Thermochemistry
thermodynamics: the study of energy and its transformations

-- thermochemistry: the subdiscipline involving chemical reactions and energy changes
Energy

**kinetic energy**: energy of motion;

-- all particles have KE

-- **Thermal energy** is due to the KE of particles.

We measure the **average** KE of a collection of particles as... **temperature**.

**potential energy**: stored energy

Chemical potential energy is due to electrostatic forces between charged particles.

-- related to the specific arrangement of atoms in the substance
Units of energy are joules (J), kilojoules (kJ), calories (cal), or nutritional calories (Cal or kcal).

-- conversions:

4184 J = 4.184 kJ = 1000 cal = 1 Cal = 1 kcal
system: the part of the universe we are studying

surroundings: everything else

• In chemistry:
  • open system – can exchange energy and matter with its surroundings
  • closed system – can exchange energy but not matter with its surroundings
  • closed system – can exchange neither energy nor matter with its surroundings

-- Usually, energy is transferred to...

  ...(1) change an object’s state of motion
  ...or...(2) cause a temperature change
**Work** \( (w) \) is done when a force moves through a distance. \[ W = F \cdot d \]

**Heat** \( (q) \) is an amount of energy transferred from a hotter object to a colder one.
Find the kinetic energy of a single dinitrogen monoxide molecule moving at 650 m/s.

\[ KE = \frac{1}{2} m v^2 \]

\[ m = 1 \text{ molec} \times \left( \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ molec}} \right) \times \left( \frac{44 \text{ g}}{1 \text{ mol}} \right) \times \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) = 7.31 \times 10^{-26} \text{ kg} \]

\[ KE = \frac{1}{2} (7.31 \times 10^{-26} \text{ kg}) (650 \text{ m/s})^2 = 1.5 \times 10^{-20} \text{ J} \]
First Law of Thermodynamics = Law of Conservation of Energy

-- Energy changes between its various forms, but the total amount remains the same.
**internal energy ($E$) of a system**: the sum of all the KE and PE of the components of a system

(this is impossible for us to know)

-- The change in the internal energy of a system would be found by:

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

And for chemistry, this equation would become:

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

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<tr>
<th>$\Delta E$ is $+$ if $E_{\text{final}} &gt; E_{\text{initial}}$ (i.e., system... gains energy)</th>
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But we ARE able to find $\Delta E$ by measuring two types of “energy” quantities:

$$\Delta E = q + w$$

$q = \text{heat}$: $+/- q = \text{system absorbs/releases heat}$

$w = \text{work}$: $+/- w = \text{work done on/by system}$

**KEY: Sign conventions are based on the system’s point of view.**

The *Titanic* was propelled by massive steam engines. The internal energy of the water molecules of the steam changed from instant to instant, depending on how much heat they were absorbing and how much work they were doing during a given time interval.
In endothermic processes, heat is **absorbed** by the system.

- e.g., melting
- boiling
- sublimation

In exothermic processes, heat is **released** by the system.

- e.g., freezing
- condensation
- deposition
To go further, we must introduce the concept of enthalpy \((H)\).

-- Enthalpy \((H)\) is defined as...

\[
H = E + PV
\]

where

\[
E = \text{system’s internal energy}
\]

\[
P = \text{pressure of the system}
\]

\[
V = \text{volume of the system}
\]

The Dutch physicist and Nobel laureate H.K. Onnes coined the term *enthalpy*, basing it on the Greek term *enthalpein*, which means “to warm.”
-- There is much that could be said about enthalpy, but what you need to know is:

*If a process occurs at constant pressure, the change in enthalpy of the system equals the heat lost or gained by the system.*

\[ \Delta H = H_{\text{final}} - H_{\text{initial}} = q_P \]

\( P \) indicates constant pressure conditions.

When \( \Delta H \) is +, the system... has gained heat. (ENDO)

When \( \Delta H \) is –, the system... has lost heat. (EXO)

Enthalpy is an **extensive** property, meaning that...

the amount of material affects its value.
In the burning of firewood at constant pressure, the enthalpy change equals the heat released. $\Delta H$ is and depends on…
For exothermic reactions, the heat content of the reactants is larger than that of the products.

