

## Unit 6 <br> Thermodynamics

6.1 Endothermic \& Exothermic Processes 6.2 Energy Diagrams
6.3 Heat Transfer \& Thermal Equilibrium

## Heat vs. Temperature

## Heat

1. A form of energy measured in Joules (J).

## Temperature

1. A measure of the average kinetic energy of atoms and molecules in a system.

- The Kelvin $(\mathbb{K})$ temperature scale is proportional to this.
- When KE doubles, the Kelvin temperature doubles.


## Boltzmann Distribution \& Temperature



Kinetic Energv $\rightarrow$

## Boltzmann Distribution \& Temperature



Kinetic Energv $\rightarrow$
The distribution of kinetic energies increases as temperature increases.

The average kinetic energy of the particles in a system increases as temperature increases.

## Indications of Energy Changes

Macroscopic indications that an energy change has occurred:

- Changes in temperature
- after mixing two solutions that are at the same temperature, the temperature of the final solution is either higher or lower than the original solution.
- Heating or cooling a substance changes its internal energy.
- Changes in volume
- The volume of a gaseous system increases or decreases.


## Causes of Energy Changes

- Heating or cooling a substance
- Adding heat to, or removing heat from, a substance changes its internal energy.
- If the temperature changes, the average KE of the particles in the system changes
- Phase changes
- Temperature does not change during a phase change.
- The energy that is released or absorbed by the system is used to form, alter, or sever intermolecular forces.
- Chemical reactions
- During chemical reactions, energy is released or absorbed in the form of heat and/or work.


## Heat Transfer (Exchange)

- Two systems at different temperatures that are in thermal contact with one another will exchange energy (heat).
- The energy transferred to system 1 is equal to the energy transferred from system 2.

Initial


Final


## Conservation of Energy

Energy can neither be created nor destroyed, but it can be transformed from one form to another.

- chemical reactions
- phase changes
- heating or cooling
- System
- The actual chemical reaction that is taking place.
- Surroundings
- The entire universe outside of the chemical reactions


## Heat and Endothermic Processes

In an isolated system, energy is conserved.

$$
\begin{array}{r}
\mathrm{CH}_{3} \mathrm{OH}_{(g)} \\
\boldsymbol{P E}+\boldsymbol{K} \boldsymbol{E}
\end{array} \rightarrow \begin{gathered}
\mathrm{CO}_{(g)}+2 \mathrm{H}_{2(g)} \\
\boldsymbol{P E} \boldsymbol{E}+\boldsymbol{K E}
\end{gathered}
$$

$$
\Delta H=+90.7 \mathrm{~kJ}
$$

- As the bonds in the products contain more PE, the product molecules must contain less KE.
- This is why the products of an endothermic reaction are at a lower temperature.
- Heat flows from the surroundings into the system until thermal equilibrium is established.


## Heat and Exothermic Processes

In an isolated system, energy is conserved.
$\mathrm{CH}_{4(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})}$

$$
\kappa E+\boldsymbol{P} E
$$



- As the bonds in the products contain less PE, the product molecules must contain more KE.
- This is why the products of an exothermic reaction are at a higher temperature.
- Heat flows from the system into the surroundings until thermal equilibrium is established.


## Energy Changes and Chemical Reactions

- During chemical reactions, the internal energy of the system can:
- Decrease (exothermic)
- Increase (endothermic)
- Remain the same



## Enthalpy Change ( $\Delta \mathrm{H}$ )

- Hydrogen Fuel for Your Car

Burning Hydrogen Fuel

$$
2 \mathrm{H}_{2(g)}+\mathrm{O}_{2(g)} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(l)} \quad \Delta H=-572
$$

$$
\Delta H=572 \mathrm{~kJ}
$$

Making Hydrogen Gas

$$
2 \mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow 2 \mathrm{H}_{2(g)}+\mathrm{O}_{2(g)} \quad \Delta H=572
$$

$$
\Delta H=-572 \mathrm{~kJ}
$$



## Energy Profile Diagrams


$\Delta E$ is the energy lost of gained in a reaction.
$\Delta E=q \cdot w \quad$ If the volume does not change, $\Delta E=\Delta H$

## Ex: Forming a $\mathrm{NaCl}_{\text {(aq) }}$ Solution ${ }^{0}$

- Ionic bonds must be broken
- Hydrogen bonds between some of the water molecules must be broken.
- Both of these are ENDOTHERMIC processes.

