal equilibrium, and the final temperature.

$$c_{\text{Cu}} = 0.385 \text{ J/g}\cdot^{\circ}\text{C}$$

$$c_{\text{ethanol}} = 2.44 \text{ J/g}\cdot^{\circ}\text{C}$$

$$m_{\text{Cu}} = 12.00 \text{ g}$$

$$m_{\text{ethanol}} = 5.00 \text{ g}$$

$$T_{\text{initial}}(\text{Cu}) = 12.0 \text{ }^{\circ}\text{C}$$

$$T_{\text{initial}}(\text{ethanol}) = 68.0 \text{ }^{\circ}\text{C}$$

$$q_{\text{Cu}} + q_{\text{ethanol}} = 0$$

$$[(12.00 \text{ g})(0.385 \text{ J/g}\cdot^{\circ}\text{C})(T_{\text{f}} - 12.0 \text{ }^{\circ}\text{C})] + [(5.00 \text{ g})(2.44 \text{ J/g}\cdot^{\circ}\text{C})(T_{\text{f}} - 68.0 \text{ }^{\circ}\text{C})] = 0$$

$$4.62 \cdot T_{\text{f}} - 55.44 + 12.2 \cdot T_{\text{f}} - 829.6 = 0$$

$$16.82 \cdot T_{\text{f}} = 885.04$$

$$T_{\text{f}} = 52.6 \text{ }^{\circ}\text{C}$$



OWL Example Problems

5.11 Predicting Thermal Equilibrium Temperatures: Tutor

5.12 Predicting Thermal Equilibrium Temperatures

Energy, Changes of State, and Heating Curves

If you heat a sample of ice at $-10 \text{ }^{\circ}\text{C}$ at 1 atm pressure, it becomes warmer. If you heat ice at $0 \text{ }^{\circ}\text{C}$ (and 1 atm), however, initially it does not become warmer. Instead, the ice melts while maintaining a constant temperature of $0 \text{ }^{\circ}\text{C}$, the melting point of water.

As stated earlier, when an object is heated, it can get warmer, it can undergo a phase change, and it can undergo a chemical change. We have discussed the energy changes associated with warming and cooling objects. We now turn to the second possible outcome, a phase change.

When a solid such as ice is heated and melts, the heat energy is used to overcome the forces holding the water molecules together in the solid phase. The heat energy is therefore changed into chemical potential energy. This potential energy can be reconverted to thermal energy when the forces between water molecules form again, when liquid water freezes to form ice (Figure 5.YY).

Figure 5.YY (To come) *Figure showing how melting involves overcoming forces between water molecules and how thermal kinetic energy is converted into chemical potential energy.*

The energy to affect a phase change has been measured for a number of substances. The enthalpy (heat) of fusion (ΔH_{fus}) for a substance is the energy needed to melt one gram or one mole of that substance. The enthalpy (heat) of vaporization (ΔH_{vap}) is the energy needed to vaporize one gram or one mole of that substance.

Chapter Goals Revisited

- Relate energy to physical change. **Calculate energy involved in phase change of a substance.**

EXAMPLE PROBLEM: Phase Changes

Given the following information for mercury, Hg (at 1 atm), calculate the amount of heat needed (at 1 atm) to vaporize a 30.0-g sample of liquid mercury at its normal boiling point of 357 °C.

boiling point = 357 °C $\Delta H_{\text{vap}}(357 \text{ °C}) = 59.3 \text{ kJ/mol}$
 melting point = -38.9 °C $\Delta H_{\text{fus}}(-38.9 \text{ °C}) = 2.33 \text{ kJ/mol}$
 specific heat (liquid) = 0.139 J/g·°C

SOLUTION:

This is a constant-temperature process in which the liquid is vaporized at its normal boiling point. Use the heat of vaporization of mercury to calculate the amount of heat needed to vaporize the liquid.

$$30.0 \text{ g} \cdot \frac{1 \text{ mol Hg}}{200.6 \text{ g}} \cdot \frac{59.3 \text{ kJ}}{1 \text{ mol Hg}} = 8.87 \text{ kJ}$$



OWL Example Problems
 5.13 Phase Changes: Tutor
 5.14 Phase Changes

We now have the tools needed to calculate both the amount of thermal energy required to warm an object in a particular physical state and the amount of thermal energy required to change the physical state of a substance. Figure 5.YY shows the energy involved in heating 1-g samples of benzene and water over a large temperature range.

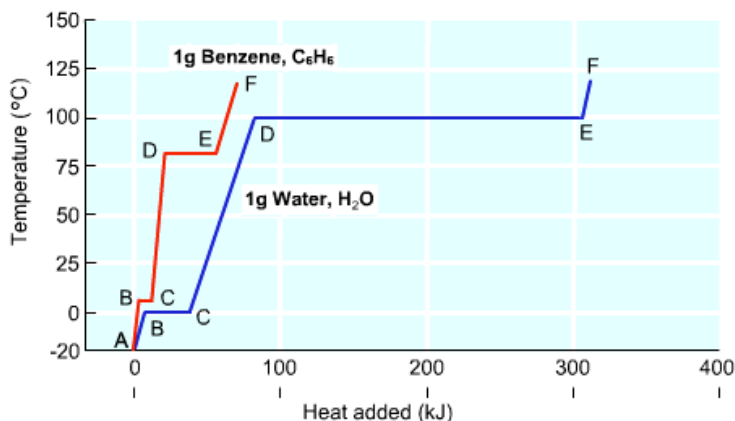


Figure 5.YY. Heating curves for 1-g samples of benzene and water

When 1-gram samples of the solids at -20 °C are heated, the following processes occur between the indicated points on the heating curves:

1. A to B: Temperature increases as added heat warms the solid to its melting point.
2. B to C: Temperature remains constant as solid is converted to liquid at the melting point.
3. C to D: Temperature increases as added heat warms the liquid to its boiling point.
4. D to E: Temperature remains constant as liquid is converted to vapor at the boiling point.
5. E to F: Temperature increases as added heat warms the vapor above its boiling point.