Enthalpy of reaction: \( \Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}} \)

(also called “heat of reaction”)
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -483.6 \text{ kJ}

What is the enthalpy change when 178 g of \text{H}_2\text{O} are produced?

\[
178 \text{ g H}_2\text{O} \left( \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) \left( \frac{-483.6 \text{ kJ}}{2 \text{ mol H}_2\text{O}} \right)
\]

\[\Delta H = -2390 \text{ kJ}\]

The space shuttle was powered by the reaction above.
$\Delta H$ for a reaction and its reverse are the opposites of each other.

\[
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad (\Delta H = \text{?})
\]

\[
2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad (\Delta H = \text{?})
\]

Enthalpy change depends on the states of reactants and products.

\[
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad (\Delta H = -483.6 \text{ kJ})
\]

\[
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})
\]
Calorimetry: the measurement of heat flow

-- device used is called a... calorimeter

**heat capacity** of an object: amount of heat needed to raise object’s temp. 1 K = 1°C

**molar heat capacity**: amt. of heat needed to raise temp. of 1 mol of a substance 1 K

**specific heat (capacity)**: amt. of heat needed to raise temp. of 1 g of a substance 1 K

i.e.,
molar heat capacity = molar mass X specific heat
We calculate the heat a substance loses or gains using:

\[ q = m \cdot c_p \Delta T \]

AND

\[ q = +/- m \cdot c_X \]

(for within a given state of matter)

(for between two states of matter)

where

- \( q \) = heat
- \( m \) = mass of substance
- \( c_p \) = substance’s heat capacity
- \( \Delta T \) = temperature change
- \( c_X \) = heat of fusion (s/l)
  or heat of vaporization (l/g)
Typical Heating Curve

- Heat removed ($-q$)
- Heat added ($+q$)
What is the enthalpy change when 679 g of water at 27.4°C are converted into water vapor at 121.2°C?

\[
c_f = 333 \text{ J/g} \\
c_v = 40.61 \text{ kJ/mol} \\
c_{P,l} = 4.18 \text{ J/g-K} \\
c_{P,s} = 2.077 \text{ J/g-K} \\
c_{P,g} = 36.76 \text{ J/mol-K}
\]

Heat liquid... \( q = m c_P \Delta T \)

\[
= 679 \text{ g} \times (4.18 \text{ J/g-K}) \times (100 - 27.4) = 206 \text{ kJ}
\]

Boil liquid... \( q = +m c_X = +37.72 \text{ mol} \times (40.61 \text{ kJ/mol}) = 1532 \text{ kJ}

Heat gas... \( q = m c_P \Delta T \)

\[
= 37.72 \text{ mol} \times (36.76 \text{ J/mol-K}) \times (121.2 - 100) = 29.4 \text{ kJ}
\]

\[\Delta H = +1767 \text{ kJ}\]
With a calorimeter, a reaction is carried out under constant pressure conditions.

-- Why is the pressure constant?

  calorimeter isn’t sealed, atmospheric pressure is constant

-- If we assume that no heat is exchanged between the system and the surroundings, then the solution must absorb any heat given off by the reaction.

  \[ q_{\text{absorbed}} = -q_{\text{released}} \]

-- For dilute aqueous solutions, it is a safe assumption that \( c_P = 4.18 \text{ J/g-K} \)
When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a coffee-cup calorimeter, the mixture’s temperature increases from 22.30°C to 23.11°C. Calculate the enthalpy change for the reaction, per mole of AgNO₃.

\[
\text{AgNO}_3 + \text{HCl} \rightarrow \text{AgCl} + \text{HNO}_3
\]

0.05 L, 0.05 L,
0.1 M 0.1 M
0.005 mol 0.005 mol

\[
q = m \cdot c_p \cdot \Delta T
\]

\[
= 100 \times (4.18) \times (23.11 - 22.30)
\]

\[
= 338.58 \text{ J (for 0.005 mol AgNO}_3\text{)}
\]

Assume:
-- mixture \(c_p = c_p\) of H₂O
-- mixture mass = 100 g

\[
\Delta H = \frac{338.58 \text{ J}}{0.005 \text{ mol AgNO}_3} = -67.7 \frac{\text{kJ}}{\text{mol AgNO}_3}
\]
Combustion reactions are studied using constant-volume calorimetry.

