

System and Surroundings

$$\text{universe} = \text{system} + \text{surroundings}$$

- the system is the sample being observed
- the surroundings is everything else
- interactions between a system and its surroundings involve exchange of energy and matter

Three types of systems based on this type of exchange are:



can exchange energy and matter with surroundings



can exchange energy, but not matter, with surroundings

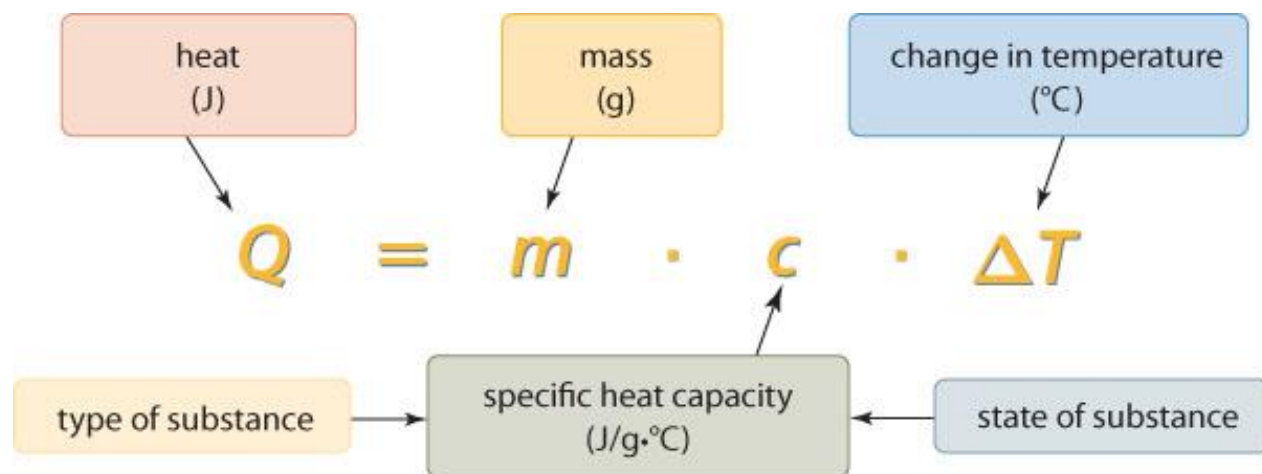


cannot exchange matter or energy with surroundings

Measurable and Calculated Variables of a System

Measurable properties of a system include volume, mass, pressure, **temperature**, and **specific heat capacity** (the amount of energy required to increase the temperature of 1 g of a substance by 1 degree C).

Calculated properties of a system include heat (Q) that enters or leaves an object when it is being heated or cooled.



The change in temperature, T , is expressed as $\Delta T = T_{\text{final}} - T_{\text{initial}}$

When heat enters a system, ΔT is positive and so is Q .

QUESTION

A 1.0 g sample of copper is heated from 25.0°C to 31.0°C.

How much heat did the sample absorb?



ANSWER

$$Q = mc\Delta T$$

$$Q = (1.0 \text{ g})(0.385 \text{ J/g}^\circ\text{C})(6^\circ\text{C})$$

$$Q = 2.3 \text{ J}$$

The First Law of Thermodynamics: Energy is Conserved

The **first law of thermodynamics** states that energy can be converted from one form to another but cannot be created or destroyed.

Therefore, change in the energy of the universe must be zero.

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

And therefore:

- if a system gains energy, that energy must come from the surroundings
- if a system loses energy, that energy must enter the surroundings

Enthalpy

One way chemists express thermochemical changes is by a variable called **enthalpy**, H . The change in enthalpy, ΔH , of a system can be measured.