As shown in the following example, the amount of heat required to heat a substance can be calculated when specific heat capacities, enthalpy of fusion, and enthalpy of vaporization values are known.

Chapter Goals Revisited

- Relate energy to physical change.
Interpret a heating curve for a pure substance.

EXAMPLE PROBLEM: Heating Curves

The following information is given for ethanol at 1 atm:

boiling point = 78.40 °C	$\Delta H_{\text{vap}}(78.40\text{ °C}) = 837.0\text{ J/g}$
melting point = -114.5 °C	$\Delta H_{\text{fus}}(-114.5\text{ °C}) = 109.0\text{ J/g}$
specific heat (gas) = 1.430 J/g·°C	specific heat (liquid) = 2.460 J/g·°C

A 33.50-g sample of liquid ethanol is initially at 13.50 °C. If the sample is heated at constant pressure ($P = 1\text{ atm.}$), calculate the amount of energy needed to raise the temperature of the sample to 94.50 °C.

SOLUTION:

This is a three step process: (1) raise the temperature of the liquid to its boiling point, (2) vaporize the liquid at its boiling point and (3) raise the temperature of the resulting gas to the final temperature.

(1) Calculate the amount of energy required to heat the liquid from 13.50 °C to 78.40 °C.

$$q(1) = m \cdot c_{\text{liquid}} \cdot \Delta T = (33.50\text{ g})(2.460\text{ J/g}\cdot\text{°C})(78.40\text{ °C} - 13.50\text{ °C}) = 5348\text{ J}$$

(2) Calculate the amount of energy required to vaporize the liquid at its boiling point.

$$q(2) = m \cdot \Delta H_{\text{vap}} = (33.50\text{ g})(837.0\text{ J/g}) = 2.804 \times 10^4\text{ J}$$

(3) Calculate the amount of energy required to heat the vapor from 78.40 °C to 94.50 °C.

$$q(3) = m \cdot c_{\text{gas}} \cdot \Delta T = (33.50\text{ g})(1.430\text{ J/g}\cdot\text{°C})(94.50\text{ °C} - 78.40\text{ °C}) = 771.3\text{ J}$$

The total amount of energy needed to heat the sample of ethanol is the sum of the energy required for the three steps.

$$q_{\text{total}} = q(1) + q(2) + q(3) = 5348\text{ J} + 2.804 \times 10^4\text{ J} + 771.3\text{ J} = 3.416 \times 10^4\text{ J} = 34.16\text{ kJ}$$



OWL Example Problems
5.16 Heating Curves: Simulation

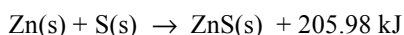
5.4. Enthalpy Changes and Chemical Reactions



OWL Opening Exploration
5.X

We have examined the ways in which energy transferred to or from a sample can change its temperature or phase. Of far greater interest and importance is the energy associated with chemical change. When elements or compounds combine to form a new compound, bonds between the atoms in the reactants are broken and new bonds form in the products. Breaking and forming chemical bonds leads to a change in enthalpy, which is observed as a release or absorption of thermal energy.

For example, when zinc and sulfur react, a large amount of thermal energy is released (Figure 5.YY).



The energy released is the **enthalpy change for a reaction** (ΔH_{rxn}).

$$\Delta H_{\text{rxn}} = -205.98\text{ kJ}$$

Chapter Goals Revisited

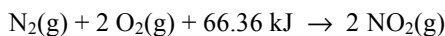
- Relate energy to chemical change.
Use enthalpy change of reaction in calculations.



Figure 5.YY. Zinc and sulfur (a) react (b) to form zinc sulfide (c)

The negative sign of ΔH_{rxn} indicates that the reaction is exothermic. The enthalpy of the system (zinc and sulfur) decreases, and energy is released.

In contrast, when nitrogen and oxygen react to form nitrogen dioxide (Figure 5.YY), thermal energy is absorbed.



This reaction is endothermic and the enthalpy change for the reaction has a positive value.

$$\Delta H_{\text{rxn}} = +66.36 \text{ kJ}$$

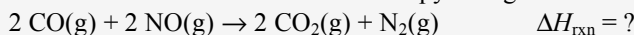
The enthalpy change for a reaction is the energy associated when the reaction occurs as written. That is, 66.36 kJ of energy is absorbed when 1 mole of N_2 reacts with 2 moles of O_2 to form 2 moles of NO_2 .



Figure 5.YY. Nitrogen dioxide is a brown gas.

EXAMPLE PROBLEM: Enthalpy Changes and Chemical Reactions

When CO reacts with NO according to the following reaction, 373 kJ of energy are evolved for each mole of CO that reacts. Use this information to calculate the enthalpy change for the reaction.



