

Chapter 6

Energy of Reactions

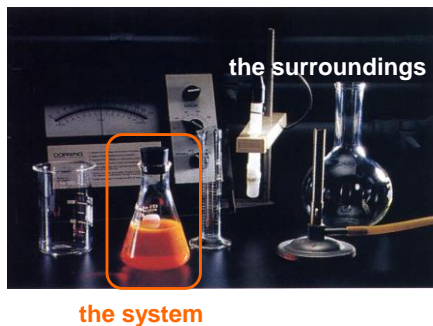
If the expanding combustion gases do 451 J of work on the pistons of an engine and the system loses 325 J as heat, calculate the change in energy (ΔE) of the system in J and kJ.

Forms of Energy and Their Interconversion

During a chemical or physical change, a loss or gain of energy takes place.

System – the part of the universe that we will focus on

Surroundings - everything outside what is defined as the system



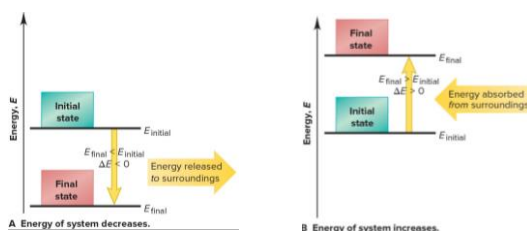
Energy Transfer to and from the System

E of the system = sum of potential and kinetic of each particle in a system.

Energy change (ΔE) is the difference between the **system's** internal energy after (E_{final}) and before (E_{initial}) the change:

Reactant \rightarrow Products

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}}$$



Note: The sign of ΔE indicates whether energy is lost to ($-\Delta E$) or gained from ($+\Delta E$) the surroundings.

Heat and Work: Two Forms of Energy Transfer

- **Heat** (or thermal energy, q) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures only.
- **Work** (w) is the energy transferred when an object is moved by force.

The total change in a system's internal energy is the sum of the energy transferred as heat and/or work:

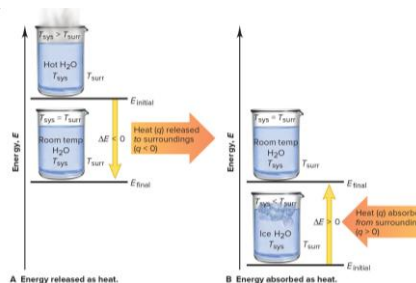
$$\Delta E = q + w$$

Let's consider four simple cases of energy transfer. . .

Energy Transfer as Heat Only ($w = 0$)

$$\Delta E = q + 0 = q$$

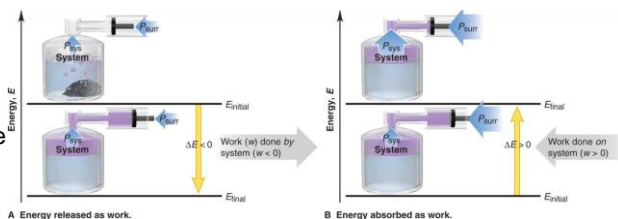
1. $-q$, heat flow out of system and gained by surroundings
2. $+q$, heat gained by system and lost by surroundings



Energy Transfer as Work Only ($q = 0$)

$$\Delta E = 0 + w = w$$

3. $-w$, work done **by** the system thus energy lost from system
4. $+w$, work done **on** the system thus energy gained by system



If the expanding combustion gases do 451 J of work on the pistons of an engine and the system loses 325 J as heat, calculate the change in energy (ΔE) of the system in J and kJ.

The Law of Energy Conservation

The ***law of conservation of energy*** states that the total energy of the universe is constant – that is, energy can be converted from one form to another but can not be created or destroyed.

The change in energy of the system (ΔE_{system}) plus the change in energy of the surroundings ($\Delta E_{\text{surroundings}}$) must equal zero.

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

Units of Energy

The SI unit of energy is the **joule** (J).

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

Both heat and work are expressed in joules.