It depends only on the initial and final states of the system

For reactions of solids and liquids in solutions

If heat enters a system

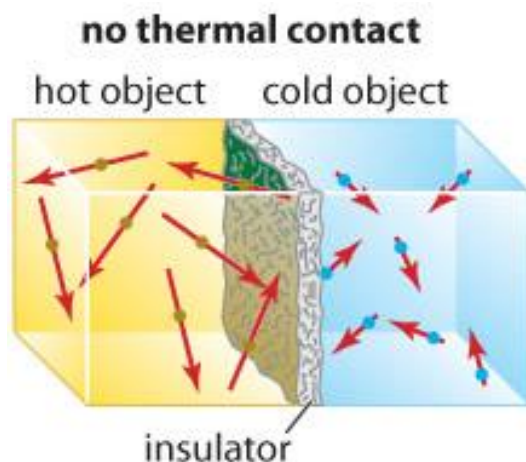
- ΔH is positive
- the process is **endothermic**

If heat leaves a system

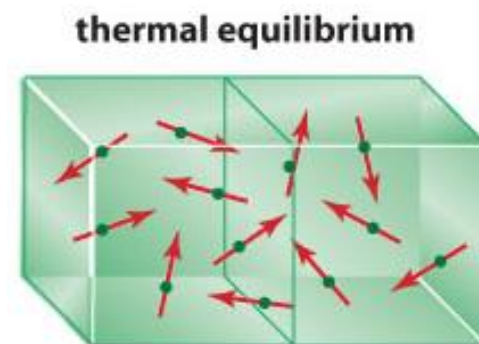
- ΔH is negative
- the process is **exothermic**

The Second Law of Thermodynamics

The **second law of thermodynamics** states that when two objects are in thermal contact, heat is transferred from the object at a higher temperature to the object at the lower temperature until both objects are the same temperature (in *thermal equilibrium*).



When in thermal contact, energy from hot particles will transfer to cold particles until the energy is equally distributed and thermal equilibrium is reached.



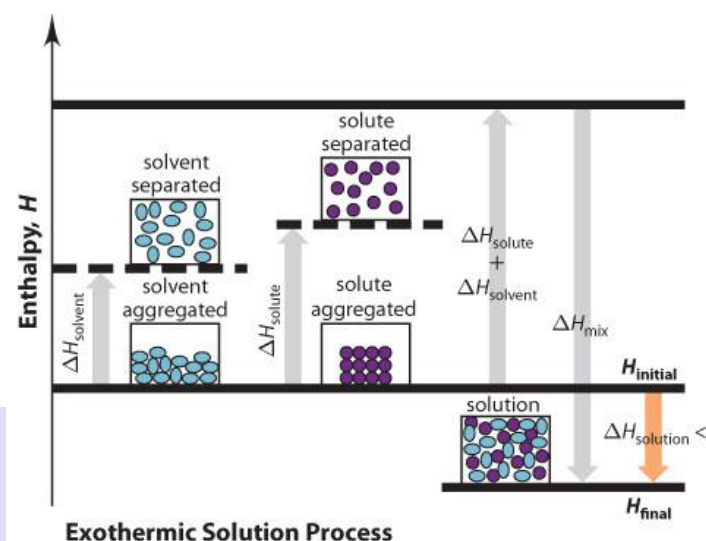
Comparing Categories of Enthalpy Changes: Enthalpy of Solution

Three processes occur when a substance dissolves, each with a ΔH value.

1. bonds between solute molecules or ions break
2. bonds between solvent molecules break
3. bonds between solvent molecules and solute molecules or ions form

Sum of the enthalpy changes:
enthalpy of solution, $\Delta H_{\text{solution}}$

The orange arrow shows the overall ΔH .
Enthalpies can be exothermic (shown) or endothermic.