SOLUTION:

Energy is evolved in this reaction, so the sign of ΔH_{rxn} is negative. The equation shows the reaction of two moles of CO, so the energy change for the reaction is

$$\Delta H_{\text{rxn}} = 2 \text{ mol CO} \cdot \frac{-373 \text{ J}}{1 \text{ mol CO}} = -746 \text{ kJ}$$



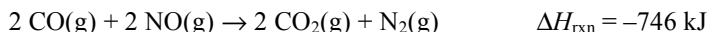
OWL Example Problems

5.18 Enthalpy Changes and Chemical Reactions: Tutor

5.19 Enthalpy Changes and Chemical Reactions

Enthalpy Change and Chemical Equations

The enthalpy change for a given reaction is a function of the stoichiometry of the chemical reaction. For example, the previous example problem showed that the reaction of carbon monoxide with nitric oxide releases 373 kJ of energy per mole of CO.

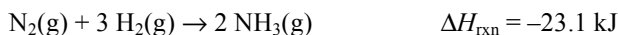


Consider, however, the reaction of 0.250 mol carbon monoxide. The amount of energy released can be calculated from the enthalpy of reaction.

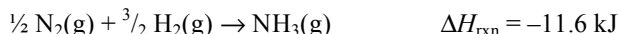
$$0.250 \text{ mol CO} \times \frac{746 \text{ kJ}}{2 \text{ mol CO}} = 93.3 \text{ kJ energy released}$$

This calculation is valid because enthalpy is an **extensive variable**, which means that it is dependent on the amount of substance present and therefore a change in enthalpy is also dependent on the amount of substance that reacts. The reaction of 250. mol of CO with NO, for example, results in the release of 9.33×10^4 kJ of energy.

Knowing that enthalpy is an extensive variable allows us to look at the relationship between the enthalpy change for a reaction and the chemical equation. Consider for example the production of ammonia from elemental nitrogen and hydrogen.

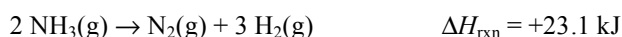


In this reaction, 23.1 kJ of energy is released when 2 mol of NH_3 is formed. The formation of 1 mol of NH_3 ,



releases half as much energy, 11.6 kJ. Thus, *when a chemical equation is multiplied by a constant, the enthalpy change is also multiplied by that constant.*

Consider the decomposition of ammonia to form elemental nitrogen and hydrogen.



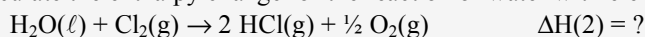
This is the reverse of the equation for the formation of ammonia from elemental nitrogen and hydrogen. Because the original equation represented an exothermic reaction (heat is evolved to the surroundings), the reverse reaction is endothermic (heat is absorbed from the surroundings). *When the reactants and products in a chemical equation are reversed, the magnitude of ΔH is identical but the sign of ΔH is reversed.*

EXAMPLE PROBLEM: Enthalpy Change and Chemical Equations

The reaction of HCl with O_2 is exothermic.



Calculate the enthalpy change for the reaction of water with elemental chlorine to produce HCl and O_2 .



SOLUTION:

The second reaction is related to the first reaction by (1) reversing reactants and products and (2) multiplication by a constant ($\times \frac{1}{2}$). Thus the enthalpy change for the second reaction is equal to $-\Delta H(1) \times \frac{1}{2}$.

$$\Delta H(2) = -\Delta H(1) \times \frac{1}{2} = -(-202.4 \text{ kJ}) \times \frac{1}{2} = 101.2 \text{ kJ}$$



OWL Example Problems
5.24 Enthalpy Change and Chemical Equations

Determining Enthalpy Change: Calorimetry

Tabulated ΔH_{rxn} values are derived from experimental data. Experiments that measure heat exchange are referred to collectively as **calorimetry** experiments, and the measurement device is called a **calorimeter**. There are two important types of calorimetry experiments, constant-pressure calorimetry (also known as coffee-cup calorimetry) and constant-volume calorimetry (also known as bomb calorimetry).

In constant-pressure calorimetry, the heat evolved or absorbed during a chemical change is measured under conditions where the pressure does not change. This typically means that the chemical change is allowed to occur in a reaction vessel that is open to the atmosphere, and thus the pressure remains essentially constant. Under these conditions, the heat evolved or absorbed, q , is equal to the enthalpy change for the reaction, ΔH .

Heat exchange under conditions of constant pressure can be measured using a simple coffee-cup calorimeter (shown Figure 5.YY). The reaction vessel consists of two nested styrofoam coffee cups that are covered with a lid. A thermometer measures the temperature change. Most coffee-cup calorimetry experiments involve a solvent such as water and a stirring device ensures thorough mixing in the reaction vessel.

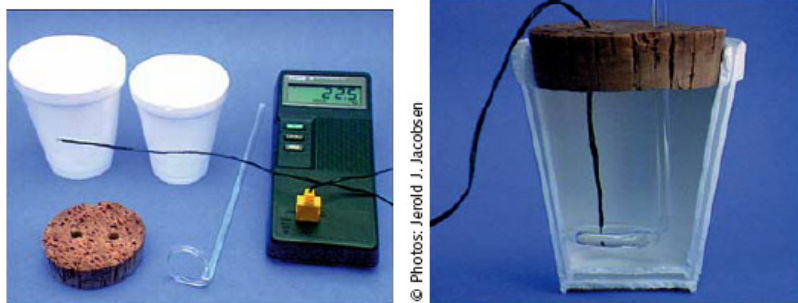


Figure 5.YY. A coffee-cup calorimeter

Chapter Goals Revisited

- Relate energy to chemical change.
Calculate enthalpy change from calorimetry experiments.

