Thermochemistry: study of the relationships between chemistry and energy

Energy: capacity to do work

Work: result of a force acting over a certain distance, one way to transfer energy

Types of energy:

- **Kinetic energy**: energy of motion
    - **Thermal energy:** energy associated with temperature, transferred by **heat**
- **Potential energy**: energy of position or composition
    - **Chemical energy**: energy associated with the composition of chemical compounds

Law of conservation of energy: energy cannot be created or destroyed, only transferred

- One object to another
- One type of energy to another

Units of energy:

- joule (J) = 1 kg · m^2 · s^{-2} (SI unit)
- calorie (cal) = 4.184 J (heat 1 g H_2O · 1 ^oC)
- Calorie (Cal) = 1 kcal = 1000 cal (food labels)
- kilowatt-hour (kWh) = 3.60×10^6 J

System and surroundings

The transfer of energy can be considered in terms of a system and its surroundings

- **System**: a specific place or substance
- **Surroundings**: everything outside of the system

In thermochemistry, the system is usually a **chemical reaction**, and it can use heat and work to transfer energy to or from its surroundings:

- Combustion of natural gas in a furnace

- Combustion of gasoline in a car's engine

- Chemical cold pack

First law of thermodynamics

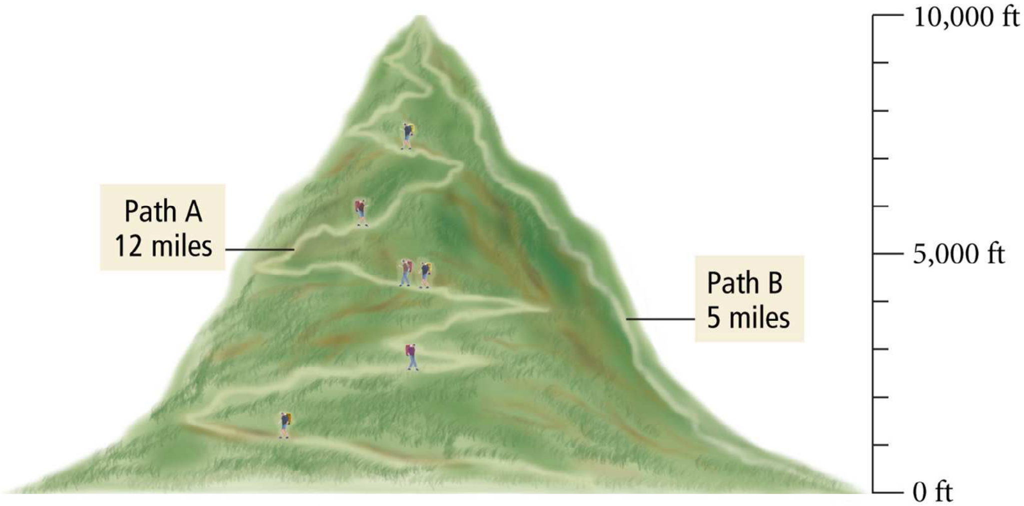
1st law: the total energy of the universe is constant

- law of conservation of energy
- perpetual motion?

Internal energy *(E):* sum of all forms of kinetic and potential energy in a certain system

Internal energy is a state function: it depends **only** on the makeup of the system itself at one point in time, not its history (it doesn't add up over time)

A State Function
Change in altitude depends only on the difference between the initial and final values, not on the path taken.



The **change** in any state function can be considered:

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

Work and heat

The change in a system's internal energy, ΔE, depends on how much work (w)was done and how much heat was transferred (q):

$\Delta E = q + w$ ($\Delta E = E_{\text{final}} - E_{\text{initial}}$)

Signs are always considered from the system's perspective.

If energy flows **out of** the system, ΔE is:
If energy flows **into** the system, ΔE is:

If heat flows **out of** the system, q is:
If heat flows **into** the system, q is:

Measuring heat:

Heat always transfers thermal energy from areas of ______ temperature to areas of _____ temperature

Heat capacity *(C)*: heat required to raise the temperature of an object by 1 °C
Units:

Specific heat capacity (C_s or s)*:* heat required to raise the temperature of **1 g of a substance** by 1 °C
Units:

Calculating heat transfers

For an object, q =

For a certain mass of a substance, q =

How much energy is required to heat 50.0 g water from 25.0 °C to 100.0 °C?

