“Thermochemistry”
Energy Transformations

- "Thermochemistry" - concerned with heat changes that occur during chemical reactions
- **Energy** - capacity for doing work or supplying heat
  - weightless, odorless, tasteless
  - if within the chemical substances - called **chemical potential energy**
Energy Transformations

- Gasoline contains a significant amount of chemical potential energy
- **Heat** - represented by "q", is energy that transfers from one object to another, because of a temperature difference between them.
  - Only changes can be detected!
  - Flows from warmer $\rightarrow$ cooler object
Heat = Transfer of Energy

- The 3 methods that heat can be transferred:
  - **Conduction** – heat transfers by direct contact
  - **Convection** - is the process in which heat is carried from one place to another by the bulk movement of a fluid.
  - **Radiation** – heat transfers by electromagnetic waves.
Exothermic and Endothermic Processes

Essentially all chemical reactions and changes in physical state involve either:

a) release of heat, or
b) absorption of heat
Exothermic and Endothermic

- The **Law of Conservation of Energy** states that in any chemical or physical process, energy is neither created nor destroyed.

  - All the energy is accounted for as work, stored energy, or heat.

https://www.youtube.com/watch?v=GqtUWvDR1fg
Bell Ringer

- What is energy?
- What is heat?
- What are the three methods of heat transfer?
- All chemical and physical changes involve a transfer of ______________?
- In which direction does energy(heat) flow?
Exothermic & Endothermic

In studying heat changes, think of defining these two parts:

- **system** - the part of the universe on which you focus your attention
- the **surroundings** - includes everything else in the universe
- Together, the system and its surroundings constitute the **universe**
Endothermic Processes

- Heat **flowing into** a system from it’s surroundings:
  - defined as positive
  - \( q \) has a positive value
  - called **endothermic**
    - system **gains heat** (gets warmer) as the surroundings cool down
Exothermic Processes

- Heat flowing **out of** a system into its surroundings:
  - defined as negative
  - \( q \) has a negative value
  - called **exothermic**
    - system **loses heat** (gets cooler) as the surroundings heat up
1) A calorie is defined as the quantity of heat needed to raise the temperature of 1 g of pure water 1 °C.
- Used except when referring to food
- A Calorie, (written with a capital C), always refers to the energy in food
- 1 Calorie = 1 kilocalorie = 1000 cal.
Units for Measuring Heat Flow

2) The calorie is also related to the **Joule**, the SI unit of heat and energy
   - named after James Prescott Joule
   - $4.184 \text{ J} = 1 \text{ cal}$
Specific Heat Capacity

Specific Heat Capacity (abbreviated “C”) - the amount of heat it takes to raise the temperature of 1 gram of a substance by 1 °C

- Depends on both the object’s mass and its chemical composition
- Water $C = 4.18 \text{ J}/(\text{g } \circ\text{C})$
  or $= 1.00 \text{ cal}/(\text{g } \circ\text{C})$
Note the tremendous difference in Specific Heat. Water’s value is VERY HIGH.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific heat J/(g·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (l)</td>
<td>4.18</td>
</tr>
<tr>
<td>Water (s)</td>
<td>2.06</td>
</tr>
<tr>
<td>Water (g)</td>
<td>1.87</td>
</tr>
<tr>
<td>Ammonia (g)</td>
<td>2.09</td>
</tr>
<tr>
<td>Benzene (l)</td>
<td>1.74</td>
</tr>
<tr>
<td>Ethanol (l)</td>
<td>2.44</td>
</tr>
<tr>
<td>Ethanol (g)</td>
<td>1.42</td>
</tr>
<tr>
<td>Aluminum (s)</td>
<td>0.897</td>
</tr>
<tr>
<td>Calcium (s)</td>
<td>0.647</td>
</tr>
<tr>
<td>Carbon, graphite (s)</td>
<td>0.709</td>
</tr>
<tr>
<td>Copper (s)</td>
<td>0.385</td>
</tr>
<tr>
<td>Gold (s)</td>
<td>0.129</td>
</tr>
<tr>
<td>Iron (s)</td>
<td>0.449</td>
</tr>
<tr>
<td>Mercury (l)</td>
<td>0.140</td>
</tr>
<tr>
<td>Lead (s)</td>
<td>0.129</td>
</tr>
</tbody>
</table>
Specific Heat