In a constant-pressure calorimetry experiment, the system consists of the chemicals undergoing change, and the surroundings consist of the other contents of the calorimeter, the calorimeter itself, and all materials around the calorimeter. However, the calorimeter is designed to minimize energy transfer, and thus it is possible to assume that the surroundings consist only of the contents of the calorimeter. Therefore, the temperature change measured by the thermometer allows calculation of $q_{\text{surroundings}}$ for a chemical change in a coffee-cup calorimeter.

$$q_{\text{surroundings}} = (\text{mass of calorimeter contents})(\text{specific heat of solution})(\Delta T)$$

Because $0 = q_{\text{system}} + q_{\text{surroundings}}$, the enthalpy change for a chemical process taking place in a coffee-cup calorimeter is

$$\Delta H = q_{\text{system}} = -q_{\text{surroundings}}$$

In a typical experiment, enthalpy change is reported per mol of reactant (kJ/mol). Note that in constant-pressure calorimetry experiments, an increase in temperature indicates an exothermic reaction ($q_{\text{surroundings}}$ is positive, q_{system} and ΔH are negative) and a decrease in temperature indicates an endothermic reaction ($q_{\text{surroundings}}$ is negative, q_{system} and ΔH are positive).

**Constant-pressure calorimetry:
Sign of ΔT , q , and ΔH**

Exothermic reactions

- Temperature increases ($+\Delta T$)
- $+q_{\text{surroundings}}$
- $-q_{\text{system}}$
- $-\Delta H$

Endothermic reactions

- Temperature decreases ($-\Delta T$)
- $-q_{\text{surroundings}}$
- $+q_{\text{system}}$
- $+\Delta H$

EXAMPLE PROBLEM: Constant-Pressure Calorimetry

Ammonium chloride is very soluble in water. When 4.50 g NH_4Cl is dissolved in 53.00 g of water, the temperature of the solution decreases from 20.40 °C to 15.20 °C. Calculate the enthalpy of dissolution of NH_4Cl in kJ/mol.

Assume that the specific heat of the solution is 4.18 J/g·°C and that the heat absorbed by the calorimeter is negligible.

SOLUTION:

First calculate the energy change for the surroundings (q_{solution}) in the coffee-cup calorimeter.

$$c_{\text{solution}} = 4.18 \text{ J/g}\cdot^\circ\text{C}$$

$$m_{\text{solution}} = 4.50 \text{ g} + 53.00 \text{ g} = 57.50 \text{ g}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 15.20 \text{ }^\circ\text{C} - 20.40 \text{ }^\circ\text{C} = -5.20 \text{ }^\circ\text{C}$$

$$q_{\text{solution}} = m \cdot c_{\text{solution}} \cdot \Delta T = (57.50 \text{ g})(4.18 \text{ J/g}\cdot^\circ\text{C})(-5.20 \text{ }^\circ\text{C}) = -1250 \text{ J}$$

Next calculate q for the dissolution of NH_4Cl , q_{system} .

$$q_{\text{dissolution}} + q_{\text{solution}} = 0$$

$$q_{\text{solution}} = -q_{\text{dissolution}} = 1250 \text{ J}$$

Finally, calculate the amount of NH_4Cl dissolved (mol) and ΔH for the dissolution of NH_4Cl (kJ/mol).

$$4.50 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g}} = 0.0841 \text{ mol NH}_4\text{Cl}$$

$$\Delta H_{\text{dissolution}} = \frac{q_{\text{dissolution}}}{\text{mol NH}_4\text{Cl}} = \frac{1250 \text{ J}}{0.0841 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 14.9 \text{ kJ/mol}$$

Notice that the temperature of the solution decreased, indicating an endothermic process and a positive value for $\Delta H_{\text{dissolution}}$.



OWL Example Problems

5.20 Constant-Pressure Calorimetry: Tutor

5.21 Constant-Pressure Calorimetry

Many constant-pressure calorimetry experiments assume that no heat is transferred to the calorimeter or to the outside surroundings. A more precise experiment is performed using constant-volume calorimetry. Constant-volume experiments can be performed using a bomb calorimeter (Figure 5.YY), a reaction vessel designed to measure the energy change involved in combustion reactions.

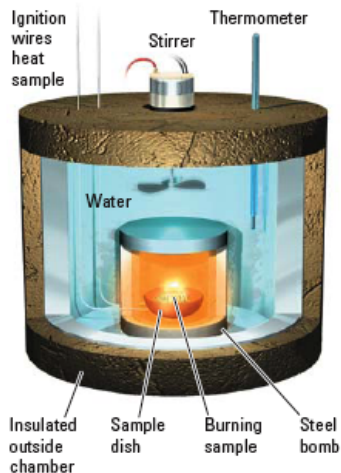


Figure 5.YY. A bomb calorimeter

The chemical reaction studied in a bomb calorimeter takes place inside a sealed steel vessel (the bomb) that is completely surrounded by a water bath, and an insulated jacket surrounds the water bath. The temperature change of the chemical reaction is determined by measuring the temperature change of the water surrounding the bomb.

Because the reaction studied in a bomb calorimetry experiment takes place in a sealed bomb, this is a constant-volume calorimetry experiment, not a constant-pressure experiment. Under constant volume conditions the heat evolved or absorbed by a chemical change, q , is equal to the change in energy, ΔE , not the change in enthalpy, ΔH . However, the difference between ΔE and ΔH is quite small for most chemical reactions.