How long will this take a 1000 W hotplate (assuming all of the heat is transferred to the water)? (1 W = 1 J/s)

TABLE 6.4 Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity, C_s (J/g · °C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

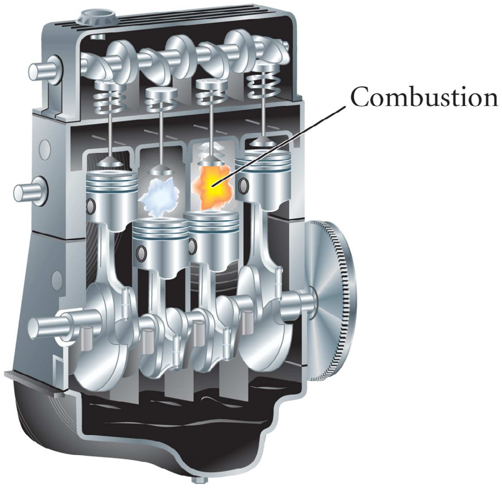
*At 298 K.

Reaction work

What if the system is a **chemical reaction** that gives off or absorbs heat?

$\Delta E_{rxn} = q + w$

The most common work a chemical reaction does is expanding gases against an exterior pressure (pressure-volume work).



$w = -P\Delta V$

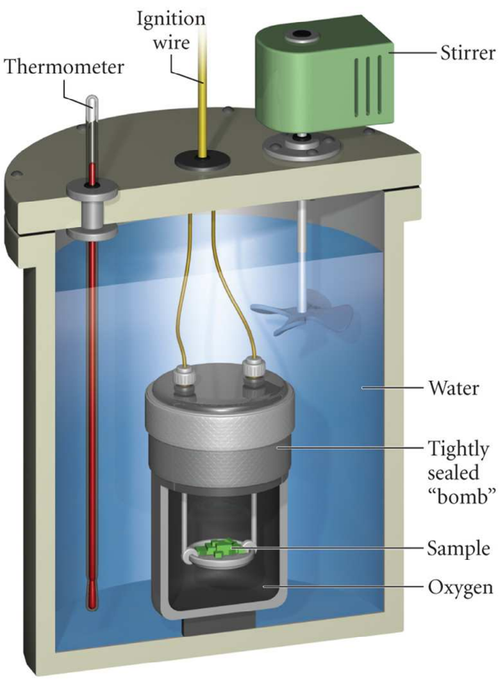
But usually we are mostly interested in the heat exchanged with the surroundings

If $\Delta V = 0$, $w = 0$ and $\Delta E_{rxn} = q_V$ (constant volume)

If P is constant, we can use a different state function called enthalpy to only consider heat transferred.

Constant-volume calorimetry

A **bomb calorimeter** is used to measure ΔE_{rxn}



The Bomb Calorimeter

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

$w = -P\Delta V$

If $\Delta V = 0$, $w = 0$ and $\Delta E_{\text{rxn}} = q_V$ (constant volume)

- q is a measurable energy transfer for a certain experimental process
- State functions like ΔE are more general - they're given for a balanced chemical equation or per mole of a substance

$q_{\text{cal}} = C_{\text{cal}}\,\Delta t$ (C_{cal} is given)

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

$\Delta E_{\text{rxn}} = q_{\text{rxn}} / n$

Constant-volume calorimetery

$q_{\text{cal}} = C_{\text{cal}}\, \Delta t$ (C_{cal} is given)

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

$\Delta E_{\text{rxn}} = (q_{\text{rxn}}) / n$

2.14 g C_5H_{12} is combusted in a bomb calorimeter and the temperature rises from 25.50 ^{o}C to 41.23 ^{o}C. The heat capacity of the calorimeter is 6.23 kJ/^{o}C. What is ΔE for the combustion of C_5H_{12} in kJ/mol?

Δ*H*, Change in enthalpy

It's more convenient to do a reaction open to the atmosphere, where pressure is constant.

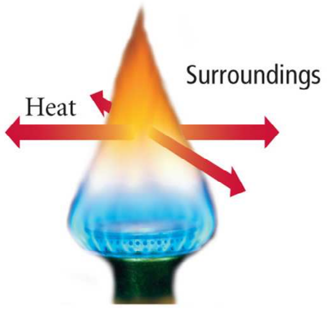
The heat exchanged in a specific experiment is q_P and its related state function for a general process is **Δ*H*** : change in enthalpy.

Since Δ*H* only involves the heat given off or absorbed, it has the same sign conventions as *q*:

Endothermic reaction: heat is transferred from surroundings to system (inwards)
Δ*H* is:

Exothermic reaction: heat is transferred from system to surroundings (outwards)
Δ*H* is:

Endothermic



Exothermic

Thermochemical equations

ΔH_{rxn} is always given per a balanced chemical equation.