- More energy is required to break the ionic bonds and H -bonds than is released when the ion-dipole forces are established, so the overall process is endothermic.
lon-dipole forces of attraction are established between $\mathrm{Na}^{+}$and $\mathrm{H}_{2} \mathrm{O}$ and between $\mathrm{Cl}^{-}$and $\mathrm{H}_{2} \mathrm{O}$.
- These are EXOTHERMIC processes.



# 6.4 Heat Capacity \& Calorimetry <br> 6.6 Introduction to Enthalpy of Reaction 

## First Law of Thermodynamics

- Energy is conserved in chemical and physical processes.
- The internal energy of a system may be transferred into or out of that system in the form of heat or work, but it cannot be created or destroyed.

The First Law of Thermodynamics
Energy
transformation


## Heating \& Cooling

- When heat flows into a system, the energy of that system increases.


The internal energy of the system increases as heat flows into the system.

- When heat flows out of a system, the energy of that system decreases.


The internal energy of the system decreases as heat flows out of the system.

## Specific Heat Capacity (C)

- Specific heat capacity, $C$, is the amount of heat required to raise the temperature of 1.0 g of a substance by 1.0 K .
- A large value for water ( $4.184 \mathrm{~J} / \mathrm{g} \bullet \mathrm{K}$ )
- It takes a lot of heat to increase the temperature of 1.0 g of water by 1.0 K .
- A small value for iron ( $0.45 \mathrm{~J} / \mathrm{g} \bullet \mathrm{K}$ )
- It takes much less heat to raise the temperature of 1.0 g of Fe by 1.0 K .


## Example: Specific Heat Capacity (C)

- 10.0 J of heat are absorbed by a 1.0 g sample of water at $25.0^{\circ} \mathrm{C}$ and 10.0 J of heat are absorbed by a 1.0 g sample of iron at $25.0^{\circ} \mathrm{C}$. Which sample will experience the greatest temperature? Justify your answer.


## Specific Heat Capacity (C)

- The heat transfer equation shows that the transfer of equal quantities of heat to two materials of equal masses with different specific heat capacities will produce different temperature changes.
- The material with the higher specific heat capacity will experience a smaller increase in temperature (logically).


## $q=m C \Delta T$

$\mathrm{q}=$ heat lost or gained
$\mathrm{m}=$ mass of that substance
$C=$ specific heat capacity
$\Delta T=$ Temperature change of that substance $\left(\Delta T=T_{f}-T_{i}\right)$

## $q=m C \Delta T$ <br> Calorimetry

- The measure of heat transfer using a calorimeter.
- A device used to determine the amount of heat transferred.
- Heat flow cannot be measured directly.
- We measure the temperature before and after a reaction, and use that data to calculate heat transfer.



## Coffee Cup Calorimetry

- The reactants and products are the system.
- The water in which they are dissolved and the calorimeter make up the surroundings.
- The heat lost or gained by the solution is equal to the heat lost or gained by the reaction.
- e.g. - if you calculated qsolution to be +568 J , the solution gained heat. This means the reaction was exothermic, as the heat gained by the solution is equal to the heat lost by the reaction ( $\left.q_{1 \times n}=-568 \mathrm{~J}\right)$.