The **calorie** is an older unit, originally defined as the quantity of energy needed to raise the temperature of 1 g of water by 1°C (specifically, 14.5°C to 15.5°C).

N2K: 1 cal \equiv 4.184 J

Note: This is **not** a nutritional calorie (Cal). 1 Cal = 1000 cal

State Functions and Path Independence of the Energy Change

State function – a property dependent only on the current state of the system (its composition, volume, pressure and temperature)

Does not depend on the path the system took to reach that state.

ARE State Functions

- Volume
- Pressure
- Temperature
- Energy
- Changes in all as well

ARE NOT State Functions

- Heat
- Work

Enthalpy (H) is defined as the internal energy (E) plus the product of pressure times volume.

$$H = E + PV$$

The **change in enthalpy** (ΔH) is equal to the change in energy (ΔE) plus the product of constant pressure times the change in volume (ΔV).

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

Substituting definitions of $\Delta E = q + w$ and $w = -P\Delta V$, we find. . .

$$\Delta H = (q + w) - w$$

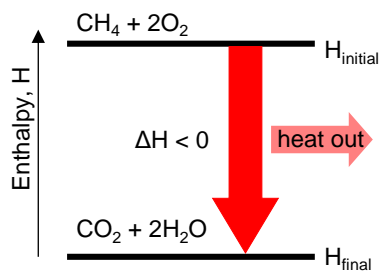
$$\Delta H = q$$

In other words, the change in enthalpy equals the heat gained or lost at constant pressure!

Exothermic and Endothermic Processes

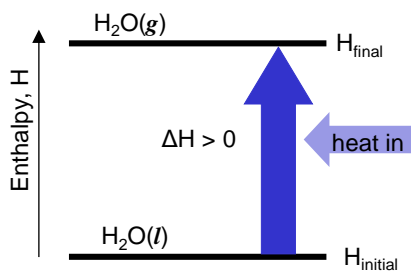
$$\Delta H = H_{\text{final}} - H_{\text{initial}} = H_{\text{products}} - H_{\text{reactants}}$$

An **exothermic process** releases heat ($\Delta H < 0$), and an **endothermic process** absorbs heat ($\Delta H > 0$) (**Figure 6.6**).



A Exothermic process

Think: Heat is a **PRODUCT**



B Endothermic process

Think: Heat is a **REACTANT**

A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300°C? The specific heat capacity (c) of copper is 0.387 J/g•K.

Calorimetry: Measuring the Heat of a Chemical or Physical Change

Specific Heat Capacity

The quantity of heat absorbed by an object is proportional to its temperature change. . .

$$q \propto \Delta T \quad \text{OR} \quad q = \text{constant} \times \Delta T \quad \text{OR} \quad \text{constant} = \frac{q}{\Delta T}$$

Heat capacity –the quantity of heat required to change its temperature by 1K and is equal to $q/\Delta T$

$$\text{Heat capacity} = \frac{q}{\Delta T} \text{ in units of J/K}$$

Specific heat capacity (c) - the quantity of heat required to change the temperature of 1 gram of a substance by 1K.

$$\text{Specific heat capacity, } c = \frac{q}{\text{mass} \times \Delta T} \text{ in units of J/g} \cdot \text{K}$$

$$q = m \times c \times \Delta T$$

A layer of copper welded to the bottom of a skillet weighs 125 g. How much heat is needed to raise the temperature of the copper layer from 25°C to 300°C? The specific heat capacity (c) of copper is 0.387 J/g•K.

Suppose you heat 25.64 g solid in a test tube to 100.00°C and carefully add it to 50.00 g of water in a coffee-cup calorimeter. The water changes temperature from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

The Practice of Calorimetry

A **calorimeter** is a device used to measure the heat released (or absorbed) by a physical or chemical process. The calorimeter is the “surroundings” that changes temperature when heat is transferred to or from the system.