Thermochemical equation:

- balanced chemical equation
- thermochemical state function (ΔH_{rxn})
- molar interpretation (coefficients = # moles)

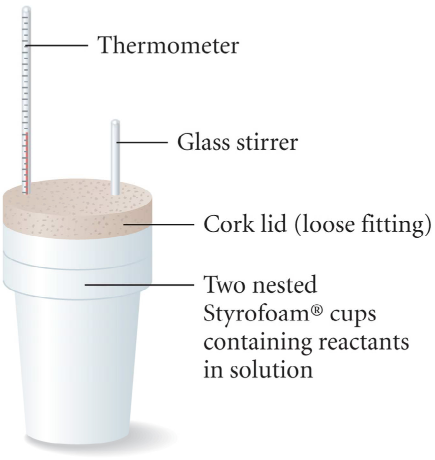
$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g);\ \ \Delta H_{rxn} = -483.7\ \text{kJ}$

How much heat (in kJ) is given off when 20.0 g H_2 react with excess oxygen?

Constant-pressure calorimetry

ΔH_{rxn} can be measured using a constant-pressure calorimeter

The Coffee-Cup Calorimeter



We assume all of the heat lost by the reaction is gained by the solution (or vice-versa), and since there is a varying amount of solution, we use its specific heat capacity (C_s or s)

$q_{soln} = (m_{soln})(C_{s,soln})(\Delta t)$
$q_{rxn} =$

If the reaction is made only of dilute solutions, you can make these assumptions:

- $C_{s,soln} = C_{s,water} = 4.184$ J/g°C
- $m_{solutions} = m_{water}$
- $d_{solutions} = 1$ g/mL

Constant-pressure calorimetry problem

50.0 mL of 0.500 *M* $H_2SO_4(aq)$ were added to 20.0 mL of 0.500 *M* NaOH in a coffee-cup calorimeter. The temperature rose from 25.00 ^oC to 27.20 ^oC. Assume C_s = 4.184 J/g^{o}C. What is q_{rxn} in kJ?

What is ΔH_{rxn} for the following balanced chemical equation?

$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$; $\Delta H_{rxn} = ?$

Find the limiting reactant (LR):

What is n_{LR} for the reaction that was performed?

$$\Delta H_{rxn} = \text{coefficient}_{LR} \times \frac{q_{rxn}}{n_{LR}}$$

Thermochemical state functions like Δ*H* are given for a certain chemical equation, where coefficients = # mol

1. Doubling coefficients doubles Δ*H,* etc.

$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g);\ \Delta H = -483.6\ \text{kJ}$

$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(g);\ \Delta H =$

$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(g);\ \Delta H =$

2. Reversing an equation changes the sign of Δ*H*

$6\ H_2O(g) \longrightarrow 6\ H_2(g) + 3\ O_2(g);\ \Delta H =$

3. Adding equations adds their Δ*H* values

Find ΔH_{rxn} for the following reaction:

$CO(g) + NO(g) \longrightarrow CO_2(g) + \frac{1}{2}\ N_2(g);\quad \Delta H = ?$

Use the following reactions with known Δ*H* values:

$CO(g) + \frac{1}{2}\ O_2(g) \longrightarrow CO_2(g);\quad \Delta H = -283.0\ \text{kJ}$

$N_2(g) + O_2(g) \longrightarrow 2NO(g);\quad \Delta H = 180.6\ \text{kJ}$

Hess's law practice

Find ΔH_{rxn} for the following reaction:

$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 6\ H_2O(g);\ \Delta H = ?$

Use the following reactions with known Δ*H* values:

1. $N_2(g) + O_2(g) \longrightarrow 2\ NO(g);\quad \Delta H = 180.6\ kJ$
2. $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g);\quad \Delta H = -91.8\ kJ$
3. $2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g);\quad \Delta H = -483.6\ kJ$

Standard enthalpies of formation

Standard thermodynamic states:

- gases: 1 atm
- liquids or solids: most stable form, 1 atm, 25 °C
- solutions: 1 *M* concentration

Some common standard states:

H_2
Cl_2
C(*graphite*)
Fe
Br_2
Hg
I_2

Standard enthalpy of formation: ΔH_f^o

enthalpy change when 1 mol of a compound is formed from its elements in their standard states

Write the chemical equation for ΔH_f^o of NaCl(*s*)

Write the chemical equation for ΔH_f^o of $NH_3(g)$

ΔH_f^o for any element in its standard state = 0

Using standard enthalpies of formation

Calculate ΔH^o for the following reaction using standard enthalpies of formation:

$$4\ NH_3(g) + 5\ O_2\ (g) \longrightarrow 4\ NO(g) + 6\ H_2O(g);\ \ \Delta H^o = ?$$

Compound	ΔH_f^o (kJ/mol)
$NH_3(g)$	-45.9
$O_2(g)$	
$NO(g)$	90.3
$H_2O(g)$	-241.8

$$\Delta H^o_{rxn} = \Sigma\ n\ \Delta H_f^o\ \text{(products)} - \Sigma\ n\ \Delta H_f^o\ \text{(reactants)}$$