## Ex. Calorimetry

- A 97 g iron bar was heated to $143^{\circ} \mathrm{C}$ and placed in a coffee cup calorimeter containing 350.0 g of water at $25.00^{\circ} \mathrm{C}$. The maximum temperature of the water was measured to be $28.40^{\circ} \mathrm{C}$.
a) How much heat was gained by the water?
b) How much heat was lost by the iron bar?

$$
\begin{aligned}
q_{\mathrm{Fe}} & =m c \Delta T \\
c & =\frac{q_{\mathrm{Fe}}}{m \Delta T}
\end{aligned}
$$

$$
c=\frac{-4979 \mathrm{~J}}{(97 \mathrm{~g})\left(28.40^{\circ} \mathrm{C}-143^{\circ} \mathrm{C}\right)}
$$

$$
c=0.45 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}
$$

## Enthalpy Change

- The enthalpy change, $\Delta H$, of a reaction is the amount of heat energy that is released (exothermic) or absorbed (endothermic) by a chemical reaction at constant pressure.
- Four methods for finding $\Delta \mathrm{H}$ :

1. Find it by performing calorimetry experiments.
2. Calculate it using average bond enthalpies.
3. Calculate it using enthalpies of formation.
4. Calculate it using Hess's Law.

## Example 2: Calorimetry

- When 20.0 mL of 1.00 M NaCl at $22.00^{\circ} \mathrm{C}$ is mixed with 20.0 mL of 1.00 M $\mathrm{AgNO}_{3}$ at $22.0^{\circ} \mathrm{C}$ in a calorimeter, a white precipitate forms and the temperature of the mixture reaches $29.60^{\circ} \mathrm{C}$. Assume that the specific heat capacity of the mixture is $4.184 \mathrm{~J} / \mathrm{g} \bullet \mathrm{K}$, its density is $1.00 \mathrm{~g} / \mathrm{mL}$ and the volumes are additive.

Step 1) Calculate $q_{\text {sol }}$.
$q_{\text {sol }}=m c \Delta T$
a) Write the net ionic equation for this reaction.
b) Calculate $\Delta \mathrm{H}$ for the reaction.

$$
\begin{aligned}
& q_{\text {sol }}=(40.0 \mathrm{~g})\left(4.184 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)\left(29.60^{\circ} \mathrm{C}-22.00^{\circ} \mathrm{C}\right) \\
& q_{\text {sol }}=(40.0 \mathrm{~g})\left(4.184 \mathrm{~J} / \mathrm{g} \cdot{ }^{\circ} \mathrm{C}\right)\left(7.60^{\circ} \mathrm{C}\right) \\
& q_{\text {sol }}=+1270 \mathrm{~J}
\end{aligned}
$$

Step 2) Calculate $q_{r x n}$.

$$
\begin{aligned}
& q_{r x n}=-q_{s o l} \\
& q_{r x n}=-1270 \mathrm{~J}
\end{aligned}
$$

## Example 2: Calorimetry

## Step 3) Calculate Moles of $\mathrm{Ag}^{+}$or $\mathrm{Cl}^{-}$.

$$
0.0200 \mathrm{~L} \times \frac{1.0 \mathrm{moles} \mathrm{Ag}^{+}}{1 \mathrm{~L}}=0.0200 \text { moles } \mathrm{Ag}^{+}
$$

## Step 4) Calculate $\Delta H_{r x n}$.

$\Delta H_{r x n}=\frac{q_{r x n}}{n_{\mathrm{AgCl}}}$

$$
\begin{aligned}
\Delta H_{r x n} & =\frac{-1270 \mathrm{~J}}{0.0200 \mathrm{moles} \mathrm{AgCl}} \\
\Delta H_{r x n} & =-63500 \mathrm{~J} / \mathrm{mol}=-63.5 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

## Molar Heat Capacity

- $C_{m}$ is the amount of heat required to raise the temperature of 1.0 mole of a substance by 1.0 K .
- The transfer of equal quantities of heat to equal numbers of moles of two substances with different molar heat capacities will produce different temperature changes.
- The substance with the higher molar heat capacity will experience a smaller increase in temperature.