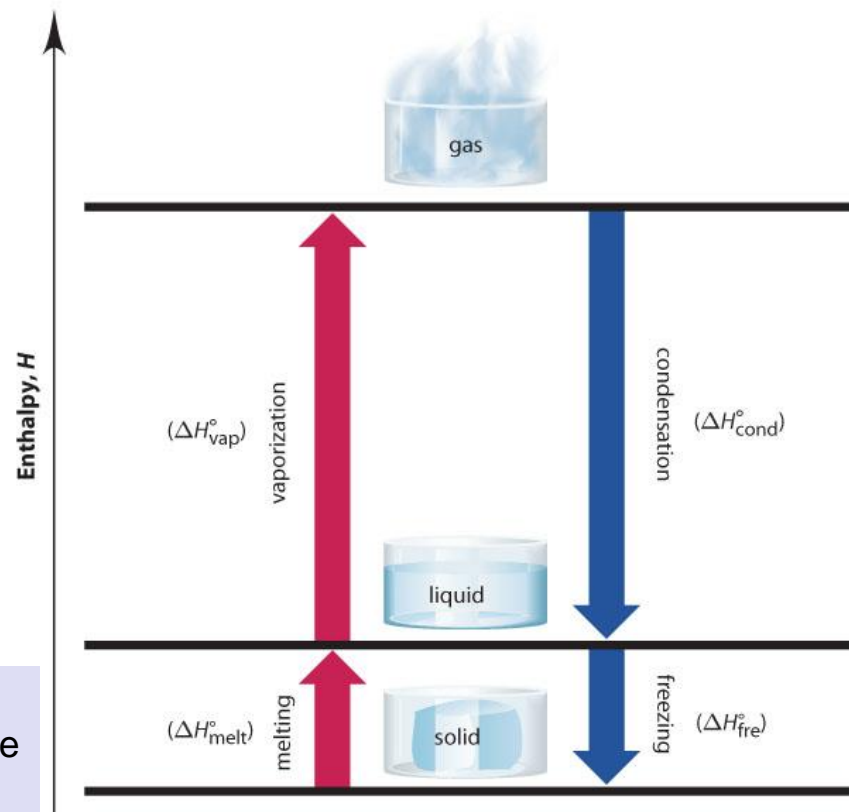


Comparing Categories of Enthalpy Changes: Enthalpy of Phase Changes

Heat must be added to or removed from a substance in order for the phase of the substance to change.

The ΔH for each phase change has a particular symbol. For example, ΔH_{melt} is called the *enthalpy of melting*.

The ΔH for one phase change is the negative of the ΔH for the opposite phase change.

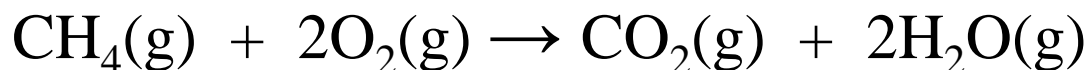


Comparing Categories of Enthalpy Changes: Chemical Changes

Every chemical reaction is associated with an enthalpy of reaction, ΔH_r .

For example:

