

EBBING - GAMMON

General
Chemistry
ELEVENTH EDITION

Chapter 6 Thermochemistry

Contents and Concepts

Understanding Heats of Reaction

The first part of the chapter lays the groundwork for understanding what we mean by heats of reaction.

- Energy and Its Units
First Law of Thermodynamics; Work and Heat
- Heat of Reaction; Enthalpy of Reaction
- Thermochemical Equations
- Applying Stoichiometry to Heats of Reaction
- Measuring Heats of Reaction

Using Heats of Reaction

Now that we understand the basic properties of heats of reaction and how to measure them, we can explore how to use them.

7. Hess's Law

8. Standard Enthalpies of Formation

9. Fuels—Foods, Commercial Fuels, and Rocket Fuels

Learning Objectives

Understanding Heats of Reaction

- **Energy and Its Units**
 - Define *energy*, *kinetic energy*, and *internal energy*.
 - Define the SI unit of energy *joule*, as well as the common unit of energy *calorie*.
 - Calculate the kinetic energy of a moving object.
 - State the law of conservation of energy.

2. Heat of Reaction

- Define a thermodynamic system and its surroundings.
- Define *work* and *heat*.
- Define the change of internal energy of a system.
- Express the *first law of thermodynamics* verbally and mathematically.

3. Heat of Reaction; Enthalpy of Reaction

- Define the heat of reaction.
- Distinguish between an exothermic process and an endothermic process.
- Explain how enthalpy and internal energy are related.
- Describe *pressure-work* verbally and mathematically.
- Define enthalpy and enthalpy of reaction.
- Relate the heat of reaction at constant pressure and the enthalpy of reaction.

4. Thermochemical Equations

- Define a *thermochemical equation*.
- Write a thermochemical equation given pertinent information.
- Learn the two rules for manipulating (reversing and multiplying) thermochemical equations.
- Manipulate a thermochemical equation using these rules.

5. Applying Stoichiometry to Heats of Reaction

- Calculate the heat absorbed or evolved from a reaction given its enthalpy of reaction and the mass of a reactant or product.

6. Measuring Heats of Reaction

- a. Define *heat capacity* and *specific heat*.
- b. Relate the heat absorbed or evolved to the specific heat, mass, and temperature change.
- c. Calculate the heat involved in changing the temperature of a material, given its specific heat.
- d. Define a *calorimeter*.
- e. Calculate the enthalpy of reaction from calorimetric data (its temperature change and heat capacity).

Using Heats of Reaction

7. Hess's Law

- a. State Hess's law of heat summation.
- b. Apply Hess's law to obtain the enthalpy change for one reaction from the enthalpy changes of a number of other reactions.

8. Standard Enthalpies of Formation

- a. Define *standard state* and *reference form*.
- b. Define *standard enthalpy of formation*.
- c. Calculate the heat of a phase transition using standard enthalpies of formation for the different phases.
- d. Calculate the heat (enthalpy) of reaction from the standard enthalpies of formation of the substances in the reaction.

9. Fuels—Foods, Commercial Fuels, and Rocket Fuels

- Define a *fuel*.
- Describe the three needs of the body that are fulfilled by foods.
- Give the approximate average values quoted (per gram) for the heat values (heats of combustion) for fats and for carbohydrates.
- List the three major fossil fuels.
- Describe the processes of coal gasification and coal liquefaction.
- Describe some fuel-oxidizer systems used in rockets.

Thermodynamics

The science of the relationship between heat and other forms of energy.

Thermochemistry

An area of thermodynamics that concerns the study of the heat absorbed or evolved by a chemical reaction.

Energy

The potential or capacity to move matter.

Energy can exist in the different forms such as heat, light, and electricity. These forms can be interconverted.

Kinetic Energy, E_K

The energy associated with an object by virtue of its motion.

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

In the equation:

m = mass

v = velocity

Joule

The SI unit of energy

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

Calorie

A commonly-used non-SI unit of energy.

It is the amount of energy required to raise the temperature of one gram of water by one degree Celsius.

The exact definition is given by the equation:

$$1 \text{ cal} = 4.184 \text{ J}$$

A regulation baseball weighing 143 g (0.143 kg) travels 75 miles per hour (33.5 m/s). Calculate the kinetic energy of the baseball in joules as well as in calories.

Using the formula to calculate kinetic energy,

$$E_k = \frac{1}{2} \times 0.143 \text{ kg} \times (33.5 \text{ m/s})^2 = 80.2 \text{ J}$$

Converting joules to calories,

$$80.2 \text{ J} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 19.2 \text{ cal}$$

Potential Energy, E_p

The energy an object has by virtue of its position in a field of force.

Gravitational potential energy is given by the equation

$$E_p = mgh$$

m = mass (kg)

g = gravitational constant (9.80 m/s²)

h = height (m)

Internal Energy, U

The sum of the kinetic and potential energies of the particles making up a substance.

Formula for determining total energy

$$E_{\text{tot}} = E_K + E_P + U$$

Law of Conservation of Energy

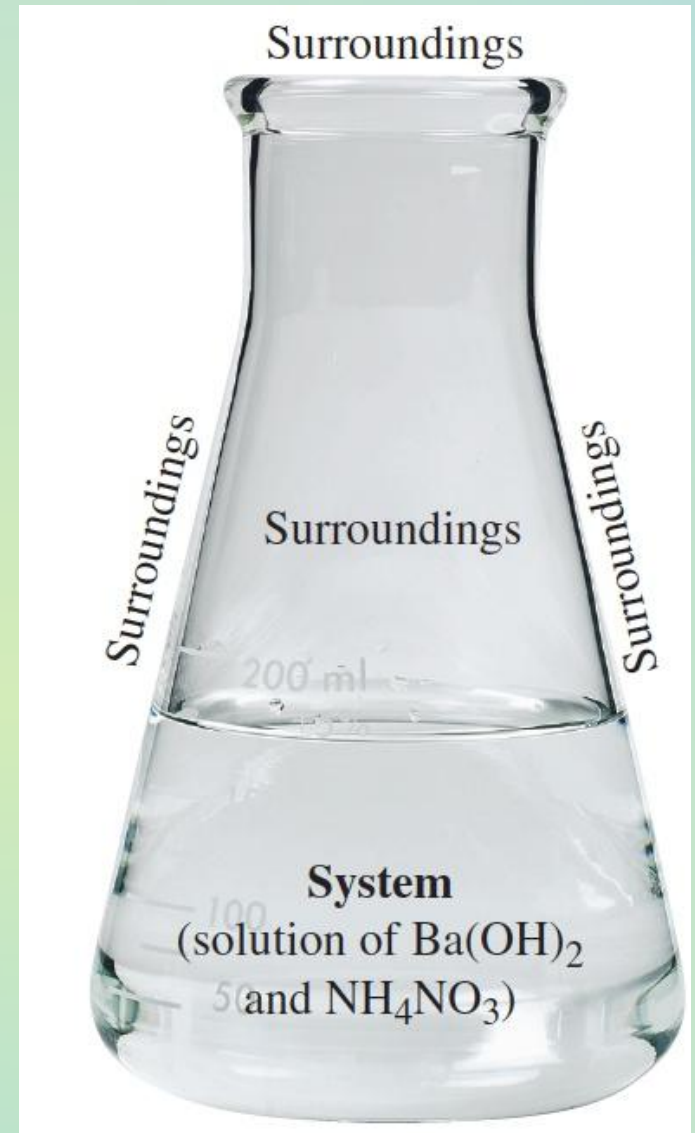
Energy may be converted from one form to another, but the total quantity of energy remains constant.