## Ex. Molar Heat Capacity

- The specific heat capacity of gold is $0.129 \mathrm{~J} / \mathrm{g} \cdot \mathrm{K}$.
a) Find the molar heat capacity of gold.
b) If 743 J of heat are added to 3.4 moles of gold at $2^{\circ} \mathrm{C}$, what is the final temperature of the gold?

$$
C_{m_{\mathrm{An}}}=\frac{0.129 \mathrm{~J}}{\mathrm{gK}} \times \frac{196.97 \mathrm{~g} \mathrm{Au}}{1 \mathrm{~mol} \mathrm{Au}}=25.4 \mathrm{~J} /(\mathrm{molK})
$$



## Ex. Molar Heat Capacity

$$
\begin{aligned}
q & =n C_{m_{\mathrm{Au}}} \Delta T \\
q & =n C_{m_{\mathrm{Au}}}\left(T_{f}-T_{i}\right) \\
T_{f} & =\frac{q}{n C_{m_{\mathrm{Au}}}}+T_{i}
\end{aligned}
$$

$$
\begin{aligned}
T_{f} & =\frac{743 \mathrm{~J}}{(3.4 \mathrm{moles})(25.4 \mathrm{~J} /(\mathrm{molK}))}+(2+273) \mathrm{K} \\
& =8.6 \mathrm{~K}+275 \mathrm{~K}=284 \mathrm{~K}
\end{aligned}
$$

## Enthalpy \& Stoichiometry

- How much heat is released when 3.56 g of $\mathrm{H}_{2} \mathrm{O}_{2(\mathrm{aq)}}$ decomposes into water and oxygen gas?

$$
2 \mathrm{H}_{2} \mathrm{O}_{2(a q)} \rightarrow \mathrm{O}_{2(g)}+2 \mathrm{H}_{2} \mathrm{O}_{(l)} \quad \Delta H=-186 \mathrm{~kJ}
$$

$$
3.56 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2} \times \frac{1 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}}{34.02 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}_{2}} \times \frac{-186 \mathrm{~kJ}}{2 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}_{2}}=-9.73 \mathrm{~kJ}
$$

There are $\mathbf{2}$ moles $\mathrm{H}_{2} \mathrm{O}_{2}$ in the balanced equation

## Thermodynamics

### 9.1 Introduction to Entropy

9.2 Absolute Entropy \& Entropy Change

## Laws of Thermodynamics

- First Law:
- The energy contained within the universe is constant.
- Second Law:
- The entropy of the universe is constantly increasing.


## Entropy (S)

- A measure of the disorder of a system.
- Entropy increases when matter becomes more dispersed.
- A greater degree of disorder is favorable.
- A positive value for $\Delta S$ is favorable.


## $\Delta \mathrm{S}=\mathrm{S}_{\text {(products) }}-\mathrm{S}_{\text {(reactants) }}$

## Increases in Entropy are Favored

- Your house gets dirty
- Making a stir-fry
- The impossibility of maintaining a perfect lawn
- Spilling a glass of milk
- Breaking a window


Highly Ordered


More disordered

## $\Delta S>0$ for the following processes:

- Melting
- Vaporizing
- Reactions where the products are in the same phase as the reactants but contain more particles than the reactants.
- Making most solutions
- Adding heat
- Increasing the volume of a gas


## $\Delta S>0$ when Melting



## $\Delta S>0$ when Vaporizing


$\mathrm{H}_{2} \mathrm{O}(l)$
Relatively Low $S$
High $S$

## $\Delta S>0$ when Products have more Particles

## $4 \mathrm{C}_{3} \mathrm{H}_{5} \mathrm{~N}_{3} \mathrm{O}_{9}(\mathrm{l}) \rightarrow 6 \mathrm{~N}_{2}(\mathrm{~g})+12 \mathrm{CO}_{2}(\mathrm{~g})+10 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g})$

- 4 liquid molecules are converted into 29 gaseous molecules.
- Increasing the number of moles increases the number of potential arrangements.
- Changing from liquid to gas increases the number of potential arrangements.


## $\Delta \mathrm{S}>0$ when (usually) when making solutions with solids and/or liquids

- An ionic compound is very organized.