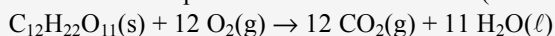
The heat evolved in a bomb calorimeter combustion reaction (q_{reaction}) is absorbed by the steel bomb (q_{bomb}) and the water in the water bath (q_{water}).

$$0 = q_{\text{reaction}} + q_{\text{bomb}} + q_{\text{water}}$$

The heat absorbed by the steel bomb is calculated from the temperature change of the water bath (ΔT) and the bomb heat capacity (c_{bomb} , J/°C). The heat absorbed by the water bath is calculated from the mass of water, the specific heat of water, and the water bath temperature change.

EXAMPLE PROBLEM: Constant-Volume Calorimetry

A 0.444-g sample of sucrose ($C_{12}H_{22}O_{11}$) is burned in a bomb calorimeter and the temperature increases from 20.00 °C to 22.06 °C. The calorimeter contains 748 g of water and the bomb has a heat capacity of 420. J/°C. Calculate ΔE for the combustion reaction per mole of sucrose burned (kJ/mol).

**SOLUTION:**

First, calculate the energy absorbed by the water bath and the bomb.

Water bath:

$$c_{\text{water}} = 4.184 \text{ J/g}\cdot^{\circ}\text{C}$$

$$m_{\text{water}} = 748 \text{ g}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.06 \text{ }^{\circ}\text{C} - 20.00 \text{ }^{\circ}\text{C} = 2.06 \text{ }^{\circ}\text{C}$$

$$q_{\text{water}} = m \cdot c_{\text{water}} \cdot \Delta T = (748 \text{ g})(4.184 \text{ J/g}\cdot^{\circ}\text{C})(2.06 \text{ }^{\circ}\text{C}) = 6450 \text{ J}$$

Bomb:

$$c_{\text{bomb}} = 420. \text{ J/}^{\circ}\text{C}$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.06 \text{ }^{\circ}\text{C} - 20.00 \text{ }^{\circ}\text{C} = 2.06 \text{ }^{\circ}\text{C}$$

$$q_{\text{bomb}} = c_{\text{bomb}} \cdot \Delta T = (420 \text{ J/g}\cdot^{\circ}\text{C})(2.06 \text{ }^{\circ}\text{C}) = 865 \text{ J}$$

Next, calculate the energy released by the combustion reaction.

$$0 = q_{\text{reaction}} + q_{\text{bomb}} + q_{\text{water}}$$

$$q_{\text{reaction}} = -(q_{\text{bomb}} + q_{\text{water}}) = -(865 \text{ J} + 6450 \text{ J}) = -7320 \text{ J}$$

Finally, calculate the amount (mol) of sucrose burned in the combustion reaction and the energy change for the reaction.

$$0.444 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g}} = 0.00130 \text{ mol } C_{12}H_{22}O_{11}$$

$$\Delta E = \frac{q_{\text{reaction}}}{\text{mol } C_{12}H_{22}O_{11}} = \frac{-7320 \text{ J}}{0.00130 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = -5640 \text{ kJ/mol}$$

This is an exothermic reaction. Temperature increased and q_{reaction} and ΔE are negative. In addition, because the difference between ΔE and ΔH is quite small, this energy change can be taken as the enthalpy of combustion (ΔH_{comb}) for sucrose.



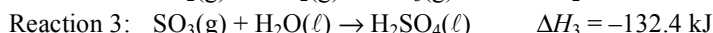
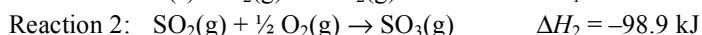
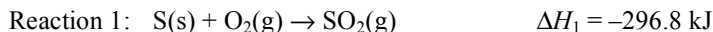
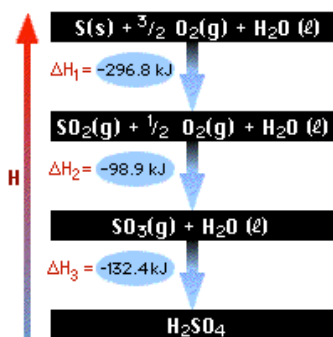
OWL Example Problems
5.22 Bomb Calorimetry: Simulation
5.23 Bomb Calorimetry

5.5. Hess's Law

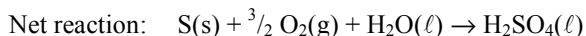
OWL Opening Exploration
5.25 Hess's Law: Simulation

Enthalpy is a **state function**, which means its value for a system depends only on the current state of the system and not on its history. Therefore, the change in enthalpy for a process depends only on the initial and final states for a system and not on the path between the two. For example, the altitude of a given location is like a state function: the difference in altitude between the top and bottom of a mountain has a fixed value, but the length of the hike from bottom to top does not, as there is more than one possible route, each with a different length. The state function nature of enthalpy is expressed in **Hess's Law**, which states that *if a chemical reaction can be expressed as the sum of two or more chemical reactions, the enthalpy change for the net reaction is equal to the sum of the enthalpy changes for the individual steps.*

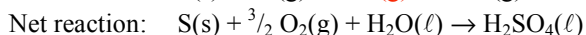
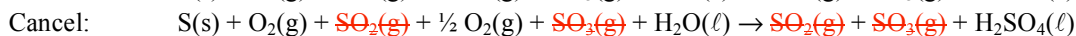
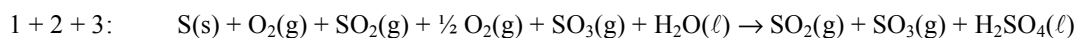
Consider the enthalpy changes for three reactions involved in the formation of sulfuric acid.



The net reaction is the production of sulfuric acid from sulfur, oxygen, and water.



To apply Hess's law, sum reactions 1, 2 and 3 and cancel any species common to the products and reactants in the reaction.