Thermodynamic System

The substance or mixture of substances that are the focus of a study.

Thermodynamic Surroundings

Everything in the vicinity of the thermodynamic system.



Work, w

An energy transfer into or out of a thermodynamic system whose effect on the surroundings is equivalent to moving an object through a field of force.

Work is chosen to be positive when work is done on the thermodynamic system and negative when work is done by the thermodynamic system.

Heat, q

A transfer of energy into or out of a thermodynamic system caused by a temperature difference between the system and its surroundings.

Heat flows spontaneously from a region of higher temperature to a region of lower temperature.

- q is defined as positive if heat is absorbed by the system (heat is added to the system)
- q is defined as negative if heat is evolved by a system (heat is subtracted from the system)

Change in Internal Energy

It is determined by the formula

$$\Delta U = U_f - U_i$$

U_f = final internal energy

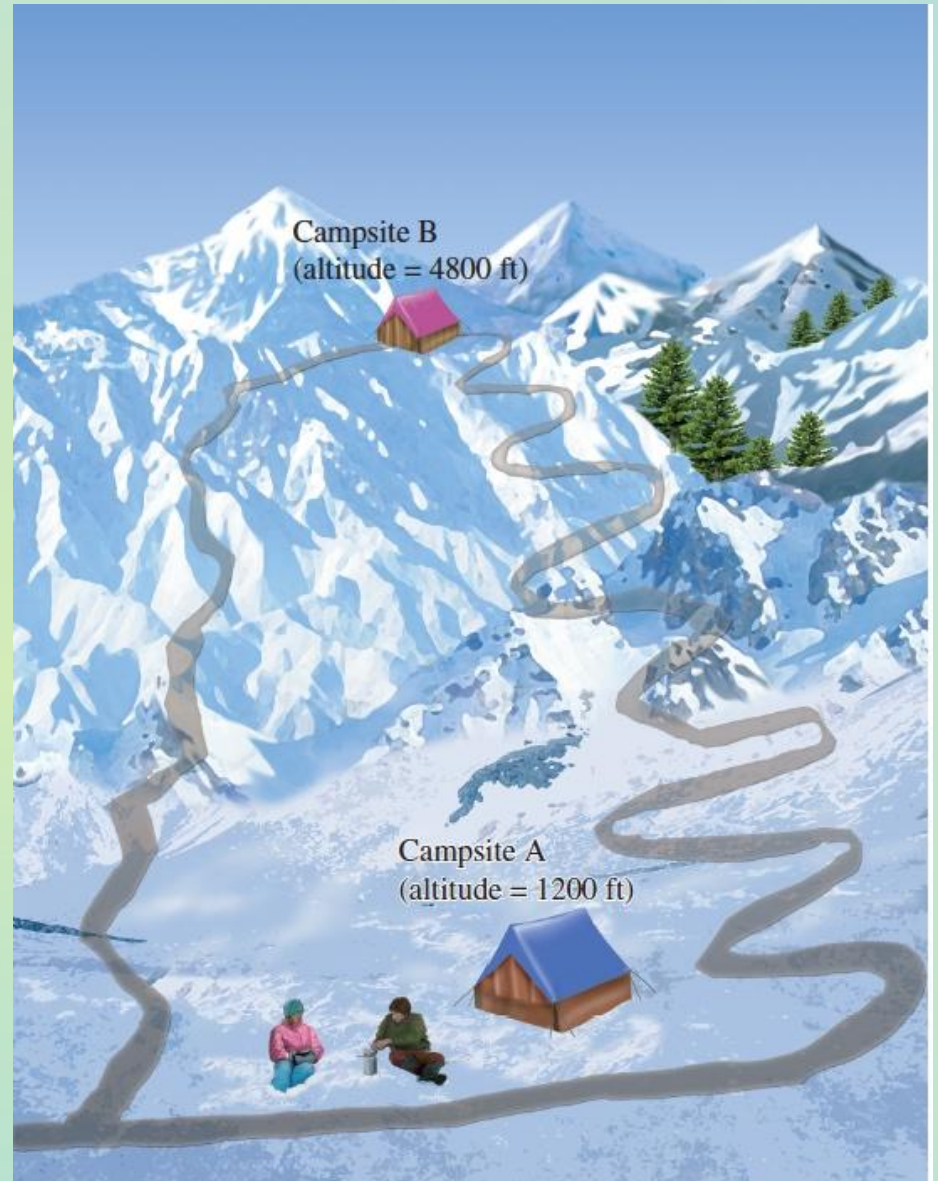
U_i = initial internal energy

State function

A property of a system that depends only on its present state. It is independent of any previous history of the system.

The altitude of a campsite is a state function.

It is independent of the path taken to reach it.



First Law of Thermodynamics

The change in the internal energy of a system, ΔU , is the sum of heat, q , and work, w .

$$\Delta U = q + w$$

Heat of Reaction

The heat absorbed or evolved from a reaction system to retain a fixed temperature of the system under the conditions specified for the reaction.

Exothermic Process

A chemical reaction or process in which heat is evolved by the system (q is negative).

Endothermic Process

A chemical reaction or process in which heat is absorbed by the system (q is positive).

In an **endothermic** reaction:

The reaction vessel cools.

Heat is absorbed.

Energy is added to the system.

q is positive.

In an **exothermic** reaction:

The reaction vessel warms.

Heat is evolved.

Energy is subtracted from the system.

q is negative.

Pressure-Volume Work

A reaction in which the work done equals the product between the negative of the pressure and the change in the system's volume.

$$w = -P\Delta V$$

Enthalpy, H

It is the sum of internal energy, U , and the product of pressure, P , and volume, V .

$$H = U + PV$$

As U , P , and V are state functions, H is also a state function.

Enthalpy of Reaction

The change in enthalpy for a reaction at a given temperature and fixed pressure:

Change in enthalpy is determined by the formula:

$$\Delta H = H_f - H_i$$

According to the first law of dynamics,

$$\Delta U = q + w = q - P\Delta V$$

Solving for heat of reaction (q),

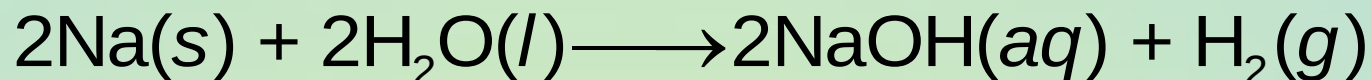
$$q = \Delta U + P\Delta V = (U_f - U_i) + P(V_f - V_i)$$