- A solution containing the same ions is much more disordered.




## $\Delta S>0$ when adding heat, as the distribution of KE increases



## $\Delta S>0$ when volume increases (at constant temperature)


$\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
High $S$

$\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
Higher $S$

## Calculating $\Delta \mathbf{S}^{0}$


stoichiometric
coefficients

## Example: Calculating $\Delta S$

$$
\Delta S_{\mathrm{rv}}^{\mathrm{o}}=\Sigma n S_{\text {(roducts) }}^{\mathrm{o}}-\Sigma n S_{\text {(reactants) }}^{\mathrm{o}}
$$

- Calculate $\Delta S$ for the following reaction at 298K.

$$
\begin{aligned}
& \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \\
& \left.\Delta S^{\mathrm{o}}=\Sigma n S_{(\text {products })}^{\mathrm{o}}-\Sigma n S_{(\text {reactants })}^{\mathrm{o}}\right) \\
& \Delta S^{\mathrm{o}}=\left[1\left(S^{\mathrm{o}}\left(\mathrm{~N}_{2} \mathrm{O}_{4(\mathrm{~g})}\right)\right)\right]-\left[1\left(S^{\mathrm{o}}\left(\mathrm{~N}_{2(g)}\right)\right)+2\left(S^{\mathrm{o}}\left(\mathrm{O}_{2(\mathrm{~g})}\right)\right)\right] \\
& \Delta S^{\mathrm{o}}=[1(304.2)]-[1(191.5)+2(205.0)] \\
& \Delta S^{\mathrm{o}}=-297.3 \mathrm{~J} / \mathrm{K} \cdot \mathrm{~mol}
\end{aligned}
$$

## Example \#2: Calculating $\Delta S$

$$
\Delta S_{\mathrm{rv}}^{\mathrm{o}}=\sum n S_{(\text {products })}^{\mathrm{o}}-\sum n S_{\text {(reacants) }}^{\mathrm{o}}
$$

- Calculate $\Delta \mathrm{S}$ for the following phase change at 298 K .

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

$$
\begin{aligned}
& \Delta S^{\mathrm{o}}=\sum n S^{\mathrm{o}}{ }_{\text {(products) })}-\sum n S^{\mathrm{o}}{ }_{\text {(reactants) }} \\
& \Delta S^{\mathrm{o}}=\left[1\left(S^{\mathrm{o}}\left(\mathrm{H}_{2} \mathrm{O}(g)\right)\right)\right]-\left[1\left(S^{\mathrm{o}}\left(\mathrm{H}_{2} \mathrm{O}(l)\right)\right)\right] \\
& \Delta S^{\mathrm{o}}=[1(188.72)]-[1(69.94)] \\
& \Delta S^{\mathrm{o}}=118.78 \mathrm{~J} / \mathrm{K} \cdot \mathrm{~mol}
\end{aligned}
$$

## Applications of Thermodynamics

9.3 Gibbs Free Energy \& Thermodynamic Favorability

## Entropy or Enthalpy?



Solid water
Spontaneous below $0^{\circ} \mathrm{C}$

$$
\begin{array}{cc}
\Delta S^{\circ}=-22.0 \mathrm{~J} /(\mathrm{K} \cdot \mathrm{~mol}) & \text { (Entropy decreases) } \\
\Delta H^{\circ}=-6.01 \mathrm{~kJ} / \mathrm{mol} & \text { (Exothermic) }
\end{array}
$$



Liquid water

## Entropy or Enthalpy?

- A reaction is more likely to be spontaneous if it is exothermic $(-\Delta H)$, but endothermic reactions can still be spontaneous.
- A reactions more likely to be spontaneous if there is an increase in entropy, $+\Delta S$, but a reaction that decreases disorder can still be spontaneous.
- Temperature is also crucial in determining whether a reaction is spontaneous.
- We need a way to incorporate all 3 terms!