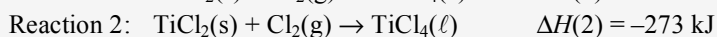
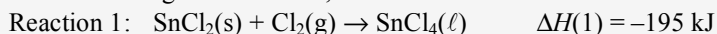
The net reaction is the sum of reactions 1, 2 and 3, and therefore the enthalpy change for the net reaction is equal to the sum of the enthalpy changes for reactions 1, 2 and 3.

$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3 = (-296.8 \text{ kJ}) + (-98.9 \text{ kJ}) + (-132.4 \text{ kJ}) = -528.1 \text{ kJ}$$

As shown in the following example, reactions might need to be reversed or multiplied by a constant before summing to obtain a net reaction.

EXAMPLE PROBLEM: Hess's Law

Given the following two reactions,

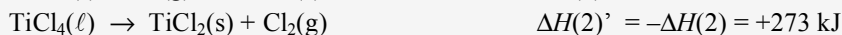
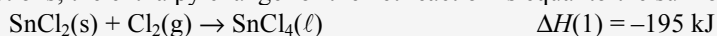


calculate the enthalpy change for the following chlorine exchange reaction.



SOLUTION:

In order to use Hess's Law, the sum of two or more chemical reactions must result in the net reaction. In this example, reversing the second reaction and adding it to the first reaction results in the net reaction. Notice that reversing the second reaction requires changing the sign of $\Delta H(2)$. Because the net reaction can be expressed as the sum of two chemical reactions, the enthalpy change for the net reaction is equal to the sum of the enthalpy changes for the individual steps.



Chapter Goals Revisited

- Relate energy to chemical change.
Calculate enthalpy change using Hess's Law.



OWL Example Problems
5.26 Hess's Law

5.6. Standard Heats of Reaction



OWL Opening Exploration
5.X

Enthalpies vary with experimental conditions such as temperature, pressure, and solution concentration. It is helpful therefore to specify a standard set of conditions under which to tabulate enthalpy change as well as a standard set of enthalpy change values that can be used to calculate the enthalpy change for a reaction.

Standard conditions for enthalpy values are

- gases, liquids, and solids in their pure form at a pressure of 1 bar at a specified temperature; and
- solutions with concentrations of 1 mol/L at a specified temperature.

Notice that standard conditions do not specify a temperature. Most standard enthalpy values are tabulated at 25 °C (298 K), but it is possible to report standard enthalpy change values at other temperatures.

Enthalpy change values that are tabulated under standard conditions are indicated with a superscripted ° symbol, as in $\Delta H_{\text{rxn}}^{\circ}$.

Standard Heat of Formation

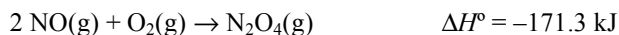
Creating a list of all possible standard enthalpy values is impossible. Fortunately, tabulating only one type of standard enthalpy change is all that is needed in order to calculate the standard enthalpy change for almost any chemical reaction. The **standard heat of formation** (or standard enthalpy of formation) for a species is the enthalpy change for the formation of one mole of a species from its constituent elements in their most stable form. Standard heat of formation values are given the symbol ΔH_f°

For example, the standard heat of formation for solid N_2O_5 is the enthalpy change when one mole of the compound is formed from its constituent elements, nitrogen and oxygen, both in their standard states.



Notice that the chemical reaction for the standard heat of formation of N_2O_5 includes a fractional coefficient. It is often necessary to include fractional coefficients in chemical reactions representing ΔH_f° values because the enthalpy change must be for the formation of one mole of a species.

A chemical reaction that does not represent a standard heat of formation is the formation of gaseous N_2O_4 from nitric oxide and oxygen. The enthalpy change for this reaction is not a ΔH_f° value because NO is not a constituent element of N_2O_4 .



Some standard heat of formation values are shown in Table 5.X and a more complete table is found in the appendix in this textbook.

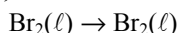
TABLE 5.X Standard Heat of Formation values for selected compounds (kJ/mol) at 25 °C

Formula	Name	Standard molar enthalpy of formation (kJ/mol)	Formula	Name	Standard molar enthalpy of formation (kJ/mol)
Al ₂ O ₃ (s)	Aluminum oxide	-1675.7	HI(g)	Hydrogen iodide	+26.48
BaCO ₃ (s)	Barium carbonate	-1216.3	KF(s)	Potassium fluoride	-567.27
CaCO ₃ (s)	Calcium carbonate	-1206.92	KCl(s)	Potassium chloride	-436.747
CaO(s)	Calcium oxide	-635.09	KBr(s)	Potassium bromide	-393.8
CCl ₄ (l)	Carbon tetrachloride	-135.44	MgO(s)	Magnesium oxide	-601.70
CH ₄ (g)	Methane	-74.81	MgSO ₄ (s)	Magnesium sulfate	-1284.9
C ₂ H ₅ OH(l)	Ethyl alcohol	-277.69	Mg(OH) ₂ (s)	Magnesium hydroxide	-924.54
CO(g)	Carbon monoxide	-110.525	NaF(s)	Sodium fluoride	-573.647
CO ₂ (g)	Carbon dioxide	-393.509	NaCl(s)	Sodium chloride	-411.153
C ₂ H ₂ (g)	Acetylene (ethyne)	+226.73	NaBr(s)	Sodium bromide	-361.062
C ₂ H ₄ (g)	Ethylene (ethene)	+52.26	NaI(s)	Sodium iodide	-287.78
C ₂ H ₆ (g)	Ethane	-84.68	NH ₃ (g)	Ammonia	-46.11
C ₃ H ₈ (g)	Propane	-103.8	NO(g)	Nitrogen monoxide	+90.25
C ₄ H ₁₀ (g)	Butane	-126.148	NO ₂ (g)	Nitrogen dioxide	+33.18
C ₆ H ₁₂ O ₆ (s)	α-D-Glucose	-1274.4	PCl ₃ (l)	Phosphorus trichloride	-319.7
CuSO ₄ (s)	Copper(II) sulfate	-771.36	PCl ₅ (s)	Phosphorus pentachloride	-443.5
H ₂ O(g)	Water vapor	-241.818	SiO ₂ (s)	Silicon dioxide (quartz)	-910.94
H ₂ O(l)	Liquid water	-285.830	SnCl ₂ (s)	Tin(II) chloride	-325.1
HF(g)	Hydrogen fluoride	-271.1	SnCl ₄ (l)	Tin(IV) chloride	-511.3
HCl(g)	Hydrogen chloride	-92.307	SO ₂ (g)	Sulfur dioxide	-296.830
HBr(g)	Hydrogen bromide	-36.40	SO ₃ (g)	Sulfur trioxide	-395.72

