## Chapter 5. Thermochemistry

## Lecture Outline

### 5.1 The Nature of Energy

- Thermodynamics is the study of energy and its transformations.
- Thermochemistry is the study of the relationships between chemical reactions and energy changes involving heat.
- Definitions:
- Energy is the capacity to do work or to transfer heat.
- Work is energy used to cause an object with mass to move.

$$
w=F x d
$$

- Heat is the energy used to cause the temperature of an object to increase.
- A force is any kind of push or pull exerted on an object.
- The most familiar force is the pull of gravity.


## Kinetic Energy and Potential Energy

- Kinetic energy is the energy of motion:

$$
E_{k}=\frac{1}{2} m v^{2}
$$

- Potential energy is the energy an object possesses by virtue of its position or composition.
- Electrostatic energy is an example.
- It arises from interactions between charged particles.

$$
E_{e l}=\frac{k Q_{1} Q_{2}}{d}
$$

- Potential energy can be converted into kinetic energy.
- An example is a ball of clay dropped off a building.


## Units of Energy

- SI unit is the joule, J.
- From $\quad E_{k}=\frac{1}{2} m v^{2}, \quad 1 \mathrm{~J}=1 \mathrm{kgx} \frac{\mathrm{m}^{2}}{\mathrm{~s}^{2}}$
- Traditionally, we use the calorie as a unit of energy.
- $1 \mathrm{cal}=4.184 \mathrm{~J}$ (exactly)
- The nutritional Calorie, $\mathrm{Cal}=1,000 \mathrm{cal}=1 \mathrm{kcal}$.


## System and Surroundings

- A system is the part of the universe we are interested in studying.
- Surroundings are the rest of the universe (i.e., the surroundings are the portions of the universe that are not involved in the system).
- Example: If we are interested in the interaction between hydrogen and oxygen in a cylinder, then the $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ in the cylinder form a system.


## Transferring Energy: Work and Heat

- From physics:
- Force is a push or pull on an object.
- Work is the energy used to move an object against a force.

$$
w=F \times d
$$

- Heat is the energy transferred from a hotter object to a colder one.
- Energy is the capacity to do work or to transfer heat.


### 5.2 The First Law of Thermodynamics

- The first law of thermodynamics states that energy cannot be created or destroyed.
- The first law of thermodynamics is the law of conservation of energy.
- That is, the energy of system + surroundings is constant.
- Thus, any energy transferred from a system must be transferred to the surroundings (and vice versa).


## Internal Energy

- The total energy of a system is called the internal energy.
- It is the sum of all the kinetic and potential energies of all components of the system.
- Absolute internal energy cannot be measured, only changes in internal energy.
- Change in internal energy, $\infty E=E_{\text {final }}-E_{\text {initital }}$.
- Example: A mixture of $\mathrm{H}_{2}(g)$ and $\mathrm{O}_{2}(g)$ has a higher internal energy than $\mathrm{H}_{2} \mathrm{O}(g)$.
- Going from $\mathrm{H}_{2}(g)$ and $\mathrm{O}_{2}(g)$ to $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ results in a negative change in internal energy, indicating that the system has lost energy to the surroundings:

$$
\mathrm{H}_{2}(g)+\mathrm{O}_{2}(g) \square 2 \mathrm{H}_{2} \mathrm{O}(g) \quad \infty E<0
$$

- Going from $\mathrm{H}_{2} \mathrm{O}(g)$ to $\mathrm{H}_{2}(g)$ and $\mathrm{O}_{2}(g)$ results in a positive change in internal energy, indicating that the system has gained energy from the surroundings:

$$
2 \mathrm{H}_{2} \mathrm{O} \square \mathrm{H}_{2}(g)+\mathrm{O}_{2}(g) \quad \infty E>0
$$

## Relating $\propto E$ to Heat and Work

- From the first law of thermodynamics:
- When a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or liberated from the system plus the work done on or by the system:

$$
\infty E=q+w
$$

- Heat flowing from the surroundings to the system is positive, $q>0$.
- Work done by the surroundings on the system is positive, $w>0$.


## Endothermic and Exothermic Processes

- An endothermic process is one that absorbs heat from the surroundings.
- An endothermic reaction feels cold.
- An exothermic process is one that transfers heat to the surroundings.
- An exothermic reaction feels hot.