- To calculate, use the formula:
  \[ q = \text{mass (in grams)} \times \Delta T \times C \]

- Heat is abbreviated as “q”

- \( \Delta T \) = change in temperature

- \( C \) = Specific Heat

- Units are either: \( J/(g \ ^{\circ}C) \) or \( \text{cal}/(g \ ^{\circ}C) \)
Calorimetry

- Calorimetry - the measurement of the heat into or out of a system for chemical and physical processes.
  - Based on the fact that the heat released = the heat absorbed

The device used to measure the absorption or release of heat in chemical or physical processes is called a “Calorimeter”
Calorimetry

- **Foam cups** are excellent heat insulators, and are commonly used as simple calorimeters under **constant pressure**.

- For systems at constant pressure, the "**heat content**" is the same as a property called **Enthalpy (H)** of the system.
Calorimetry

- Changes in enthalpy $= \Delta H$
- $q = \Delta H$ These terms will be used interchangeably
  - Thus, $q = \Delta H = m \times C \times \Delta T$

✓ $\Delta H$ is **negative** for an **exothermic** reaction

✓ $\Delta H$ is **positive** for an **endothermic** reaction

https://www.youtube.com/watch?v=JuWtBR-rDQk
Enthalpy

- The *heat content* a substance has at a given temperature and pressure
  - Can’t be measured directly because there is no set starting point
- The reactants *start* with a heat content
- The products *end up* with a heat content
- So we can measure how much enthalpy *changes*
Enthalpy

- Symbol is $H$
- Change in enthalpy is $\Delta H$ (delta H)
- If heat is *released*, the heat content of the products is *lower*
  $\Delta H$ is negative (exothermic)
- If heat is *absorbed*, the heat content of the products is *higher*
  $\Delta H$ is positive (endothermic)
C + O₂ → CO₂ + 395 kJ
Exothermic

- The products are *lower* in energy than the reactants.
- Thus, energy is *released*.
- \( \Delta H = -395 \text{ kJ} \)
  - The negative sign does not mean negative energy, but instead that *energy is lost.*
$\text{CaCO}_3 + 176 \text{ kJ} \rightarrow \text{CaO} + \text{CO}_2$
Endothermic

- The products are *higher* in energy than the reactants.
- Thus, energy is *absorbed*.
- $\Delta H = +176$ kJ
  - The positive sign means *energy is absorbed*.
An equation that *includes energy* is called a **thermochemical equation**

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 802.2 \text{ kJ}
\]

- 1 mole of \(\text{CH}_4\) releases 802.2 kJ of energy.
- When you make 802.2 kJ you also make 2 moles of water
Thermochemical Equations

- The **heat of reaction** is the heat change for the equation, exactly as written.
  - The physical state of reactants and products **must** also be given.
  - *Standard conditions* (SC) for the reaction is 101.3 kPa (1 atm.) and 25 °C (different from STP)
If 10.3 grams of CH\(_4\) are burned completely, how much heat will be produced?

\[ \Delta H = -514 \text{ kJ} \], which means the heat is released for the reaction of 10.3 grams CH\(_4\).

\[
\begin{align*}
10.3 \text{ g CH}_4 & \quad 1 \text{ mol CH}_4 \\
16.05 \text{ g CH}_4 & \quad 1 \text{ mol CH}_4 \\
802.2 \text{ kJ} & \quad 1 \text{ mol CH}_4
\end{align*}
\]

\[ = 514 \text{ kJ} \]
Heat of Reaction

- The heat that is released or absorbed in a chemical reaction
- Equivalent to $\Delta H$