This technique requires a **bomb calorimeter**.

-- The heat capacity of the bomb calorimeter ($C_{\text{cal}}$) must be known.

unit is J/K
(or the equivalent)
-- Again, we assume that no energy escapes into the surroundings, so that the heat absorbed by the bomb calorimeter equals the heat given off by the reaction.

Solve bomb calorimeter problems by unit cancellation.
A 0.343-g sample of propane, $\text{C}_3\text{H}_8$, is burned in a bomb calorimeter with a heat capacity of 3.75 $\text{kJ/}^\circ\text{C}$. The temperature of the material in the calorimeter increases from 23.22$^\circ\text{C}$ to 27.83$^\circ\text{C}$. Calculate the molar heat of combustion of propane.

\[
3.75 \frac{\text{kJ}}{^\circ\text{C}} (27.83^\circ\text{C} - 23.22^\circ\text{C})
\]

\[
\frac{17.29 \text{ kJ}}{0.343 \text{ g}} \left( \frac{44 \text{ g}}{1 \text{ mol C}_3\text{H}_8} \right)
\]

$-2220 \text{ kJ/mol}$
Hess’s Law: states that, whatever mathematical operations are performed on a chemical equation, the same mathematical operations are applied also to the heat of reaction.

1. If the coefficients of a chemical equation are all multiplied by a constant, the $\Delta H^\circ_{\text{react}}$ is multiplied by that same constant.

2. If two or more equations are added together to obtain an overall reaction, the heats of these equations are also added to give the heat of the overall reaction.

The area of a composite shape can be found by adding/subtracting the areas of simpler shapes. Similarly, the heats of reaction for individual reactions can be added to determine the heat of the overall reaction.
The $\Delta H_{\text{rxn}}$’s have been calculated and tabulated for many basic reactions. Hess’s law allows us to put these simple reactions together like puzzle pieces such that they add up to a more complicated reaction that we are interested in. By adding or subtracting the $\Delta H_{\text{rxn}}$’s as appropriate, we can determine the $\Delta H_{\text{rxn}}$ of the more complicated reaction.

The area of a composite shape can be found by adding/subtracting the areas of simpler shapes.
Calculate the heat of reaction for the combustion of sulfur to form sulfur dioxide.

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad (\Delta H = -198.2 \text{ kJ}) \]

\[ \text{S}_8(s) + 12 \text{O}_2(g) \rightarrow 8 \text{SO}_3(g) \quad (\Delta H = -3161.6 \text{ kJ}) \]

\[ \text{S}_8(s) + 8 \text{O}_2(g) \rightarrow 8 \text{SO}_2(g) \quad \text{(TARGET)} \]

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad (\Delta H = -198.2 \text{ kJ}) \]

\[ \text{S}_8(s) + 12 \text{O}_2(g) \rightarrow 8 \text{SO}_3(g) \quad (\Delta H = -3161.6 \text{ kJ}) \]

\[ \text{S}_8(s) + 8 \text{O}_2(g) \rightarrow 8 \text{SO}_2(g) \quad (\Delta H = -2368.8 \text{ kJ}) \]

need to cancel…
Calculate $\Delta H$ for the reaction... $5 \text{C} + 6 \text{H}_2 \rightarrow \text{C}_5\text{H}_{12}$ given the following:

$\text{C}_5\text{H}_{12} + 8 \text{O}_2 \rightarrow 5 \text{CO}_2 + 6 \text{H}_2\text{O}$ \hspace{1cm} (\Delta H = -3535.6 \text{ kJ})

$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ \hspace{1cm} (\Delta H = -393.5 \text{ kJ})