## Multiple Entropy Changes?

- We have 2 entropy changes, $\Delta \mathrm{S}_{\text {system }}$ and $\Delta \mathrm{S}_{\text {surroundings, }}$ and if the overall entropy increases then the reaction will be spontaneous.

$$
\Delta \mathrm{S}_{\text {total }}^{0}=\Delta \mathrm{S}_{\text {syst }}+\Delta \mathrm{S}_{\text {surr }}
$$

- The second law of thermodynamics says, in simple terms, that entropy always increases which we translate to be spontaneous, a reaction must lead to an increase in entropy.


## Determination of $\Delta \mathrm{S}$

- $\Delta S_{\text {surroundings }}$ is determined by the $\Delta H_{\text {system }}$ and by temperature.

$$
\begin{aligned}
& \Delta S_{\text {surr }}^{o}=-\frac{\Delta H^{o}}{T} \text { syst } \\
& \Delta S_{\text {total }}^{o}=\Delta S_{\text {syst }}^{0} \frac{-\Delta H^{o}}{T} \text { syst }
\end{aligned}
$$

- We have methods of calculating $\Delta \mathrm{S}$ and $\Delta \mathrm{H}$, but we actually use a modified version of this equation which introduces Gibbs (Free) Energy, $\Delta \mathrm{G}$.


## Free Energy: $\Delta \mathbf{G}$

- Gibbs energy is a useful quantity as it represents the energy of a reaction that is available 'to do work' and is given by

$$
\Delta \mathrm{G}^{0}=\mathrm{T} \Delta \mathrm{~S}_{\text {total }}^{0}
$$

- If we multiply both sides of our previous equation by $-T$, we get:

$$
-\mathrm{T} \Delta \mathrm{~S}^{0_{\text {total }}}=\Delta \mathrm{H}_{\text {syst }}-\mathrm{T} \Delta \mathrm{~S}_{\text {syst }}
$$

- If we combine these two equations we get Gibbs Free Energy Equation

$$
\Delta G^{0}=\Delta H^{0}{ }_{\text {syst }}-T \Delta S^{0}{ }_{\text {syst }}
$$

## Free Energy: $\Delta \mathbf{G}$

## $\Delta H<0$

$\Delta H>0$


## Calculating $\Delta G$

- At Standard Conditions

$$
\Delta G_{r \times n}=\sum \Delta G_{f(\text { products) })}^{\circ}-\sum \Delta G_{f(\text { freactants })}^{\circ}
$$

- At Temperatures other than 298K

$$
\Delta G_{\text {syst }}=\Delta H_{\text {syst }}-T \Delta S_{\text {syst }}
$$

## Example

- Calculate $\Delta \mathrm{G}^{\circ}{ }_{\text {rxn }}$ for the following reaction:

$$
2 \mathrm{Al}_{(\mathrm{s})}+\mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})} \rightarrow 2 \mathrm{Fe}_{(\mathrm{s})}+\mathrm{Al}_{2} \mathrm{O}_{3(\mathrm{~s})}
$$

| COMPOUND | $\Delta \mathbf{G}^{\mathbf{o}}{ }_{\mathrm{f}} \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :---: | :---: |
| $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})$ | -742 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}(\mathrm{~s})$ | -1582 |

## Example

- Calculate the $\Delta G_{r \times n}$ for the thermal decomposition of calcium carbonate @ 298K from the following data

| Compound | $\Delta \mathbf{H}^{\circ}{ }_{\mathrm{f}} \mathbf{k J} \mathrm{mol}^{-\mathbf{1}}$ | $\Delta \mathbf{S}^{\circ}{ }_{\mathrm{f}} \mathbf{J ~ K}^{-1} \mathrm{~mol}^{-\mathbf{1}}$ |
| :---: | :---: | :---: |
| $\mathrm{CaCO}_{3}(\mathrm{~s})$ | -1207 | 92.9 |
| $\mathrm{CaO}(\mathrm{s})$ | -635 | 39.7 |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | -394 | 214 |