## State Functions

- A state function depends only on the initial and final states of a system.
- Example: The altitude difference between Denver and Chicago does not depend on whether you fly or drive, only on the elevation of the two cities above sea level.
- Similarly, the internal energy of 50 g of $\mathrm{H}_{2} \mathrm{O}(l)$ at $25 \square \mathrm{C}$ does not depend on whether we cool 50 g of $\mathrm{H}_{2} \mathrm{O}(l)$ from $100 \square \mathrm{C}$ to $25 \square \mathrm{X}$ or heat 50 g of $\mathrm{H}_{2} \mathrm{O}(l)$ at $0 \square \mathrm{C}$ to $25 \square \mathrm{X}$.
- A state function does not depend on how the internal energy is used.
- Example: A battery in a flashlight can be discharged by producing heat and light. The same battery in a toy car is used to produce heat and work. The change in internal energy of the battery is the same in both cases.


### 5.3 Enthalpy

- Chemical changes may involve the release or absorption of heat.
- Many also involve work done on or by the system.
- Work is often either electrical or mechanical work.
- Mechanical work done by a system involving expanding gases is called pressure-volume work or $P-V$ work.
- The heat transferred between the system and surroundings during a chemical reaction carried out under constant pressure is called enthalpy, $H$.
- Again, we can only measure the change in enthalpy, $\infty H$.
- Mathematically,

$$
\begin{gathered}
\propto H=H_{\text {final }}-H_{\text {initial }}=\infty E+P \propto V \\
w=-P \infty V ; \infty E=q+w \\
\infty H=\propto E+P \infty V=\left(q_{\mathrm{p}}+w\right)-w=q_{\mathrm{p}}
\end{gathered}
$$

- For most reactions $P \propto V$ is small thus $\propto H=\infty \mathrm{E}$
- Heat transferred from surroundings to the system has a positive enthalpy (i.e., $\infty H>0$ for an endothermic reaction).
- Heat transferred from the system to the surroundings has a negative enthalpy (i.e., $\infty H<0$ for an exothermic reaction).
- Enthalpy is a state function.


## A Closer Look at Energy, Enthalpy, and P-V Work

- Consider:
- A cylinder has a cross-sectional area $A$.
- A piston exerts a pressure, $P=F / A$, on a gas inside the cylinder.
- The volume of gas expands through $\infty V$ while the piston moves a height $\infty h=h_{\mathrm{f}}-h_{\mathrm{i}}$.
- The magnitude of work done $=F \mathrm{x} \infty h=P \mathrm{x} A \mathrm{x} \infty h=P \mathrm{x} \propto V$.
- Since work is being done by the system on the surroundings, then
- $w=-P \infty V$.
- Using the first law of thermodynamics,
- $\infty E=q-P \infty V$.
- If the reaction is carried out under constant volume,
- $\infty V=0$ and $\infty E=q_{v}$.
- If the reaction is carried out under constant pressure,
- $\infty E=q_{\mathrm{p}}-P \infty V$, or
- $q_{\mathrm{p}}=\infty H=\infty \mathrm{E}+P \propto V$
- and $\infty E=\infty H-P \infty V$


### 5.4 Enthalpies of Reaction

- For a reaction, $\propto H_{\mathrm{rxn}}=H_{\text {products }}-H_{\text {reactants }}$.
- The enthalpy change that accompanies a reaction is called the enthalpy of reaction or heat of reaction $\left(\infty H_{\mathrm{rxn}}\right)$.
- Consider the thermochemical equation for the production of water:

$$
2 \mathrm{H}_{2}(g)+\mathrm{O}_{2}(g) \square 2 \mathrm{H}_{2} \mathrm{O}(g) \quad \infty H=-483.6 \mathrm{~kJ}
$$

- The equation tells us that 483.6 kJ of energy are released to the surroundings when water is formed.
- $\infty H$ noted at the end of the balanced equation depends on the number of moles of reactants and products associated with the $\infty H$ value.
- These equations are called thermochemical equations.
- Enthalpy diagrams are used to represent enthalpy changes associated with a reaction.
- In the enthalpy diagram for the combustion of $\mathrm{H}_{2}(g)$, the reactants, $2 \mathrm{H}_{2}(g)+\mathrm{O}_{2}(g)$, have a higher enthalpy than the products $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$; this reaction is exothermic.
- Enthalpy is an extensive property.
- Therefore, the magnitude of enthalpy is directly proportional to the amount of reactant consumed.
- Example: If one mol of $\mathrm{CH}_{4}$ is burned in oxygen to produce $\mathrm{CO}_{2}$ and water, 890 kJ of heat are released to the surroundings. If two mol of $\mathrm{CH}_{4}$ are burned, then 1780 kJ of heat are released.
- The sign of $\infty H$ depends on the direction of the reaction.
- The enthalpy change for a reaction is equal in magnitude but opposite in sign to $\infty H$ for the reverse reaction.
- Example: $\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l) \quad \infty H=-890 \mathrm{~kJ}$,
- But $\mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l) \square \mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \quad \infty H=+890 \mathrm{~kJ}$.
- Enthalpy change depends on state.
- $2 \mathrm{H}_{2} \mathrm{O}(g) \square 2 \mathrm{H}_{2} \mathrm{O}(l)$
$\infty H=-88 \mathrm{~kJ}$