$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ \hspace{1cm} (\Delta H = -285.8 \text{ kJ})

$\Delta H = -146.7 \text{ kJ}$
Calculate \( \Delta H \) for the reaction… \( 5 \text{ C} + 6 \text{ H}_2 \rightarrow \text{C}_5\text{H}_{12} \) given the following:

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\text{C}_5\text{H}_{12} + 8 \text{ O}_2 \rightarrow 5 \text{ CO}_2 + 6 \text{ H}_2\text{O} \quad (\Delta H = -3535.6 \text{ kJ})
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\text{C} + \text{ O}_2 \rightarrow \text{ CO}_2 \quad (\Delta H = -393.5 \text{ kJ})
\]

\[
\text{H}_2 + \frac{1}{2} \text{ O}_2 \rightarrow \text{ H}_2\text{O} \quad (\Delta H = -285.8 \text{ kJ})
\]

\[
5 \text{ CO}_2 + 6 \text{ H}_2\text{O} \rightarrow \text{C}_5\text{H}_{12} + 3535.6 \text{ kJ}
\]

\[
5 \text{ C} + 5 \text{ O}_2 \rightarrow 5 \text{ CO}_2 + 1963.5 \text{ kJ}
\]

\[
6 \text{ H}_2 + \frac{3}{2} \text{ O}_2 \rightarrow 6 \text{ H}_2\text{O} + 1284.8 \text{ kJ}
\]

\[
5 \text{ C} + 6 \text{ H}_2 \rightarrow \text{C}_5\text{H}_{12} + 146.7 \text{ kJ}
\]

\( \Delta H = -146.7 \text{ kJ} \)
enthalpy of formation ($\Delta H_f$): the enthalpy change associated with the formation of a compound from its constituent elements

-- also called…

When finding the **standard enthalpy of formation** ($\Delta H_f^\circ$), all substances must be in their standard states. The “standard state” of a substance has arbitrarily been chosen to be the state of the substance at 25°C (298 K). If more than one form of the element exists at 298 K, then the standard state is the most stable form, e.g.,
-- By definition, $\Delta H_f^\circ$ for the most stable form of any element in its standard state is zero.

e.g., $\Delta H_f^\circ$ for O$_2$(g) or Al(s) or S$_8$(s), etc. is ZERO

-- $\Delta H_f$ values are for 1 mol of substance, so the units are typically kJ/mol.

-- Many $\Delta H_f$ values have been tabulated.

$\Delta H_f^\circ$ for Ni(s) = 0, but is $\neq 0$ for Fe$_2$O$_3$. 
standard enthalpy of a reaction ($\Delta H^o_{rxn}$):

$\Delta H^o_{rxn}$ is the change in enthalpy of a reaction when all substances are in their standard states (i.e., at 25°C).

-- Using Hess’s law, we can easily calculate $\Delta H^o_{rxn}$ from the $\Delta H_f^o$ of all R and P.

-- equation:

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

where $n$ and $m$ are the coefficients in the balanced equation
Approximate the enthalpy change for the combustion of 246 g of liquid methanol.

\[
\begin{align*}
2 \text{ CH}_3\text{OH}(l) + 3 \text{ O}_2(g) & \rightarrow 2 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(g) \\
-238.6 \text{ kJ/mol} & \quad 0 \text{ kJ/mol}\quad \rightarrow \quad -393.5 \text{ kJ/mol} & \quad -241.8 \text{ kJ/mol} \\
\times 2 & \quad \times 2 & \quad \times 4 \\
-477.2 \text{ kJ} & \quad -1754.2 \text{ kJ} \\
\Delta H^\circ_{\text{rxn}} &= -1754.2 \text{ kJ} - (-477.2 \text{ kJ}) = -1277 \text{ kJ} \\
\text{So...} & \quad \frac{-1277 \text{ kJ}}{64 \text{ g}} = \frac{X \text{ kJ}}{246 \text{ g}} \quad \text{for 2 mol (i.e., 64 g) of CH}_3\text{OH} \\
X &= \Delta H = -4910 \text{ kJ}
\end{align*}
\]