Regrouping the terms,

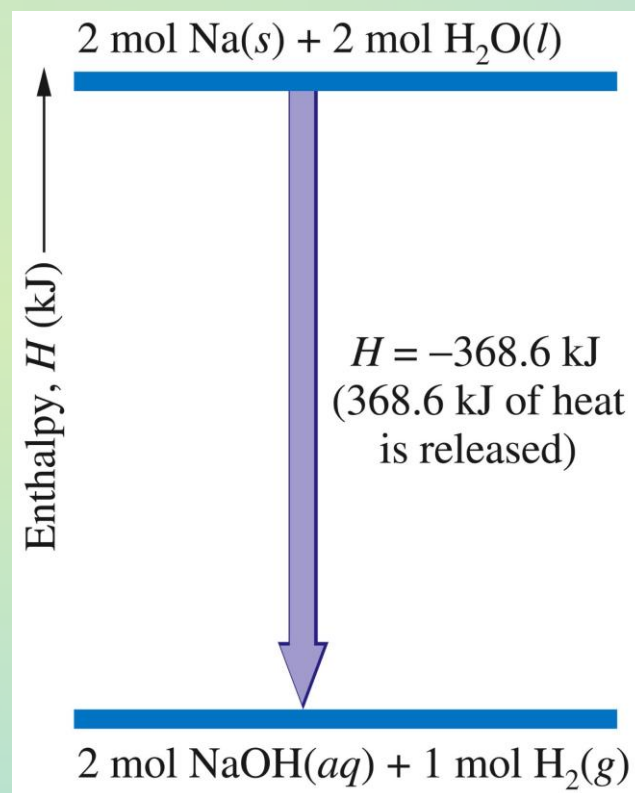
$$q = (U_f + PV_f) - (U_i + PV_i) = H_f - H_i$$

Thus, $q = \Delta H$

The diagram illustrates the enthalpy change for the reaction



The reactants are at the top. The products are at the bottom. The products have less enthalpy than the reactants, so enthalpy is evolved as heat. The signs of both q and ΔH are negative.



Thermochemical Equation

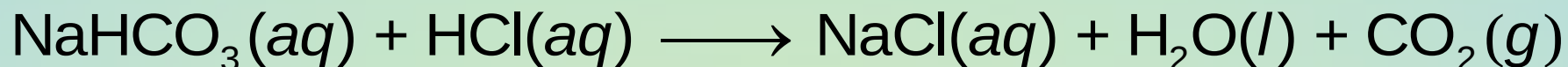
The chemical equation for a reaction (including phase labels) in which the equation is given a molar interpretation, and the enthalpy of reaction for these molar amounts is written directly after the equation.

For the reaction of sodium metal with water, the thermochemical equation is:



Aqueous sodium hydrogen carbonate solution (baking soda solution) reacts with hydrochloric acid to produce aqueous sodium chloride, water, and carbon dioxide gas. The reaction absorbs 12.7 kJ of heat at constant pressure for each mole of sodium hydrogen carbonate. Write the thermochemical equation for the reaction.

The balanced chemical equation is:



The thermochemical equation is:

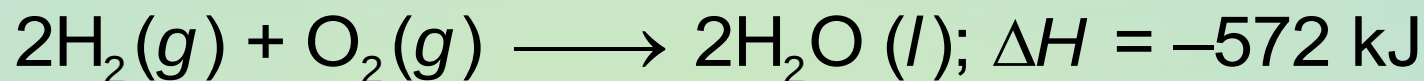


Manipulating a Thermochemical Equation

When the thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that same factor.

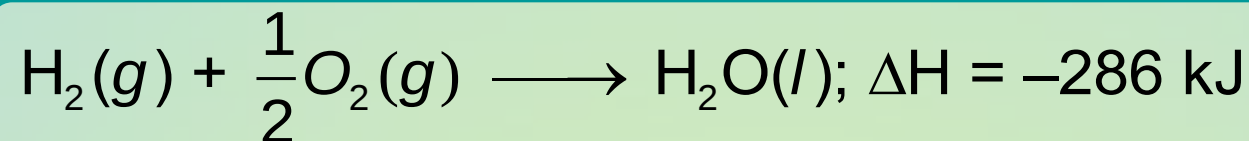
When a chemical equation is reversed, the sign of ΔH is reversed.

When 2 mol $\text{H}_2(g)$ and 1 mol $\text{O}_2(g)$ react to give water, 572 kJ of heat evolves.

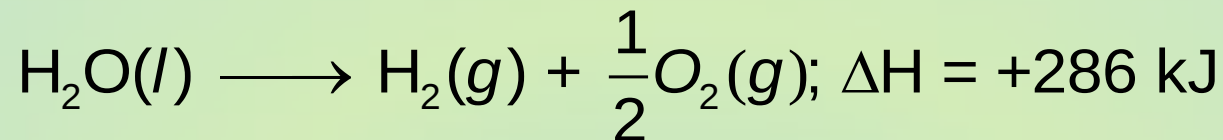


Write this equation for 1 mol of liquid water. Give the reverse equation, in which 1 mol of liquid water dissociates into hydrogen and oxygen.

Multiplying the coefficients and ΔH by $\frac{1}{2}$,



Reversing the equation gives:

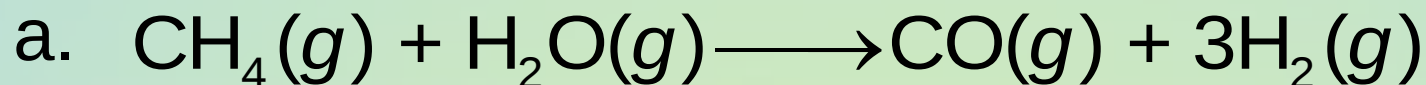
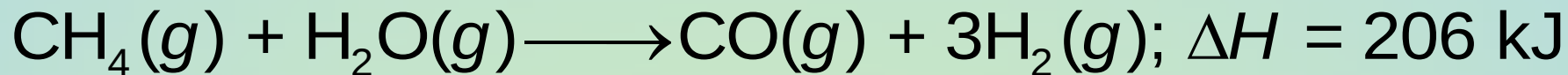


Natural gas consists primarily of methane, CH_4 . It is used in a process called steam reforming to prepare a gaseous mixture of carbon monoxide and hydrogen for industrial use.



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

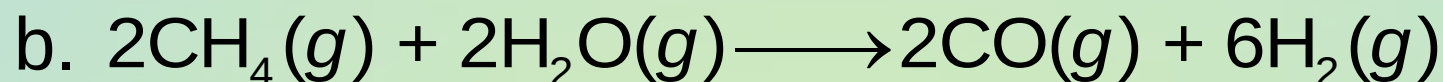
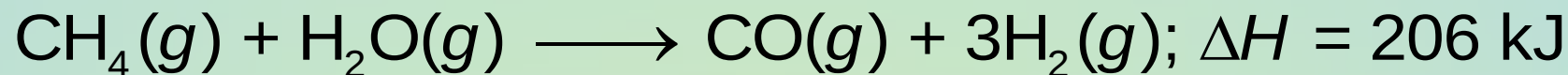
- a.** $\text{CH}_4(g) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + 3\text{H}_2(g)$
- b.** $2\text{CH}_4(g) + 2\text{H}_2\text{O}(g) \longrightarrow 2\text{CO}(g) + 6\text{H}_2(g)$
- c.** $\text{CO}(g) + 3\text{H}_2(g) \longrightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g)$
- d.** $2\text{CO}(g) + 6\text{H}_2(g) \longrightarrow 2\text{CH}_4(g) + 2\text{H}_2\text{O}(g)$



This reaction is identical to the given reaction.

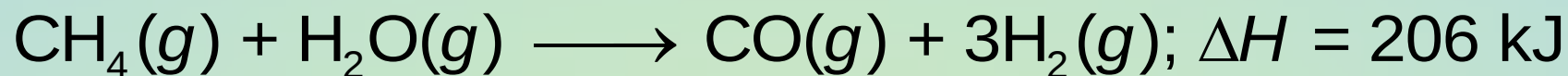
It is endothermic.

$$\Delta H = 206 \text{ kJ}$$



This reaction is double the given reaction.
It is endothermic.