### 5.5 Calorimetry

- Calorimetry is a measurement of heat flow.
- A calorimeter is an apparatus that measures heat flow.


## Heat Capacity and Specific Heat

- Heat capacity is the amount of energy required to raise the temperature of an object by $1 \square \mathrm{C}$.
- Molar heat capacity is the heat capacity of 1 mol of a substance.
- Specific heat, or specific heat capacity, is the heat capacity of 1 g of a substance.
- Heat, $q=$ (specific heat) x (grams of substance) $\mathrm{x} \propto T$.
- Be careful of the sign of $q$.


## Constant-Pressure Calorimetry

- The most common technique is to use atmospheric pressure as the constant pressure.
- Recall $\propto H=q_{\mathrm{p}}$.
- The easiest method is to use a coffee cup calorimeter.

$$
q_{\text {soln }}=(\text { specific heat of solution }) \times(\text { grams of solution }) \times \infty T=-q_{\mathrm{rxn}}
$$

- For dilute aqueous solutions, the specific heat of the solution will be close to that of pure water.


## Bomb Calorimetry (Constant-Volume Calorimetry)

- Reactions can be carried out under conditions of constant volume instead of constant pressure.
- Constant volume calorimetry is carried out in a bomb calorimeter.
- The most common type of reaction studied under these conditions is combustion.
- If we know the heat capacity of the calorimeter, $C_{\text {cal }}$, then the heat of reaction,

$$
q_{\mathrm{rxn}}=-C_{\mathrm{cal}} \mathrm{X} \propto T .
$$

- Since the reaction is carried out under constant volume, $q$ relates to $\infty E$.


### 5.6 Hess's Law

- Hess's Law: If a reaction is carried out in a series of steps, $\infty H$ for the reaction is the sum of $\infty H$ for each of the steps.
- The total change in enthalpy is independent of the number of steps.
- Total $\infty H$ is also independent of the nature of the path.

$$
\begin{array}{ll}
\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(g) & \infty H=-802 \mathrm{~kJ} \\
2 \mathrm{H}_{2} \mathrm{O}(g) \square 2 \mathrm{H}_{2} \mathrm{O}(l) & \infty H=-88 \mathrm{~kJ} \\
\hline \mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l) & \infty H=-890 \mathrm{~kJ}
\end{array}
$$

- Therefore, for the reaction $\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l), \infty H=-890 \mathrm{~kJ}$.
- Note that $\propto H$ is sensitive to the states of the reactants and the products.
- Hess's law allows us to calculate enthalpy data for reactions that are difficult to carry out directly: $\mathrm{C}(s)+\mathrm{O}_{2}(g)$ produces a mixture of $\mathrm{CO}(g)$ and $\mathrm{CO}_{2}(g)$.


### 5.7 Enthalpies of Formation

- Hess's law states that if a reaction is carried out in a number of steps, $\infty H$ for the overall reaction is the sum of the $\infty H$ s for each of the individual steps.
- Consider the formation of $\mathrm{CO}_{2}(g)$ and $2 \mathrm{H}_{2} \mathrm{O}(l)$ from $\mathrm{CH}_{4}(g)$ and $2 \mathrm{O}_{2}(g)$.
- If the reaction proceeds in one step:

$$
\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l),
$$

then $\propto H_{1}=-890 \mathrm{~kJ}$.