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

In thermochemical equation, it is important to indicate the **physical state**

a) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$ $\Delta H = -241.8 \text{ kJ}$

b) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$ $\Delta H = -285.8 \text{ kJ}$
Bell Ringer

- Find the heat of the reaction for the following: Is it endothermic or exothermic?
- \( \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \)

\[
\Delta H^\circ_{\text{f}} \text{CH}_4 \ (g) = -74.86 \text{ kJ/mol}
\]
\[
\Delta H^\circ_{\text{f}} \text{O}_2(g) = 0 \text{ kJ/mol}
\]
\[
\Delta H^\circ_{\text{f}} \text{CO}_2(g) = -393.5 \text{ kJ/mol}
\]
\[
\Delta H^\circ_{\text{f}} \text{H}_2\text{O}(g) = -241.8 \text{ kJ/mol}
\]
There are situations in which the addition or removal of heat does not cause a temperature change.

Heat must be added or removed to make a material change its phase.

- Amount of heat added or removed depends on the type of material and nature of the phase.
Phase Changes

- Sublimation
- Melting
- Boiling/Evaporation (vaporization)
- Freezing
- Condensation
- Deposition

- Solid
- Liquid
- Gas
Latent Heat

- Latent Heat – is the heat per kilogram associated with a phase change
  - \( Q = mL \)

- Latent Heat of Fusion \((L_f)\) – change between solid & liquid phases

- Heat absorbed by a melting solid = to heat lost when a liquid solidifies Thus, \( \Delta H_{\text{fus.}} = -\Delta H_{\text{solid}} \).
Latent Heat

- **Latent Heat of Vaporization** \( (L_v) \) – change between liquid & gas phases
  - \( \Delta H_{\text{vap.}} = - \Delta H_{\text{cond.}} \)
- **Latent Heat of Sublimation** \( (L_s) \) – change between solid and gas phases

- Note: Temperatures will not change, until all materials are in the same phase/state
# Latent Heat

## Table 10-6

Latent heats of fusion and vaporization at standard pressure

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point (°C)</th>
<th>$L_f$ (J/kg)</th>
<th>Boiling point (°C)</th>
<th>$L_v$ (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen</td>
<td>-209.97</td>
<td>$2.55 \times 10^4$</td>
<td>-195.81</td>
<td>$2.01 \times 10^5$</td>
</tr>
<tr>
<td>oxygen</td>
<td>-218.79</td>
<td>$1.38 \times 10^4$</td>
<td>-182.97</td>
<td>$2.13 \times 10^5$</td>
</tr>
<tr>
<td>ethyl alcohol</td>
<td>-114</td>
<td>$1.04 \times 10^5$</td>
<td>78</td>
<td>$8.54 \times 10^5$</td>
</tr>
<tr>
<td>water</td>
<td>0.00</td>
<td>$3.33 \times 10^5$</td>
<td>100.00</td>
<td>$2.26 \times 10^6$</td>
</tr>
<tr>
<td>lead</td>
<td>327.3</td>
<td>$2.45 \times 10^4$</td>
<td>1745</td>
<td>$8.70 \times 10^5$</td>
</tr>
<tr>
<td>aluminum</td>
<td>660.4</td>
<td>$3.97 \times 10^5$</td>
<td>2467</td>
<td>$1.14 \times 10^7$</td>
</tr>
</tbody>
</table>
Heat Temperature Graph

- A - solid
- B - solid/liquid
- C - liquid
- D - liquid gas
- E - gas

- Freezing
- Melting
- Condensation
- Vaporization

Heat added
Heat of Solution

- Heat changes can also occur when a solute *dissolves* in a solvent.