The combustion of methane is

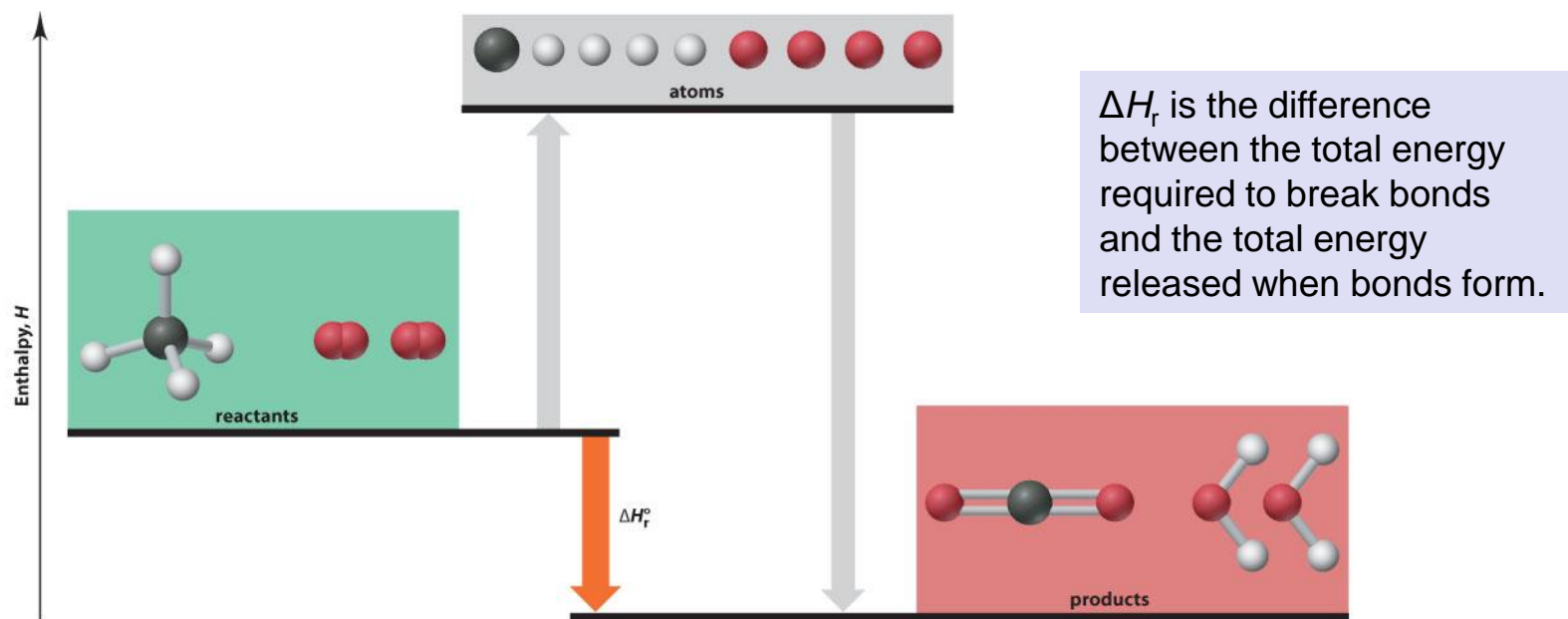


For every mole of methane combusted $\Delta H_r = -890 \text{ kJ}$

Thermochemical Equations and Calorimetry

Chemical reactions involve

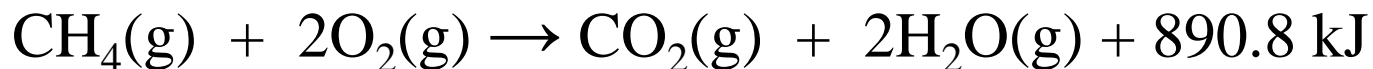
- initial breaking of chemical bonds (endothermic)
- the formation of new bonds (exothermic)



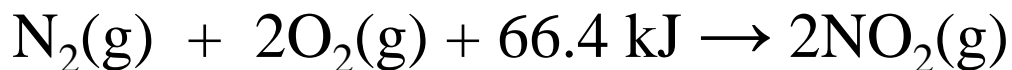
Thermochemical Equations

Thermochemical equations include the enthalpy change.

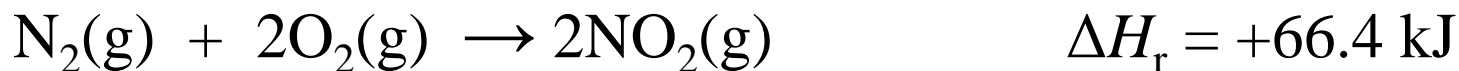
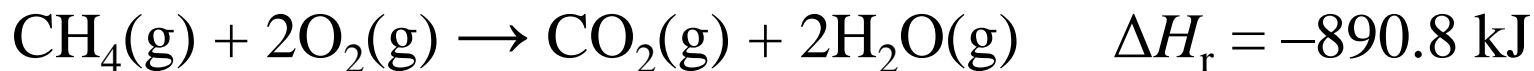
Exothermic reaction:



Endothermic reaction:



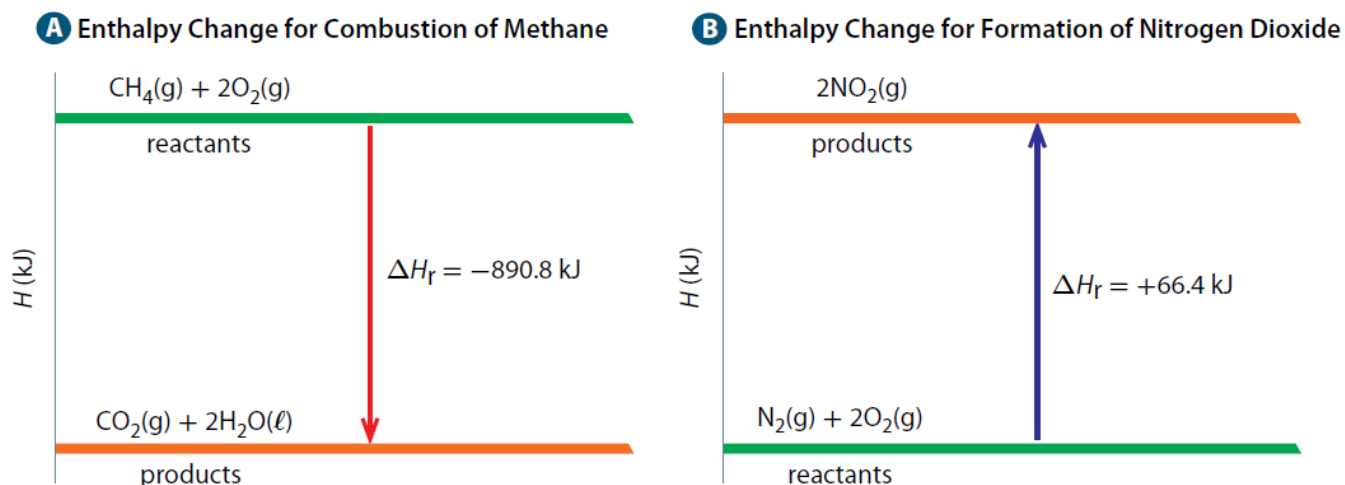
The enthalpy term can also be written beside the equation.



Enthalpy Diagrams

Enthalpy diagrams clearly show the relative enthalpies of reactants and products.

- For exothermic reactions, reactants have a larger enthalpy than products and are drawn above the products.
- For endothermic reactions, the products have a larger enthalpy and are drawn above the reactants.



Molar Enthalpy of Combustion

Combustion reactions have their own symbol: ΔH_{comb}

In standard reference tables for standard molar enthalpy of combustion data:

- reactants and products are at standard conditions
- data refers only to the compound undergoing combustion
- data are for combustion of 1 mol of the compound being combusted. For some compounds, equations are written with fractions as coefficients.

Reactant Amounts and Enthalpy of Reaction

- The enthalpy of a reaction is directly proportional to the amount of substance that reacts.
- The combustion of 2 mol of propane releases twice as much energy as the combustion of 1 mol of propane.
- Knowing the thermochemical equation, the enthalpy change associated with a certain amount of reactants or products can be calculated.

The enthalpy change of a reaction is equal to the amount in moles, n , of a specified reactant or product multiplied by the standard molar enthalpy change for the specified reactant or product.

$$\Delta H_r = n\Delta H_r^\circ$$

QUESTION

Determine ΔH_{comb} for 15.0 g of propane.



ANSWER

The molar mass of propane: 44.1 g/mol

Therefore, 15.0 g equals 0.340 mol

$$\Delta H_{\text{comb}} = \Delta H^{\circ}_{\text{comb}}$$

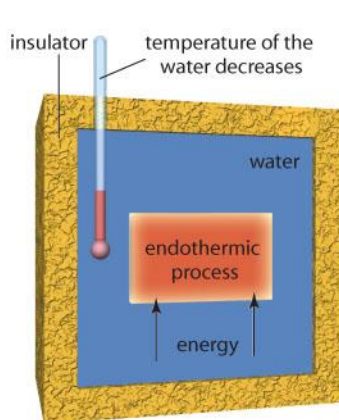
$$\Delta H_{\text{comb}} = (0.340 \text{ mol}) (-2219.2 \text{ kJ/mol})$$

$$\Delta H_{\text{comb}} = -755 \text{ kJ}$$

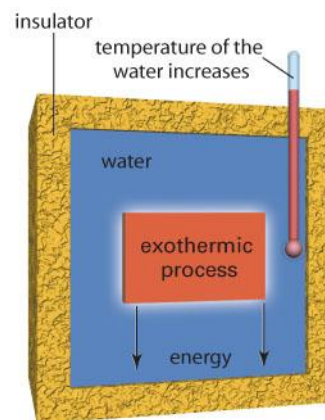
Using Calorimetry To Study Energy Changes

Calorimeters are used to measure heat released or absorbed by a chemical or physical process.