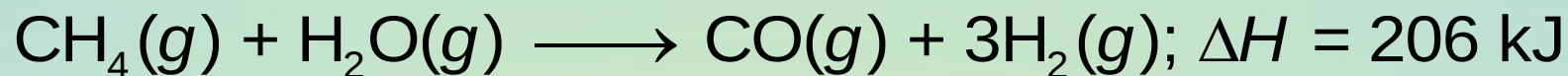
$$\Delta H = 412 \text{ kJ}$$



This reaction is the reverse of the given reaction.

It is exothermic.

$$\Delta H = -206 \text{ kJ}$$



This reaction is reverse and double the given reaction.

It is exothermic.

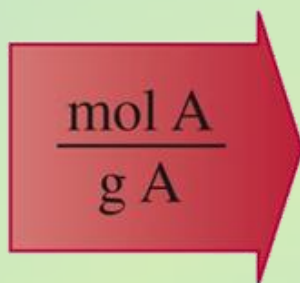
$$\Delta H = -412 \text{ kJ}$$

Equations c and d are exothermic.
Equation d is the most exothermic reaction.

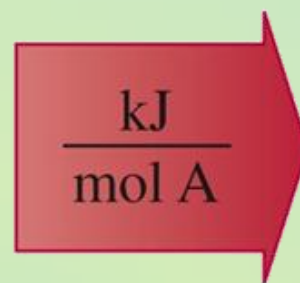
Applying Stoichiometry to Heats of Reaction

Starting Units

Grams of A
(reactant or
product)



Using molar
mass of A

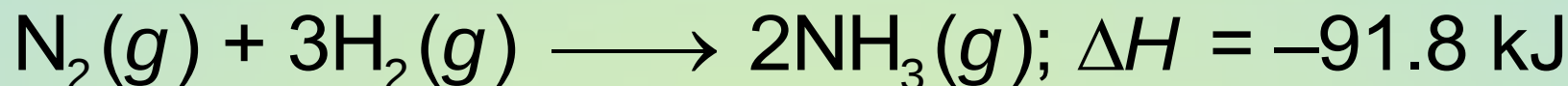


Using enthalpy
of reaction

Goal Units

Kilojoules
of heat

Determine the amount evolved when 9.07×10^5 g of ammonia is produced according to the following equation. Assume that the reaction occurs at constant pressure.



The conversion factor is obtained from the second step of the thermodynamic equation. Hence,

$$9.07 \times 10^5 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} \times \frac{-91.8 \text{ kJ}}{2 \text{ mol NH}_3} = -2.45 \times 10^6 \text{ kJ}$$

The amount of heat evolved is $2.45 \times 10^6 \text{ kJ}$

Heat Capacity, C

The quantity of heat needed to raise the temperature of the sample of substance by one degree Celsius (or one kelvin).

The heat required to raise the temperature of the sample is determined by the formula:

$$q = C\Delta t$$

The heat capacity for one mole of substance is considered its molar heat capacity.

Specific Heat Capacity, s (specific heat)

The quantity of heat needed to raise the temperature of one gram of substance by one degree Celsius (or one kelvin) at constant pressure.

The heat required to raise the temperature of the sample can be determined by the formula:

$$q = s \times m \times \Delta t$$

s = specific heat of the substance

m = mass in grams

Δt = temperature change

Calculate the heat absorbed by 15.0 g of water to raise its temperature from 20.0°C to 50.0°C. The specific heat of water is 4.18 J/(g·°C)

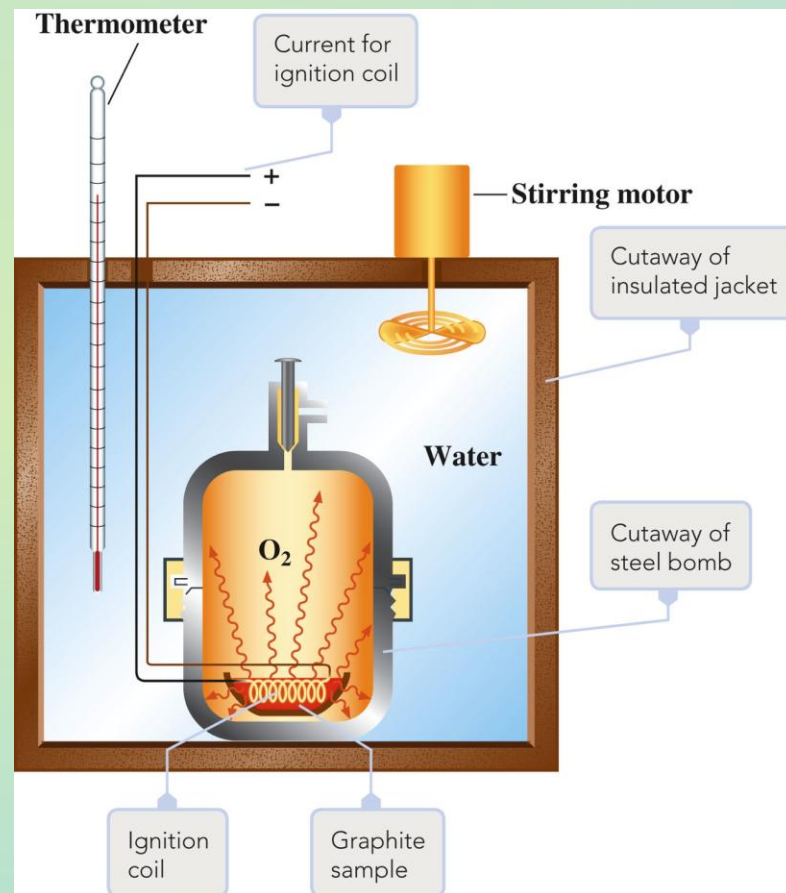
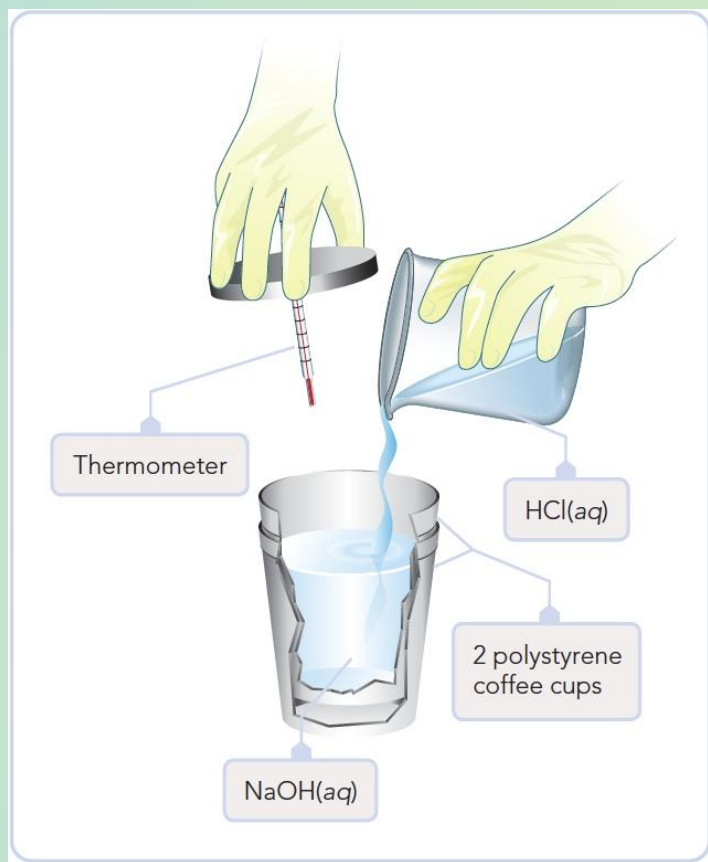
Substituting the formula for specific heat capacity,

$$\Delta t = t_f - t_i = 50.0^\circ\text{C} - 20.0^\circ\text{C} = +30.0^\circ\text{C}$$