*From Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., and Nuttall, R.: The NBS Tables of Chemical Thermodynamic Properties. *Journal of Physical and Chemical Reference Data*, Vol. 11, Suppl. 2, 1982. (NBS, the National Bureau of Standards, is now NIST, the National Institute for Standards and Technology.)

There are some important details that should be noted about ΔH_f° values.

- ΔH_f° values have units of kJ/mol because each is the enthalpy change for the formation of one mole of a chemical species.
- The ΔH_f° value for an element in its standard state is equal to 0 kJ/mol. For example, the reaction for ΔH_f° of elemental bromine is written

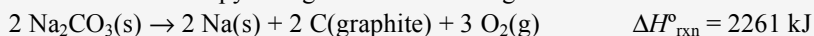


There is no change from reactants to products, so $\Delta H_f^\circ = 0$ kJ/mol.

- Most ΔH_f° values are negative. This indicates that for most species, the formation from elements in their standard states is an exothermic process.

EXAMPLE PROBLEM: Standard Heats of Formation

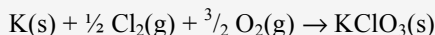
- (a) Write the balanced chemical equation that represents the standard heat of formation of KClO₃(s) at 298 K.
 (b) The standard enthalpy change for the following reaction is 2261 kJ at 298 K.



What is the standard heat of formation of Na₂CO₃(s)?

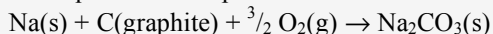
SOLUTION:

- (a) The standard heat of formation (or standard enthalpy of formation) of a substance in a specified state at 298 K is the enthalpy change for the reaction in which one mole of the substance is formed from the elements in their stable forms at 1 atm and 298 K. Potassium is a solid and chlorine and oxygen are diatomic gases at 1 atm and 298 K.



Note that equation must show the formation of one mole of product.

- (b) The equation that represents the standard heat of formation of Na₂CO₃(s) is



Reversing the equation in the problem and multiplying by $\frac{1}{2}$ results in the equation for the standard heat of formation of Na₂CO₃, so

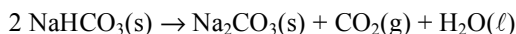
$$\Delta H_f^\circ = -\frac{1}{2}(\Delta H_{\text{rxn}}^\circ) = -\frac{1}{2}(2261 \text{ kJ}) = -1131 \text{ kJ/mol}$$



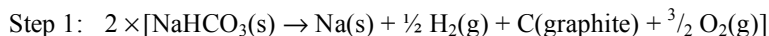
OWL Example Problems
5.28 Standard Heats of Formation

Using Standard Heats of Formation

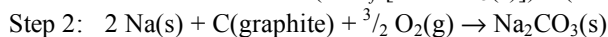
Standard heat of formation values, when combined with Hess's Law, are used to calculate the enthalpy change for a reaction under standard conditions. Consider the following reaction, at 25 °C.



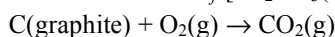
The reaction can be thought to occur in two steps. First, reactants are broken down into constituent elements in their standard states, and second, the elements are recombined to form products.



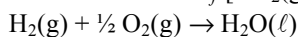
$$\Delta H^\circ = 2 \times (-\Delta H_f^\circ[\text{NaHCO}_3(\text{s})]) = (2 \text{ mol NaHCO}_3)[-(-950.81 \text{ kJ/mol})]$$



$$\Delta H^\circ = \Delta H_f^\circ[\text{Na}_2\text{CO}_3(\text{s})] = (1 \text{ mol Na}_2\text{CO}_3)(-1130.68 \text{ kJ/mol})]$$



$$\Delta H^\circ = \Delta H_f^\circ[\text{CO}_2(\text{g})] = (1 \text{ mol CO}_2)(-393.51 \text{ kJ/mol})]$$



$$\Delta H^\circ = \Delta H_f^\circ[\text{H}_2\text{O}(\ell)] = (1 \text{ mol H}_2\text{O})(-187.78 \text{ kJ/mol})]$$

Both steps involve ΔH_f° values. In step 1, the sign of $\Delta H_f^\circ[\text{NaHCO}_3(\text{s})]$ is reversed because the standard heat of formation reaction is reversed. The value is also multiplied by 2 because two moles of NaHCO_3 are broken down into constituent elements. Step 2 reactions are standard heat of formation reactions, so the enthalpy change for each is equal to ΔH_f° .