Hint: calculate $\Delta H, \Delta S \ldots$ then $\Delta G$

### 6.7 Bond Enthalpies

- Calculating $\Delta H$ with Average Bond Enthalpies


## Bond Enthalpy

- Energy is always released during the formation of a bond.
- The same amount of energy must be added in order to break that specific bond.
$\Delta H=\Sigma B E_{(\text {bonds broken })}-\sum B E_{\text {(bonds formed) }}$


## $\Delta H$ from Bond Enthalpies

- Exothermic Process
- More energy is released during formation of bonds in the products than is required to break bonds in the reactants.
- The products are at a lower potential energy than the reactants.


## $\Delta H$ from Bond Enthalpies

- Endothermic Process
- Less energy is released during formation of bonds in the products than is required to break bonds in the reactants.
- The products are at a higher potential energy than the reactants.


## Example: $\Delta \mathrm{H}$ from Bond Enthalpies

$$
\Delta H=\Sigma B E_{(\text {bonds broken })}-\Sigma B E_{(\text {bonds formed })}
$$

- Calculate the enthalpy change for the following reaction using the table of values.
$\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$

| Bond | Average Bond Enthalpy |
| :--- | :---: |
| $\mathrm{C}-\mathrm{H}$ | $413 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{O}=\mathrm{O}$ | $495 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{C}-\mathrm{O}$ | $358 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{C}=\mathrm{O}$ | $799 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{O}-\mathrm{H}$ | $467 \mathrm{~kJ} / \mathrm{mol}$ |

## Example: $\Delta \mathrm{H}$ from Bond Enthalpies

$$
\Delta H=\Sigma B E_{(\text {bonds broken })}-\Sigma B E_{(\text {bonds formed })}
$$

- Calculate the average bond energy in an $\mathrm{H}-\mathrm{H}$ bond. $2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{H}=-572 \mathrm{k} \mathrm{kJ}$

| Bond | Average Bond Enthalpy |
| :--- | :---: |
| $\mathrm{O}=\mathrm{O}$ | $495 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{O}-\mathrm{H}$ | $467 \mathrm{~kJ} / \mathrm{mol}$ |

### 6.8 Enthalpy of Formation

- Calculating $\Delta H$ with Standard Enthalpies of Formation


## Standard Enthalpy of Formation

- A hypothetical value that indicates how much heat would be lost or gained during the formation of one mole of a compound from the most common form of its elements in their standard states.
standard state $\left(25^{\circ} \mathrm{C}, 1 \mathrm{~atm}\right)$



## Standard Enthalpy of Formation

- For Methanol:

$$
\begin{gathered}
\mathrm{C}_{(s)}+2 \mathrm{H}_{2(g)}+1 / 2 \mathrm{O}_{2(g)} \rightarrow \mathrm{CH}_{3} \mathrm{OH}_{(g)} \\
\Delta \boldsymbol{H}_{f}^{0}=-\mathbf{2 0 1} \mathbf{k J} / \mathrm{mol}
\end{gathered}
$$

- Heat of formation reactions are always written so that all reactants exist as they would under standard conditions, and there is one mole of product.


## Enthalpy of Formation

The $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ value for the most stable form of any element in its standard state is zero.

| Element | $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ | Element | $\Delta H_{\mathrm{f}}^{\mathrm{o}}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ca}(s)$ | 0 | $\mathrm{Cl}_{2}(g)$ | 0 |
| $\mathrm{Ag}(s)$ | 0 | $\mathrm{H}_{2}(g)$ | 0 |
| $\mathrm{Na}(s)$ | 0 | $\mathrm{Fe}(s)$ | 0 |
| $\mathrm{O}_{2}(g)$ | 0 | $\mathrm{~N}_{2}(g)$ | 0 |

## Formula for Calculating the Enthalpy of a Reaction Under Standard Conditions



Sum of
stoichiometric

## Example: Enthalpy of Formation

$$
\Delta H_{\mathrm{rxn}}^{\mathrm{o}}=\Sigma n \Delta H_{\mathrm{f} \text { (products) }}^{\mathrm{o}}-\Sigma n \Delta H_{\mathrm{f} \text { (reactants) }}^{\mathrm{o}}
$$