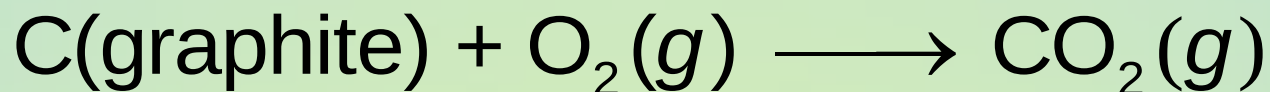
Therefore,

$$q = 4.18 \text{ J/(g} \cdot ^\circ\text{C)} \times 15.0 \text{ g} \times (+30.0^\circ\text{C}) = 1.88 \times 10^3 \text{ J}$$

A **calorimeter** is a device used to measure the heat absorbed or evolved during a physical or chemical change. Two examples are shown below.



0.562 g of graphite, placed in a bomb calorimeter with an excess of 25.00°C and 1 atm pressure burns according to the equation:



On reaction, the calorimeter temperature rises from 25.00°C to 25.89°C . The heat capacity of the calorimeter and its contents is $20.7 \text{ kJ}/^{\circ}\text{C}$. Determine the heat of reaction at 25.00°C and 1 atm pressure. Express the answer as a thermochemical equation.

Terms used

q_{rxn} - quantity of heat from the reaction mixture.

C_{cal} - Heat capacity of the calorimeter and its contents.

Calculating the heat from the graphite sample,

$$\begin{aligned} q_{rxn} &= -C_{cal} \Delta t = -20.7 \text{ kJ/}^{\circ}\text{C} \times (25.89^{\circ}\text{C} - 5.00^{\circ}\text{C}) \\ &= -20.7 \text{ kJ/}^{\circ}\text{C} \times 0.89^{\circ}\text{C} = -18.4 \text{ kJ} \end{aligned}$$

The negative sign indicates that the reaction is exothermic

The factor to convert grams C to kJ heat is 18.4 kJ/0.562 g C.

Converting 1 mol C to kJ heat for 1 mol (ΔH),

$$1 \text{ mol C} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} \times \frac{-18.4 \text{ kJ}}{0.562 \text{ g C}} = -3.9 \times 10^2 \text{ kJ}$$

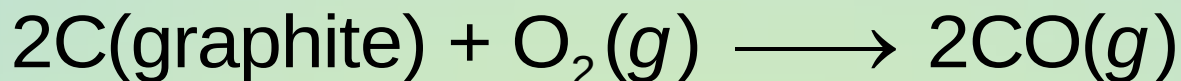
Summarizing the results in a thermodynamic equation,



Hess's Law of Heat Summation

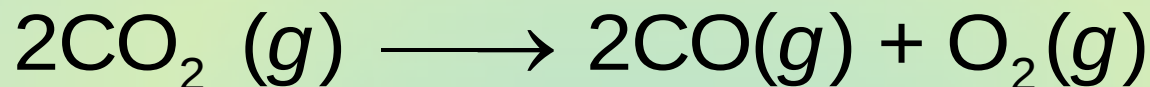
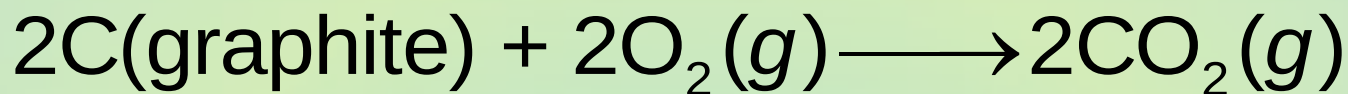
For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps.

Suppose we want ΔH for the reaction

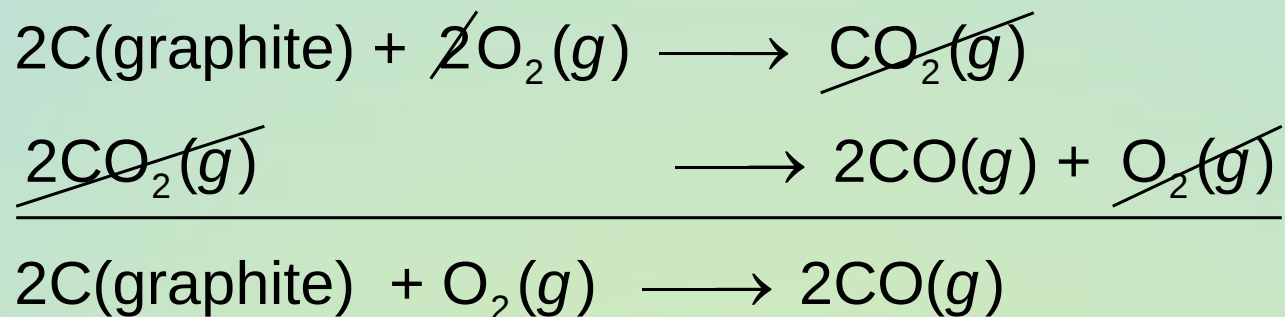


It is difficult to measure directly.

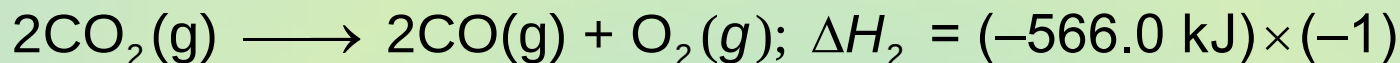
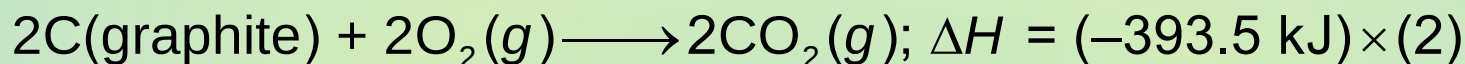
Assume that the reaction takes place in the following steps:



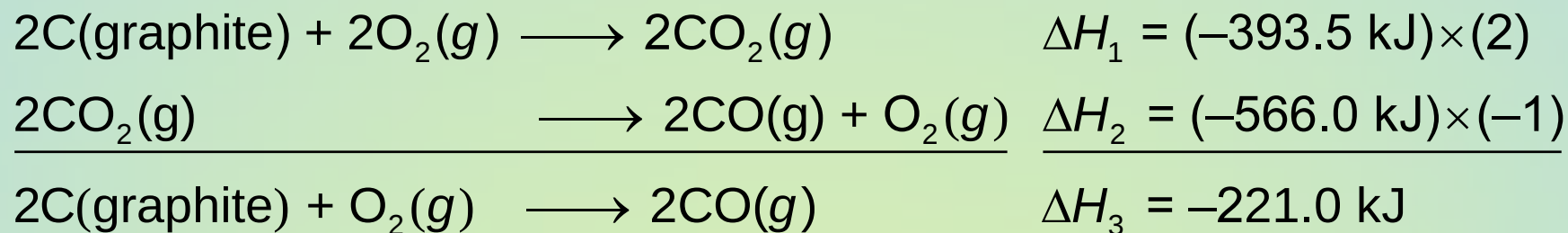
Putting the two equations together gives:

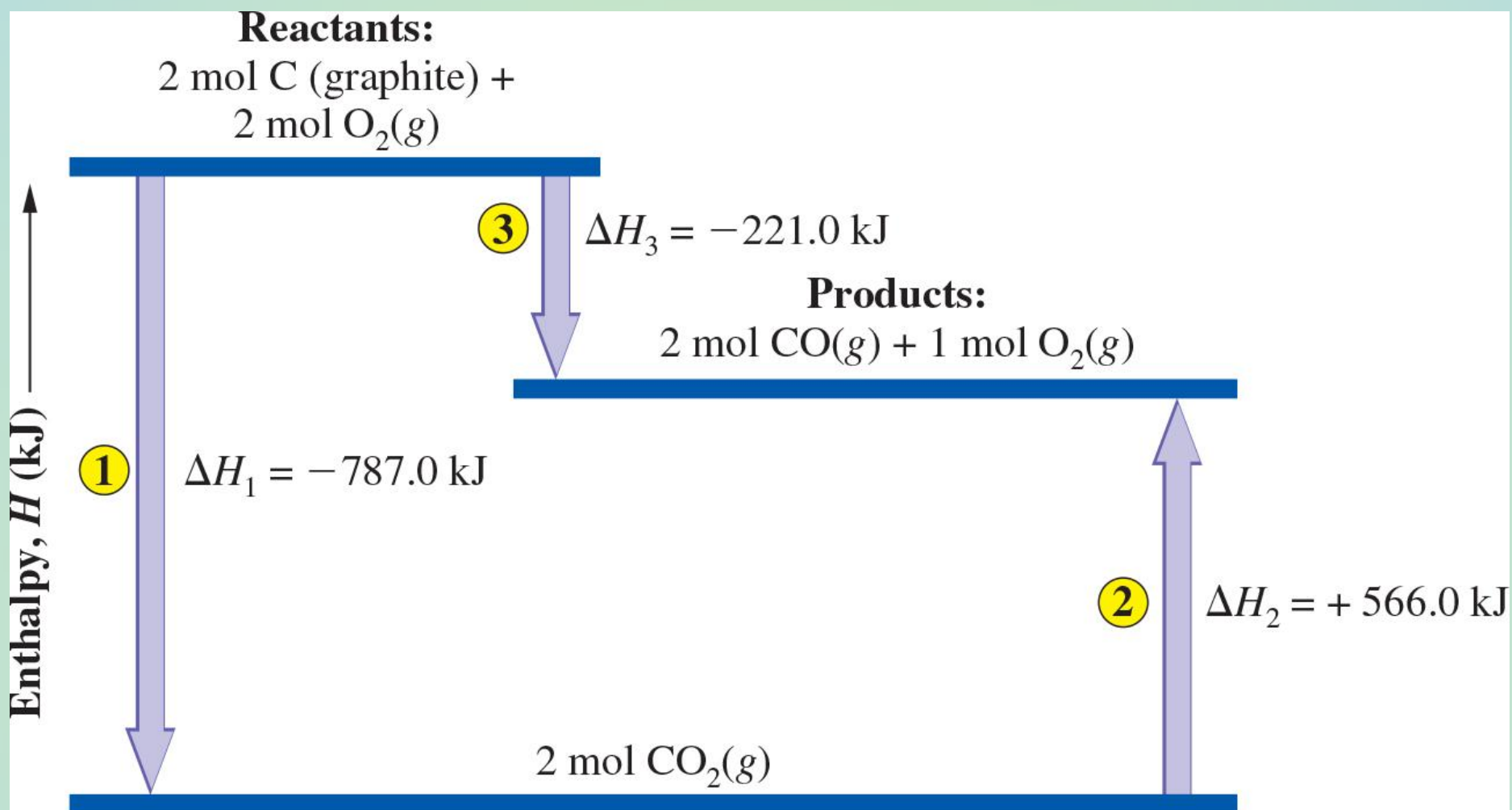


Determining the enthalpy changes for the separate steps,

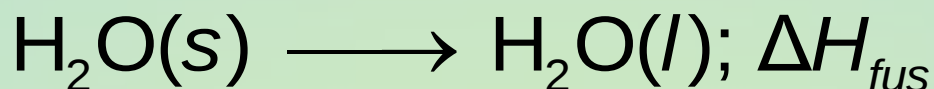


Adding the two thermochemical equations and their enthalpy changes gives the enthalpy change for the combustion of CO₂ to CO.

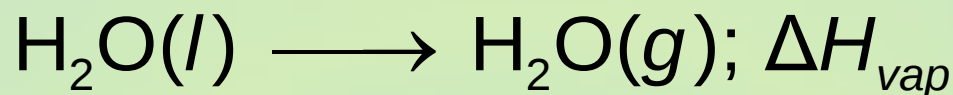




The heat of fusion (also called heat of melting), ΔH_{fus} , of ice is the enthalpy change for



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



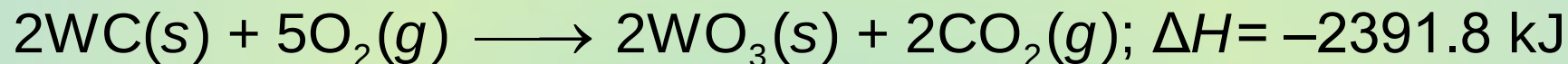
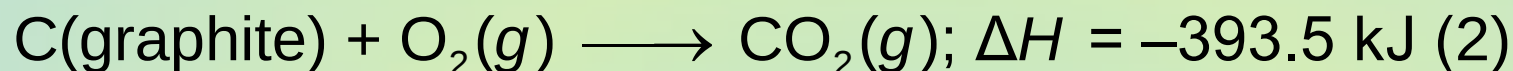
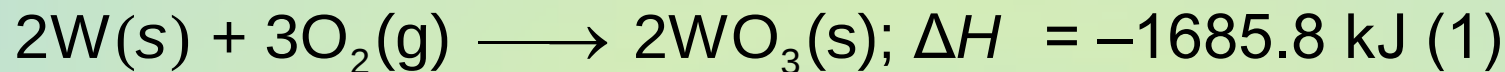
How is the heat of sublimation, ΔH_{sub} , the enthalpy change for the reaction $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{g})$; ΔH_{sub} related to ΔH_{fus} and ΔH_{vap} ?

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

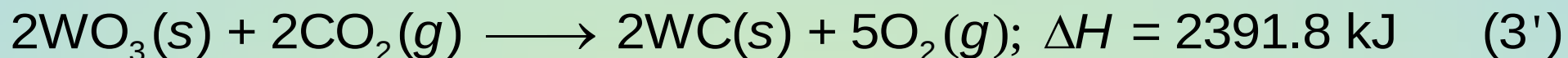
Determine the enthalpy of reaction, ΔH , for the formation of tungsten carbide, WC, from the elements.