5. **Molar Heat of Solution** \((\Delta H_{\text{soln.}})\) = heat change caused by dissolution of one mole of substance

\[
q = \text{mol} \times \Delta H_{\text{soln.}} \quad \text{(no temperature change)}
\]

- Sodium hydroxide provides a good example of an exothermic molar heat of solution (next slide)
Heat of Solution

$$\text{NaOH}_{(s)} \xrightarrow{\text{H}_2\text{O}_{(l)}} \text{Na}^{1+}_{(aq)} + \text{OH}^{1-}_{(aq)}$$

$$\Delta H_{\text{soln.}} = -445.1 \text{ kJ/mol}$$

- The heat is released as the ions separate (by dissolving) and interact with water, releasing 445.1 kJ of heat as $\Delta H_{\text{soln.}}$.
  - thus becoming so hot it steams!
Sodium Hydroxide and Heat

Preparing Sodium Hydroxide Solution?

A great amount of heat is released when sodium hydroxide dissolves in water. The temperature of the solution may increase very rapidly. In fact, the temperature may rise so fast that the solution will boil and possibly spatter a hot, caustic solution. Immerse the beaker or flask in an ice–water bath to control the solution temperature. Add ingredients slowly while stirring continuously. Use only borosilicate glassware and check to make sure that there are no scratches, chips or breaks.
Standard Heats of Formation

- The $\Delta H$ for a reaction that produces 1 mole of a compound from its elements at standard conditions
- Standard conditions: 25°C and 1 atm
- Symbol is: $\Delta H_f^0$
- The standard heat of formation of an element in its standard state is arbitrarily set at “0”
- This includes the diatomic elements Mr. BrINCiHOF
Standard Heats of Formation

The heat of a reaction can be calculated by:

- subtracting the heats of formation of the reactants from the products

\[ \Delta H^o = (\Delta H_f^0 \text{ Products}) - (\Delta H_f^0 \text{ Reactants}) \]

Remember, from balanced equation: **Products - Reactants**
Example

\[
\begin{align*}
\text{CH}_4(g) + 2\text{O}_2(g) & \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \\
\Delta H_f^0 \text{CH}_4(g) & = -74.86 \text{ kJ/mol} \\
\Delta H_f^0\text{O}_2(g) & = 0 \text{ kJ/mol} \\
\Delta H_f^0\text{CO}_2(g) & = -393.5 \text{ kJ/mol} \\
\Delta H_f^0\text{H}_2\text{O}(g) & = -241.8 \text{ kJ/mol} \\
\Delta H & = \left[ -393.5 + 2(-241.8) \right] - \left[ -74.86 + 2 \times 0 \right] \\
\Delta H & = -802.24 \text{ kJ} \quad \text{(endothermic or exothermic?)}
\end{align*}
\]
Hess’s Law
(developed in 1840)

Germain Henri Hess
(1802-1850)

If you **add** two or more thermochemical equations to give a final equation, then you can also **add** the heats of reaction to give the final heat of reaction.

Called Hess’s Law of Heat Summation
How Does It Work?

1) If you turn an equation around, you change the sign:
   If \( \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \ \Delta \text{H} = -285.5 \text{ kJ} \)
   then the reverse is:
   \( \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \ \Delta \text{H} = +285.5 \text{ kJ} \)

2) If you multiply the equation by a number, you multiply the heat by that number:
   \( 2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \ \Delta \text{H} = +571.0 \text{ kJ} \)

3) Or, you can just leave the equation “as is”
Example

Calculate $\Delta H$ for the reaction:

$$C_2H_4 \ (g) + H_2 \ (g) \rightarrow C_2H_6 \ (g)$$

- $C_2H_4(g) + 3 \ O_2(g) \rightarrow 2 \ CO_2(g) + 2 \ H_2O(l) \quad \Delta H = -1411 \ kJ$
- $C_2H_6(g) + 3\frac{1}{2} \ O_2(g) \rightarrow 2 \ CO_2(g) + 3 \ H_2O(l) \quad \Delta H = -1560 \ kJ$
- $H_2(g) + \frac{1}{2} \ O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285.8 \ kJ$