The water of a calorimeter is considered one system and the container in which the process occurs is another system. These two systems are in thermal contact.



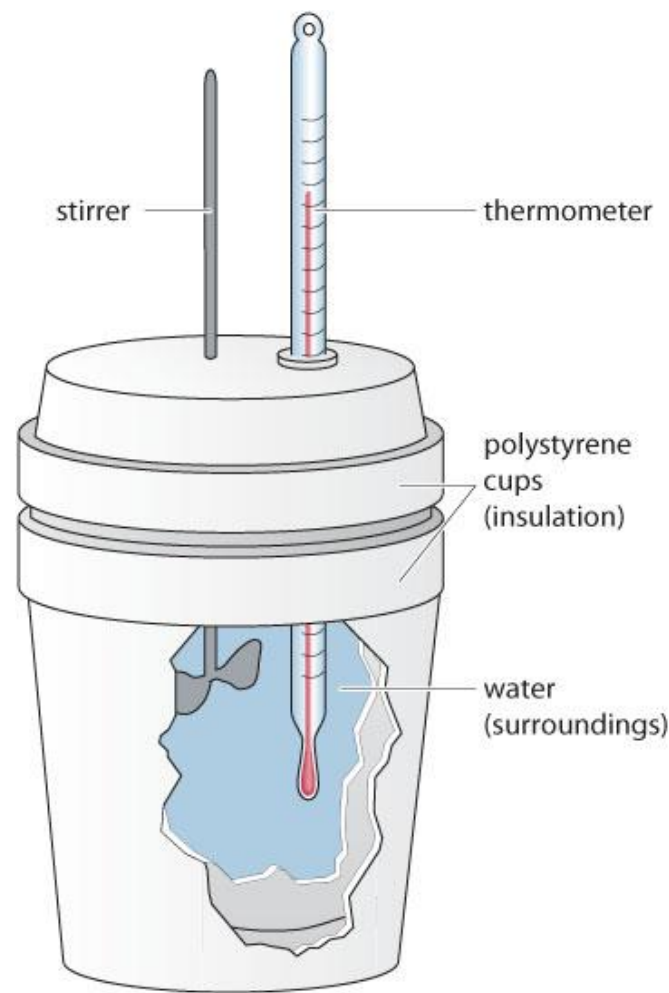
For an endothermic process, heat will be transferred from the water to the process system. The temperature of the water will decrease.



For an exothermic process, heat will be transferred from the process to the water. The temperature of the water will increase.

Using a Simple Calorimeter

- nested polystyrene cups (with a lid) can be used
- a known mass of water is in the inner cup, where the process occurs
- the process often involves compounds dissolved in water
- the change in temperature of the water is measured as the solution absorbs or releases energy
- the solution is dilute enough so that the specific heat capacity of water can be used



Using a Simple Calorimeter

If the “system” is the process being studied and the “surroundings” is the water in the calorimeter:

thermal energy released by the system = $-$ thermal energy absorbed by the surroundings
heat lost (or gained) by the system = $-$ heat gained (or lost) by the surroundings

The change in thermal energy caused by the process can be calculated using:

$$Q = mc\Delta T$$

m is the mass of the water, c is the specific heat capacity of water, and ΔT is the change in temperature of the water

How to Use a Simple Calorimeter

1. Ensure that the water in the calorimeter and all other solutions are equilibrated to room temperature before starting any investigation. Measure the initial temperature of the water in the calorimeter.
2. Add the reactants to the calorimeter. The water surrounds, and is in direct contact with, the chemical reaction (or physical change) that releases or absorbs thermal energy.
3. Allow the reaction to proceed. Stir the solution to ensure an even temperature throughout. The system is at a constant pressure because it is open to the air. Record the changing temperature of the water as the reaction proceeds. Identify the maximum or minimum temperature recorded. This temperature is the final temperature.
4. For an exothermic reaction, the final temperature is the maximum temperature recorded. It is used to calculate the thermal energy released. For an endothermic reaction, the final temperature is the minimum temperature recorded. It is used to calculate the thermal energy absorbed.