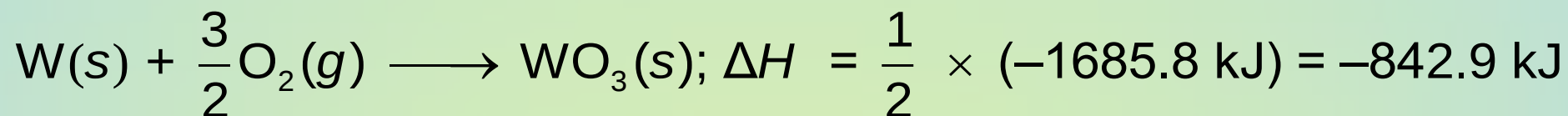
The heats of combustion of the elements and of tungsten carbide are:



Reversing Equation 3 to get WC(s) on the right side,

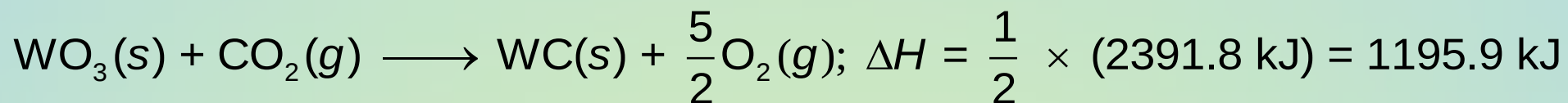


Comparing Equation 1 with the desired equation and multiplying Equation 1 by $\frac{1}{2}$ gives:

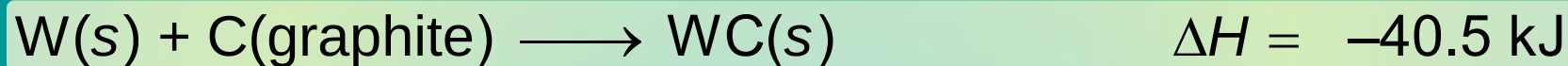
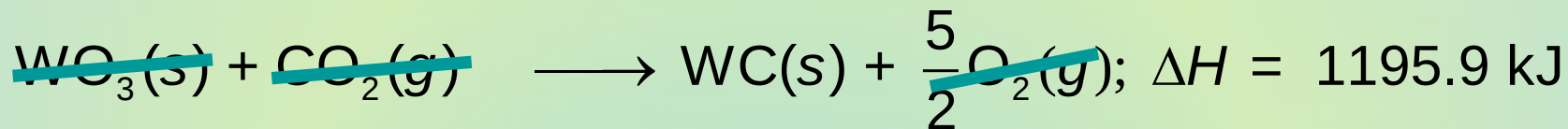
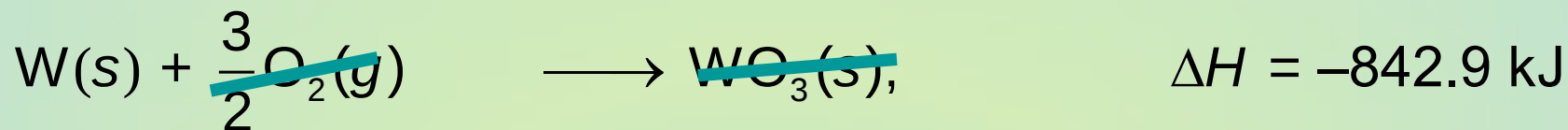


Equation 2 is left as is; it has C(graphite) on the left side.

Comparing Equation 3' with the desired equation and multiplying Equation 3' by $\frac{1}{2}$ gives:



Adding the last three equations with their corresponding ΔH 's gives:



Standard Enthalpies of Formation

The term **standard state** refers to the standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: 1 atm pressure and the specified temperature (usually 25°C). These standard conditions are indicated with a degree sign (°).

When reactants in their standard states yield products in their standard states, the enthalpy of reaction is called the **standard** enthalpy of reaction, ΔH° . (ΔH° is read “delta H zero.”)

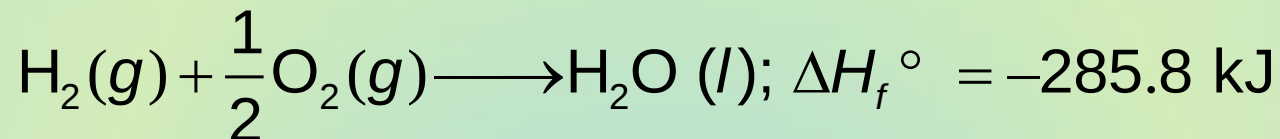
Elements can exist in more than one physical state, and some elements exist in more than one distinct form in the same physical state. For example, carbon can exist as graphite or as diamond; oxygen can exist as O_2 or as O_3 (ozone).

These different forms of an element in the same physical state are called **allotropes**.

The **reference form** is the most stable form of the element (both physical state and allotrope).

The **standard enthalpy of formation**, ΔH_f° , is the enthalpy change for the formation of one mole of the substance from its elements in their reference forms and in their standard states. ΔH_f° for an element in its reference and standard state is zero.

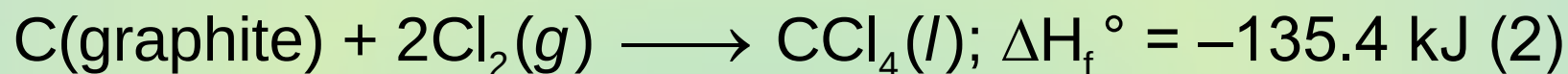
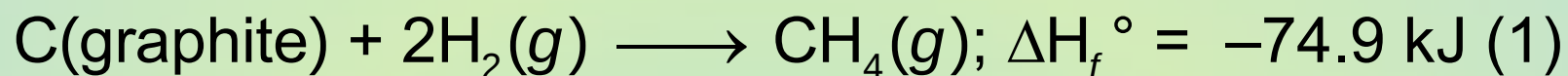
For example, the standard enthalpy of formation for liquid water is the enthalpy change for the reaction



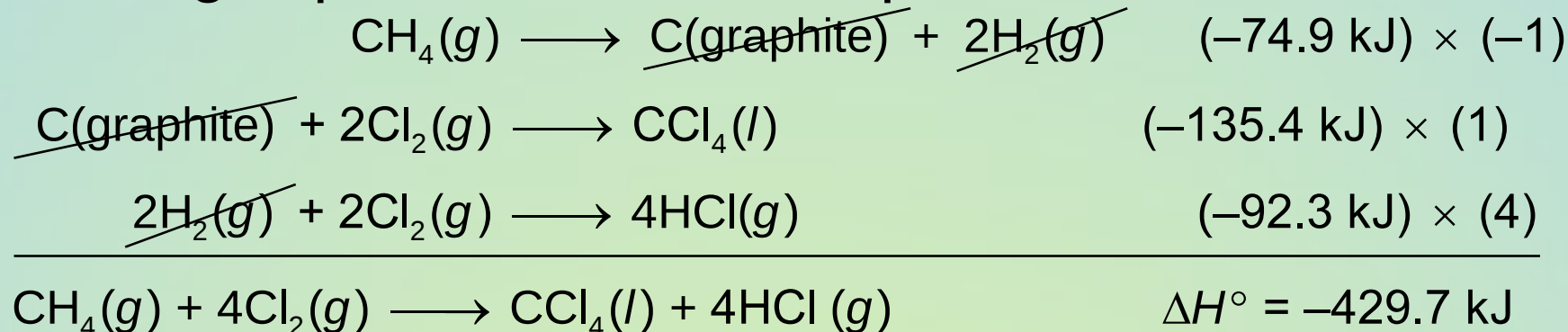
Standard enthalpies of formation can be used to calculate the standard enthalpy for a reaction, ΔH° .