Summing the four reactions in steps 1 and 2 results in the net reaction. Therefore, using Hess's Law, the enthalpy change for the net reaction is equal to the sum of the enthalpy changes for the reactions in steps 1 and 2.

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 2 \times (-\Delta H_f^\circ[\text{NaHCO}_3(\text{s})]) + \Delta H_f^\circ[\text{Na}_2\text{CO}_3(\text{s})] + \Delta H_f^\circ[\text{CO}_2(\text{g})] + \Delta H_f^\circ[\text{H}_2\text{O}(\ell)] \\ &= 1901.62 \text{ kJ} + (-1130.68 \text{ kJ}) + (-393.51 \text{ kJ}) + (-187.78 \text{ kJ}) \\ &= 189.65 \text{ kJ} \end{aligned}$$

A general formula used to calculate the standard enthalpy change for a reaction from standard heats of formation is

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \quad (5.x)$$

where each ΔH_f° value is multiplied by the stoichiometric coefficient in the balanced chemical equation. Note that the sign of the ΔH_f° values for the reactants is reversed. As shown above, this is due to the need to reverse the standard heat of formation reaction in order to break apart reactants into constituent elements. Notice also that, because each ΔH_f° value is multiplied by the number of moles of the species in the balanced equation, the standard enthalpy change calculated using equation 5.x has units of kJ. Using equation 5.x to calculate the standard enthalpy change for the reaction above,

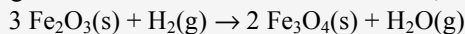
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= (1 \text{ mol Na}_2\text{CO}_3)(\Delta H_f^\circ[\text{Na}_2\text{CO}_3(\text{s})]) + (1 \text{ mol CO}_2)(\Delta H_f^\circ[\text{CO}_2(\text{g})]) \\ &\quad + (1 \text{ mol H}_2\text{O})(\Delta H_f^\circ[\text{H}_2\text{O}(\ell)]) - (2 \text{ mol NaHCO}_3)(\Delta H_f^\circ[\text{NaHCO}_3(\text{s})]) \\ &= (1 \text{ mol Na}_2\text{CO}_3)(-1130.68 \text{ kJ/mol}) + (1 \text{ mol CO}_2)(-393.51 \text{ kJ/mol}) \\ &\quad + (1 \text{ mol H}_2\text{O})(-187.78 \text{ kJ/mol}) - [(2 \text{ mol NaHCO}_3)(-950.81 \text{ kJ/mol})] \\ &= 189.65 \text{ kJ} \end{aligned}$$

Chapter Goals Revisited

- Relate energy to chemical change.
Calculate enthalpy change using standard heats of formation.

EXAMPLE PROBLEM: Standard Heats of Formation

Using the standard heats of formation below, calculate the standard enthalpy change for the following reaction.



Compound	ΔH_f° (kJ/mol)
$\text{Fe}_2\text{O}_3(\text{s})$	-824.2
$\text{Fe}_3\text{O}_4(\text{s})$	-1118.4
$\text{H}_2\text{O}(\text{g})$	-241.8

SOLUTION:

The standard enthalpy change for a reaction can be calculated from the standard heats of formation of the products and reactants, each multiplied by the stoichiometric coefficient in the balanced equation. Recall that the standard heat of formation for an element in its stable state at 298 K at 1 atm is zero.

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) \\ &= (2 \text{ mol Fe}_3\text{O}_4)(\Delta H_f^\circ[\text{Fe}_3\text{O}_4(\text{s})]) + (1 \text{ mol H}_2\text{O})(\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})]) - (3 \text{ mol Fe}_2\text{O}_3)(\Delta H_f^\circ[\text{Fe}_2\text{O}_3(\text{s})]) \\ &= (2 \text{ mol Fe}_3\text{O}_4)(-1118.4 \text{ kJ/mol}) + (1 \text{ mol H}_2\text{O})(-241.8 \text{ kJ/mol}) - (3 \text{ mol Fe}_2\text{O}_3)(-824.2 \text{ kJ/mol}) \\ &= -6.00 \text{ kJ} \end{aligned}$$



OWL Example Problems

5.29 Enthalpy of Formation and Enthalpy Change: Tutor

5.30 Enthalpy of Formation and Enthalpy Change

Chapter Review

OWL Summary Assignments

5.XX Chapter Review

5.XX Challenge Problems

Key Equations

$$\Delta E_{\text{system}} = q + w \quad (5.x)$$

$$\Delta E_{\text{universe}} = 0 \quad (5.x)$$

$$H = E + PV \quad (5.x)$$

$$c, \text{ specific heat capacity (J/g}\cdot^\circ\text{C)} = \frac{q, \text{ heat energy absorbed (J)}}{m, \text{ mass (g)} \cdot \Delta T, \text{ change in temperature (}^\circ\text{C)}} \quad (5.x)$$

$$\Delta H_{\text{rxn}}^\circ = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) \quad (5.x)$$

Key Terms**5.1 Energy**

energy

work

thermochemistry

kinetic energy

potential energy

thermodynamics

system

surroundings

isolated system

closed system

internal energy

first law of thermodynamics

5.2 Enthalpy

enthalpy

change in enthalpy

exothermic

endothermic

5.3 Energy, Temperature Changes, and Changes of State

specific heat capacity

thermal equilibrium

5.4 Enthalpy Changes and Chemical Reactions

enthalpy change for a reaction

extensive variable

calorimetry

calorimeter

5.5 Hess's Law

state function

Hess's Law

5.6 Standard Heats of Reaction

standard conditions

standard heat of formation