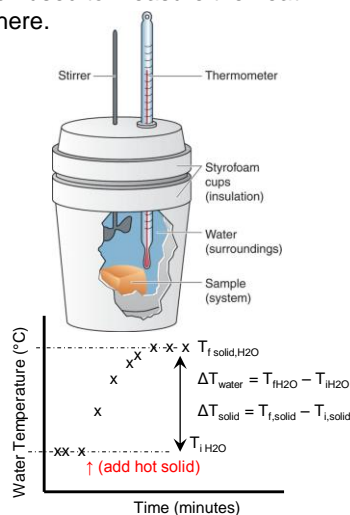
Two common types are **constant pressure** and **constant volume calorimeters**.

Constant-Pressure Calorimetry

A “coffee cup” calorimeter (**Figure 6.7**) is often used to measure the heat transferred in processes open to the atmosphere.

One common use is to find the specific heat capacity of a solid that does not react with or dissolve in water.

1. The solid (“system”) is weighed and heated to a known temperature ($T_{\text{initial, solid}}$).
2. The hot solid is added to a sample of water at a known temperature ($T_{\text{initial, H}_2\text{O}}$) and mass.
3. After stirring the water for some time, the temperature of the water stops changing ($T_{\text{final, solid \& H}_2\text{O}}$).



Suppose you heat 25.64 g solid in a test tube to 100.00°C and carefully add it to 50.00 g of water in a coffee-cup calorimeter. The water changes temperature from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

Select the phase that will make the following statement **true**.

In a constant pressure calorimetry experiment...

- A. an increase in the recorded temperature indicates heat is transferred from the system (solid) to the surroundings (water).
- B. a decrease in the recorded temperature indicates heat is transferred from the system (solid) to the surroundings (water).
- C. the measured temperature change is equal to the heat transferred (i.e., °C = J).
- D. determination of the heat transferred to the surroundings (water) does not require knowledge of the mass of the surroundings (water).
- E. the calorimeter is open to exchange of heat with the rest of the laboratory.



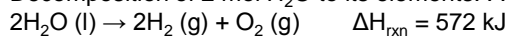
Calculate the amount of heat released when 3.76 moles of Ca(OH)_2 are allowed to react.

Stoichiometry of Thermochemical Equations

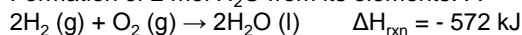
A **thermochemical equation** is a balanced equation that includes the heat of reaction (ΔH_{rxn}).

1. **Sign** – The sign of ΔH_{rxn} depends on whether the reaction is exothermic (-) or endothermic (+). The forward reaction has the opposite sign of the reverse reaction.

Example: Decomposition of 2 mol H_2O to its elements. . .

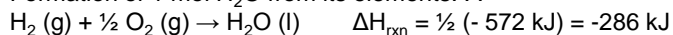


Formation of 2 mol H_2O from its elements. . .

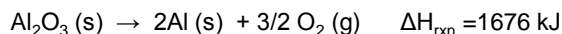


2. **Magnitude** - The magnitude of ΔH_{rxn} is proportional to the amount of substance reacting.

Example: Formation of 1 mol H_2O from its elements. . .



The major source of aluminum in the world is bauxite (mostly aluminum oxide). Its thermal decomposition can be represented by



If aluminum is produced this way, how many grams of aluminum can form when $1.000 \times 10^3 \text{ kJ}$ of heat is transferred?

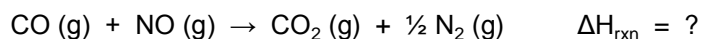
1. Write a ratio between the number of moles aluminum from the balanced chemical equation and the ΔH_{rxn} .

$$\frac{2 \text{ moles Al}}{1676 \text{ kJ}} \quad \text{OR} \quad \frac{1676 \text{ kJ}}{2 \text{ moles Al}}$$

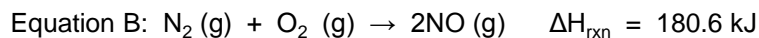
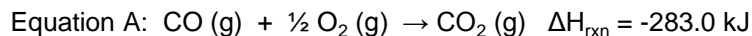
2. Convert heat transferred ($1.000 \times 10^3 \text{ kJ}$) into moles aluminum produced and then to mass aluminum.

$$\text{Mass of Al} = 1.000 \times 10^3 \text{ kJ} \times \frac{2 \text{ moles Al}}{1676 \text{ kJ}} \times \frac{26.98 \text{ g Al}}{1 \text{ mole Al}} = 32.20 \text{ g Al}$$

Two gaseous pollutants that form in auto exhaust are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following equation:



Given the following information, calculate the unknown ΔH_{rxn} .