Using Calorimetry Data To Determine the Enthalpy of Reaction

$Q = m_w c_w \Delta T_w$ is the thermal energy absorbed or released by the water.

The opposite sign of that value is the thermal energy released or absorbed by the system (compounds in solution).

Since pressure is constant, Q exchanged by the system and the water is the same as the enthalpy change of the system ΔH . This is used to determine molar enthalpy change, ΔH_r .

$$\Delta H = n\Delta H_r$$
$$\Delta H_r = \frac{\Delta H}{n}$$

QUESTION

A chemical reaction is carried out in a dilute aqueous solution using a simple calorimeter.

Calculate the enthalpy change of the reaction using the data below.

- mass of solution in calorimeter: $2.00 \times 10^2 \text{ g}$
- specific heat capacity of water: $4.19 \text{ J/g } ^\circ\text{C}$
- initial temperature: 15.0°C
- final temperature: 19.0°C



ANSWER

$$Q = m_{\text{solution}} c_{\text{solution}} \Delta T_{\text{solution}}$$

$$Q = (2.00 \times 10^2 \text{ g})(4.19 \text{ J/g}^\circ\text{C})(4.0^\circ\text{C})$$

$$Q = 3.35 \times 10^3 \text{ J}$$

This is the thermal change of the
“surroundings.”

$$\Delta H_{\text{system}} = -Q$$

$$\Delta H_{\text{system}} = -3.35 \text{ kJ}$$

5.3 Hess's Law

The enthalpy change of nearly any reaction can be determined using collected data and **Hess's law**.

Hess's Law

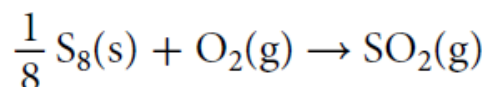
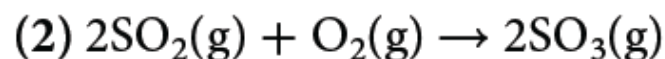
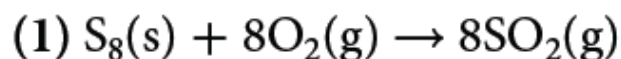
The enthalpy change of a physical or chemical process depends only on the initial and final conditions of the process. The enthalpy change of a multistep process is the sum of the enthalpy changes of its individual steps.

The enthalpy change of any reaction can be determined if:

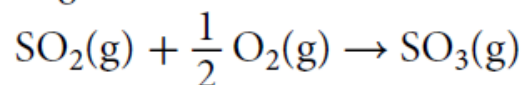
- the enthalpy changes of a set of reactions “add up to” the overall reaction of interest
- standard enthalpy change, ΔH° , values are used

Combining Sets of Chemical Equations

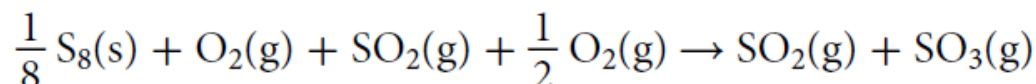
To find the enthalpy change for formation of SO_3 from O_2 and S_8 , you can use



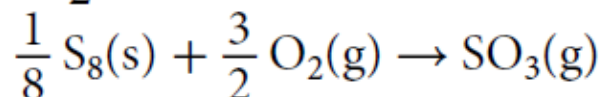
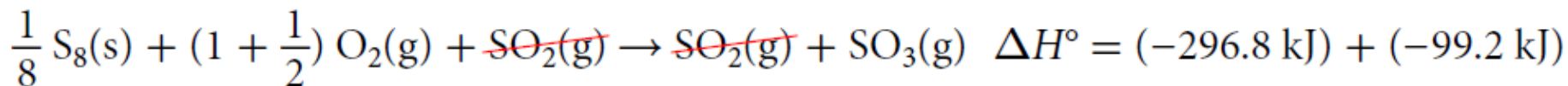
$$\Delta H^\circ = -296.8 \text{ kJ}$$



$$\Delta H^\circ = -99.2 \text{ kJ}$$



$$\Delta H^\circ = (-296.8 \text{ kJ}) + (-99.2 \text{ kJ})$$



$$\Delta H^\circ = -396.0 \text{ kJ}$$

Techniques for Manipulating Equations

Reverse an equation

- the products become the reactants, and reactants become the products
- the sign of the ΔH value must be changed