- Find $\Delta \mathrm{H}^{0}{ }^{\mathrm{rxn}}$ for the thermite reaction under standard conditions.

$$
\mathrm{Fe}_{2} \mathrm{O}_{3(s)}+2 \mathrm{Al}_{(s)} \rightarrow 2 \mathrm{Fe}_{(s)}+\mathrm{Al}_{2} \mathrm{O}_{3(s)}
$$

## Example: Enthalpy of Formation

$\Delta H_{\mathrm{rxn}}^{\mathrm{o}}=\Sigma n \Delta H_{\mathrm{f}}^{\mathrm{o}}$ (products) $-\Sigma n \Delta H_{\mathrm{f}}^{\mathrm{o}}$ (reactants)

- Find $\Delta \mathrm{H}^{0}{ }_{\mathrm{rxn}}$ for this reaction under standard conditions.

$$
2 \mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})}+3 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{SO}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

### 6.9 Hess's Law

- Calculating $\Delta H$ with Hess's Law


## Hess's Law

- If a reaction is carried out in a series of steps, the overall change in enthalpy will be equal to the sum of the enthalpy changes for the individual steps.
- The overall enthalpy change will be the same if a reaction is carried out in one step or in several steps.


## Example: Hess's Law

- Calculate $\Delta \mathrm{H}$ for the following reaction using the information in the table below.

$$
4 \mathrm{NO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{5(\mathrm{~s})}
$$

| Reaction | Chemical Equation | Enthalpy Change |
| :---: | :---: | :---: |
| 1 | $2 \mathrm{NO}_{(g)}+3 / 2 \mathrm{O}_{2(g)} \rightarrow \mathrm{N}_{2} \mathrm{O}_{5(\mathrm{~s})}$ | $\Delta H=-223.7 \mathrm{~kJ}$ |
| 2 | $2 \mathrm{NO}_{(g)}+\mathrm{O}_{2(g)} \rightarrow 2 \mathrm{NO}_{2(g)}$ | $\Delta H=-114.2 \mathrm{~kJ}$ |

## Example: Hess's Law

- Calculate $\Delta \mathrm{H}$ for the following reaction using the information in the table below.

$$
3 \mathrm{C}_{(s)}+4 \mathrm{H}_{2(g)} \rightarrow \mathrm{C}_{3} \mathrm{H}_{8(\mathrm{~g})}
$$

| Reaction | Chemical Equation | Enthalpy Change |
| :---: | :--- | :--- |
| 1 | $2 \mathrm{H}_{2(g)}+\mathrm{O}_{2(g)} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(l)}$ | $\Delta H=-571.7 \mathrm{~kJ}$ |
| 2 | $\mathrm{C}_{3} \mathrm{H}_{8(g)}+5 \mathrm{O}_{2(g)} \rightarrow 3 \mathrm{CO}_{2(g)}+4 \mathrm{H}_{2} \mathrm{O}_{(l)}$ | $\Delta H=-2220.1 \mathrm{~kJ}$ |
| 3 | $\mathrm{C}_{(s)}+\mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)}$ | $\Delta H=-393.5 \mathrm{~kJ}$ |

## Example: Hess \& Enthalpy of Formation

- Use the enthalpy of formation value below to determine $\Delta H_{r x n}$ for the reaction between $\mathrm{C}(\mathrm{s})$ and $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})$ to produce $\mathrm{Fe}(\mathrm{s})$.

$$
\begin{array}{ll}
2 \mathrm{Fe}_{(s)}+3 / 2 \mathrm{O}_{2(g)} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(s)} & \Delta H_{f}^{o}=-822 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{C}_{(\mathrm{s})}+\mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(s)} & \Delta H_{f}^{o}=-394 \mathrm{~kJ} / \mathrm{mol}
\end{array}
$$