Hess's Law of Heat Summation

One of the most powerful applications of the state function property of enthalpy (H) allows us to find ΔH of **any** reaction - even if we cannot run the reaction in the lab – we only need to be able to write the equation.

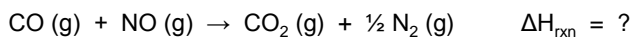
This application is based on **Hess's Law of Heat Summation**, which states the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.

$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2 + \cdots + \Delta H_n$$

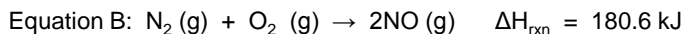
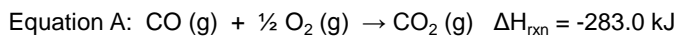
To apply Hess's Law. . .

1. Imagine the overall reaction as the sum of individual reactions steps, whether or not it actual does. Adding the steps must give the overall reaction.
2. Choose individual reaction steps for which ΔH is known.
3. Add together all the known ΔH values for the steps to get the unknown ΔH for the overall reaction.

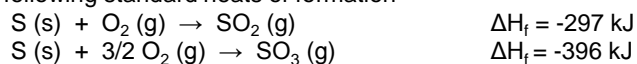
Two gaseous pollutants that form in auto exhaust are CO and NO. An environmental chemist is studying ways to convert them to less harmful gases through the following equation:



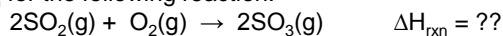
Given the following information, calculate the unknown ΔH_{rxn} .



Use the following standard heats of formation



to calculate ΔH_{rxn} for the following reaction:



Standard Heats of Reaction ($\Delta H^\circ_{\text{rxn}}$)

Changes in the enthalpy (ΔH) vary somewhat with conditions (i.e., temperature, pressure, state, etc.) Therefore, for heats of reaction data that we encounter in tables, chemists have established **standard states**, a set of specific conditions and concentrations.

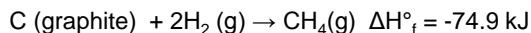
- **Gas** – 1 atm for gases behaving ideally
- **Aqueous solutions** – 1 M concentrations
- **Pure substances (elements or compounds)** – most stable form at 1 atm and 25°C

ΔH_{rxn} that has been measured with all reactants and products in their standard states is referred to a **standard heat of reaction**, $\Delta H^\circ_{\text{rxn}}$.

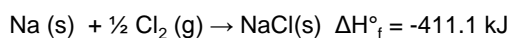
Formation Equations and Their Standard Enthalpy Changes

In a **formation equation**, 1 mole of a compound forms from its elements. The **standard heat of formation** (ΔH_f°) is the enthalpy change for the formation equation when all the substance are in their standard states.

Example: The formation equation for methane (CH_4) . . .



The formation equation for sodium chloride (NaCl) . . .



ΔH_f° values have been tabulated for several compounds (Table 6.3 shows a few) . . .

Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$
calcium				silver	
Ca(s)	0	Cl ₂ (g)	0	Ag(s)	0
CaO(s)	-635.1	HCl(g)	-92.3	AgCl(s)	-127.0
CaCO ₃ (s)	-1206.9	hydrogen		sodium	
carbon		H(g)	218	Na(s)	0
C(graphite)	0	H ₂ (g)	0	Na(g)	107.8
C(diamond)	1.9	nitrogen		NaCl(s)	-411.1
CO(g)	-110.5	N ₂ (g)	0	sulfur	
CO ₂ (g)	-393.5	NH ₃ (g)	-45.9	S ₈ (rhombic)	0
CH ₄ (g)	-74.9	NO(g)	90.3	S ₈ (monoclinic)	2
CH ₃ OH(l)	-238.6	oxygen		SO ₂ (g)	-296.8
HCN(g)	135	O ₂ (g)	0	SO ₃ (g)	-396.0
CS ₂ (l)	87.9	O ₃ (g)	143		
chlorine		H ₂ O(g)	-241.8		
Cl(g)	121.0	H ₂ O(l)	-285.8		

Note: 1. ΔH_f° is zero for an element in its standard state.

2. Most ΔH_f° are negative; most formations are exothermic.

Determining $\Delta H^\circ_{\text{rxn}}$ from ΔH°_f Values of Reactants and Products

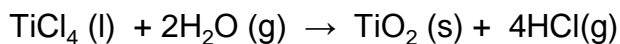
By applying Hess's law we can use ΔH°_f values to determine $\Delta H^\circ_{\text{rxn}}$ for any reaction. All we have to do is view the reaction as an imaginary two-step process:

Step 1. Each reactant decomposes to its elements ($-\Delta H^\circ_f$).

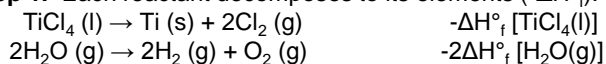
Step 2. Each product forms from its elements (ΔH°_f).

According to Hess's law we add the enthalpy changes for these steps to obtain the $\Delta H^\circ_{\text{rxn}}$.

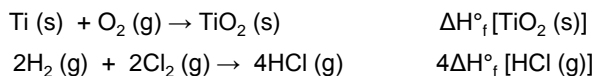
Suppose we want $\Delta H^\circ_{\text{rxn}}$ for

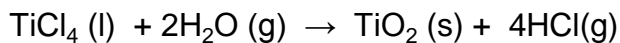


Step 1. Each reactant decomposes to its elements ($-\Delta H^\circ_f$).



Step 2. Each product forms from its elements (ΔH°_f).





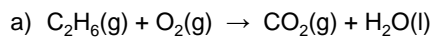
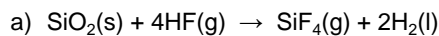
$$\Delta H_f^\circ [\text{TiCl}_4(l)] = -804.16 \text{ kJ/mol}$$

$$\Delta H_f^\circ [\text{TiO}_2(s)] = -941.4 \text{ kJ/mol}$$

$$\Delta H_f^\circ [\text{H}_2\text{O}(g)] = -241.8 \text{ kJ/mol}$$

$$\Delta H_f^\circ [\text{HCl}(g)] = -92.3 \text{ kJ/mol}$$

Calculate ΔH_{rxn} for each of the following:



Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$
calcium				silver	
Ca(s)	0	Cl ₂ (g)	0	Ag(s)	0
CaO(s)	-635.1	HCl(g)	-92.3	AgCl(s)	-127.0
CaCO ₃ (s)	-1206.9	hydrogen		sodium	
carbon		H(g)	218	Na(s)	0
C(graphite)	0	H ₂ (g)	0	Na(g)	107.8
C(diamond)	1.9	nitrogen		NaCl(s)	-411.1
CO(g)	-110.5	N ₂ (g)	0	sulfur	
CO ₂ (g)	-393.5	NH ₃ (g)	-45.9	S ₈ (rhombic)	0
CH ₄ (g)	-74.9	NO(g)	90.3	S ₈ (monoclinic)	2
CH ₃ OH(l)	-238.6	oxygen		SO ₂ (g)	-296.8
HCN(g)	135	O ₂ (g)	0	SO ₃ (g)	-396.0
CS ₃ (l)	87.9	O ₃ (g)	143		
chlorine		H ₂ O(g)	-241.8		
Cl(g)	121.0	H ₂ O(l)	-285.8		