Multiply each coefficient

- all coefficients in an equation are multiplied by the same integer or fraction
- the value of ΔH must also be multiplied by the same number

Standard Molar Enthalpies of Formation

Data that are especially useful for calculating standard enthalpy changes:

standard molar enthalpy of formation, ΔH°_f

the change in enthalpy when 1 mol of a compound is synthesized from its elements in their most stable form at SATP conditions (25°C and 100 kPa)

- enthalpies of formation for elements in their most stable state under SATP conditions are set at zero
- since formation equations are for 1 mol of compound, many equations include fractions
- standard molar enthalpies of formation are on pg 799

Formation Reactions and Thermal Stability

The **thermal stability** of a substance is the ability of the substance to resist decomposition when heated.

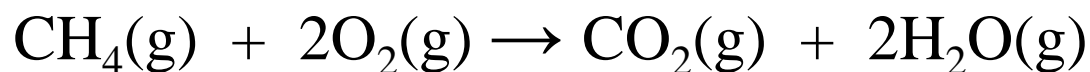
- decomposition is the reverse of formation
- the opposite sign of an enthalpy change of formation for a compound is the enthalpy change for its decomposition
- the greater the enthalpy change for the decomposition of a substance, the greater the thermal stability of the substance

Using Enthalpies of Formation and Hess's Law

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

where n represents the stoichiometric coefficient for each substance and Σ means “the sum of.”

For example:



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

$$= [(1 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{CH}_4(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{O}_2(\text{g}))]$$

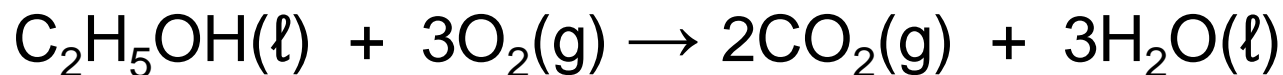
$$= \left[(1 \cancel{\text{ mol}}) \left(-393.2 \frac{\text{kJ}}{\cancel{\text{mol}}} \right) + (2 \cancel{\text{ mol}}) \left(-241.9 \frac{\text{kJ}}{\cancel{\text{mol}}} \right) \right] - \left[(1 \cancel{\text{ mol}}) \left(-74.6 \frac{\text{kJ}}{\cancel{\text{mol}}} \right) + (2 \cancel{\text{ mol}}) \left(0 \frac{\text{kJ}}{\cancel{\text{mol}}} \right) \right]$$

$$= (-877.1 \text{ kJ}) - (-74.6 \text{ kJ})$$

$$= -802.5 \text{ kJ}$$

QUESTION

Determine ΔH°_r for the following reaction using the enthalpies of formation that are provided.



- ΔH°_f of $\text{C}_2\text{H}_5\text{OH}(\ell)$: -277.6 kJ/mol
- ΔH°_f of $\text{CO}_2(\text{g})$: -393.5 kJ/mol
- ΔH°_f of $\text{H}_2\text{O}(\ell)$: -285.8 kJ/mol



ANSWER

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

$$\Delta H_r^\circ = [(2 \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + (3 \text{ mol})(\Delta H_f^\circ \text{ H}_2\text{O}(\ell))] - [(1 \text{ mol})(\Delta H_f^\circ \text{ C}_2\text{H}_5\text{OH}(\ell)) + (3 \text{ mol})(\Delta H_f^\circ \text{ O}_2(\text{g}))]$$

$$\Delta H_r^\circ = [(2 \text{ mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-285.8 \text{ kJ/mol})] - [(1 \text{ mol})(-277.6 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta H_r^\circ = (-1644.4 \text{ kJ}) - (-277.6 \text{ kJ})$$

$$\Delta H_r^\circ = -1366.8 \text{ kJ}$$