Listing down the thermochemical equations with enthalpies of formation:



Applying Hess's law, reversing Equation 1 and adding Equation 2 and 4 × Equation 3,



If the formula is written in parentheses after ΔH_f° , the calculation can be written as:

$$\begin{aligned}
 \Delta H^\circ &= [\Delta H_f^\circ(\text{CCl}_4) + 4\Delta H_f^\circ(\text{HCl})] - [\Delta H_f^\circ(\text{CH}_4) + 4\Delta H_f^\circ(\text{Cl}_2)] \\
 &= [(-135.4) + 4(-92.3)] \text{ kJ} - [(-74.9) + 4(0)] \text{ kJ} = -429.7 \text{ kJ}
 \end{aligned}$$

In general,

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

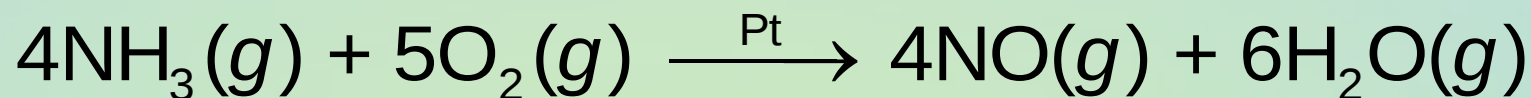
Use values of ΔH°_f to calculate the heat vaporization, $\Delta H^\circ_{\text{vap}}$, of carbon disulphide at 25°C. The vaporization process is:



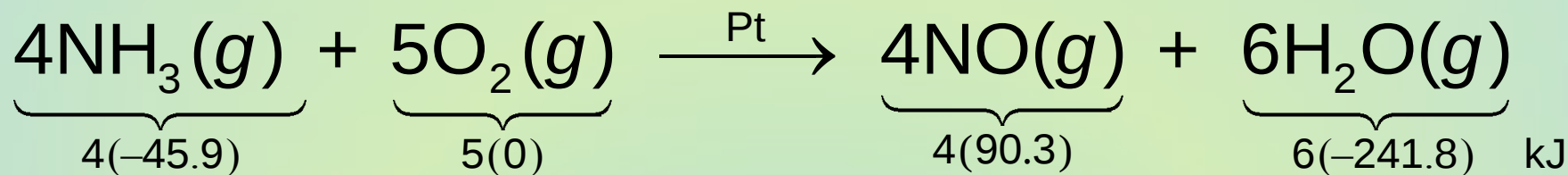
The equation, with the values of ΔH°_f multiplied by coefficients is:

$$\begin{aligned}\Delta H^\circ_{\text{vap}} &= \sum n \Delta H^\circ_f (\text{products}) - \sum m \Delta H^\circ_f (\text{reactants}) \\ &= \Delta H^\circ_f [\text{CS}_2(g)] - \Delta H^\circ_f [\text{CS}_2(l)] \\ &= (116.9 - 89.7) \text{ kJ} = 27.2 \text{ kJ}\end{aligned}$$

Determine the standard enthalpy change for the following reaction:



Adding ΔH_f° values to the components of the reaction:



The calculation is:

$$\begin{aligned}\Delta H^\circ &= \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants}) \\&= [4\Delta H^\circ_f(\text{NO}) + 6\Delta H^\circ_f(\text{H}_2\text{O})] - [4\Delta H^\circ_f(\text{NH}_3) + 5\Delta H^\circ_f(\text{O}_2)] \\&= [4(90.3) + 6(-241.8)] \text{ kJ} - [4(-45.9) + 5(0)] \text{ kJ} \\&= \boxed{-906 \text{ kJ}}\end{aligned}$$

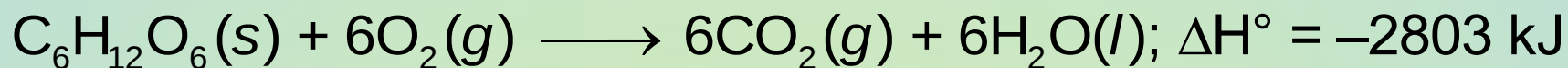
A fuel is any substance that is burned or reacts to provide heat and other forms of energy.

Foods fuel following three needs of the body:

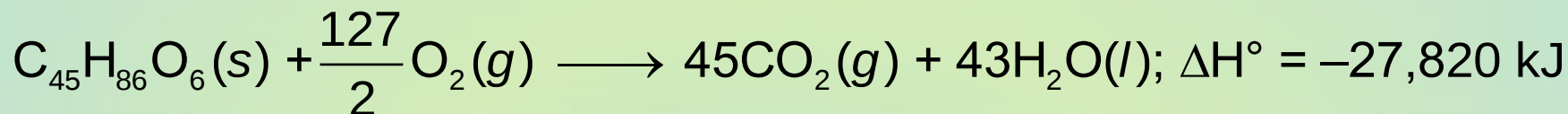
1. They supply substances for the growth and repair of tissue.
2. They supply substances for the synthesis of compounds used in the regulation processes.
3. They supply energy.

This is accomplished by a combustion process.

The thermochemical equation of the combustion of glucose is:



For glycerol trimyristate, a fat:



The average values for carbohydrates are 4.0 kcal/g and for fats is 9.0 kcal/g.

Fossil fuels were created by plants and animals buried and compressed by layers of sediment.

Over time this organic matter was converted by bacterial decay and pressure to petroleum (oil), gas, and coal.

Coal, which accounts for 18.5% of total U.S. energy consumption, varies in terms of the amount of carbon it contains and so varies in terms of the amount of energy it produces in combustion.

Anthracite (hard coal) can contain as much as 80% carbon. Bituminous coal, a younger variety, contains between 45% and 65% carbon.

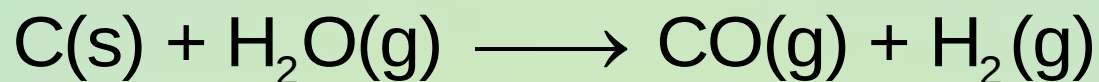
Natural gas, which accounts for 27.3% of total U.S. energy consumption, is convenient because it is fluid and can be easily transported. Purified natural gas is primarily methane, CH_4 ; plus small amounts of ethane, C_2H_6 ; propane, C_3H_8 , and butane, C_4H_{10} .

Petroleum is a mixture of compounds. Gasoline, which is obtained from petroleum, is a mixture of hydrocarbons (compounds of carbon and hydrogen).

The main issue with natural gas and petroleum is their relatively short supply. It has been estimated that petroleum deposits will be 80% depleted within this century. Natural gas supplies may last longer.

Coal deposits, however, are expected to last for several more centuries. This has led to the development of commercial methods for converting coal to the more easily handled liquid and gaseous fuels.

Coal gasification is one way. Steam is passed over hot coal:



The mixture of carbon monoxide and hydrogen can be converted by various methods into useful products such as methane, CH_4 .



Rockets are self-contained missiles propelled by the ejection of gases from an orifice. Usually these are hot gases expelled from the rocket from the reaction of a fuel with an oxidizer.

One factor in determining the appropriate fuel/oxidizer combination is its mass of the mixture.