- However, if the reaction proceeds through a CO intermediate:

$$
\begin{array}{ll}
\mathrm{CH}_{4}(g)+2 \mathrm{O}_{2}(g) \square \mathrm{CO}(g)+2 \mathrm{H}_{2} \mathrm{O}(l)+1 / 2 \mathrm{O}_{2}(g) & \infty H_{2}=-607 \mathrm{~kJ} \\
\mathrm{CO}(g)+2 \mathrm{H}_{2} \mathrm{O}(l)+1 / 2 \mathrm{O}_{2}(g) \square \mathrm{CO}_{2}(g)+2 \mathrm{H}_{2} \mathrm{O}(l) & \infty H_{3}=-283 \mathrm{~kJ},
\end{array}
$$

Then $\infty H$ for the overall reaction is:

$$
\propto H_{2}+\infty H_{3}=-607 \mathrm{~kJ}-283 \mathrm{~kJ}=-890 \mathrm{~kJ}=\propto \mathrm{H}_{1}
$$

- If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called the enthalpy of formation, $\propto H_{\mathrm{f}}$.
- Standard state (standard conditions) refer to the substance at:
- 1 atm and $25 \square \mathrm{C}(298 \mathrm{~K})$.
- Standard enthalpy, $\infty H \square$, is the enthalpy measured when everything is in its standard state.
- Standard enthalpy of formation of a compound, $\infty H \square_{\phi}$, is the enthalpy change for the formation of 1 mol of compound with all substances in their standard states.
- If there is more than one state for a substance under standard conditions, the more stable state is used. Example: When dealing with carbon we use graphite because graphite is more stable than diamond or $\mathrm{C}_{60}$.
- The standard enthalpy of formation of the most stable form of an element is zero.


## Using Enthalpies of Formation to Calculate Enthalpies of Reaction

- Use Hess's law!
- Example: Calculate $\infty H$ for

$$
\mathrm{C}_{3} \mathrm{H}_{8}(g)+5 \mathrm{O}_{2}(g) \square 3 \mathrm{CO}_{2}(g)+4 \mathrm{H}_{2} \mathrm{O}(l)
$$

- We start with the reactants, decompose them into elements, then rearrange the elements to form products. The overall enthalpy change is the sum of the enthalpy changes for each step.
- Decomposing into elements (note $\mathrm{O}_{2}$ is already elemental, so we concern ourselves with $\mathrm{C}_{3} \mathrm{H}_{8}$ ):

$$
\mathrm{C}_{3} \mathrm{H}_{8}(g) \square 3 \mathrm{C}(s)+4 \mathrm{H}_{2}(g) \quad \propto H_{l}=-\infty H \square_{\mathrm{f}}\left[\mathrm{C}_{3} \mathrm{H}_{8}(g)\right]
$$

- Next we form $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ from their elements:

$$
\begin{aligned}
3 \mathrm{C}(s)+3 \mathrm{O}_{2}(g) \square 3 \mathrm{CO}_{2}(g) & \infty H_{2}=3 \propto H \square_{\mathrm{f}}\left[\mathrm{CO}_{2}(g)\right] \\
4 \mathrm{H}_{2}(g)+2 \mathrm{O}_{2}(g) \square 4 \mathrm{H}_{2} \mathrm{O}(l) & \infty H_{3}=4 \propto H \square_{\mathrm{f}}\left[\mathrm{H}_{2} \mathrm{O}(l)\right]
\end{aligned}
$$

- We look up the values and add:

$$
\infty H \square_{\mathrm{rxn}}=-1(-103.85 \mathrm{~kJ})+3(-393.5 \mathrm{~kJ})+4(-285.8 \mathrm{~kJ})=-2220 \mathrm{~kJ}
$$

- In general:

$$
\infty H \square_{\mathrm{rxn}}=\times n \propto H \square_{\mathrm{f}} \text { (products) }-\times m \infty H \square_{\mathrm{f}} \text { (reactants) }
$$

- Where $n$ and $m$ are the stoichiometric coefficients.


### 5.8 Foods and Fuels

- Fuel value is the energy released when 1 g of substance is burned.
- The fuel value of any food or fuel is a positive value that must be measured by calorimetry.


## Foods

- Fuel value is usually measured in Calories ( 1 nutritional Calorie, $1 \underline{\underline{\mathrm{Ca}}}=1000 \mathrm{cal}$ ).
- Most energy in our bodies comes from the oxidation of carbohydrates and fats.
- In the intestines, carbohydrates are converted into glucose, $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$, or blood sugar.
- In the cells glucose reacts with $\mathrm{O}_{2}$ in a series of steps which ultimately produce $\mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}$, and energy.

$$
\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(s)+6 \mathrm{O}_{2}(g) \square 6 \mathrm{CO}_{2}(g)+6 \mathrm{H}_{2} \mathrm{O}(l) \quad \propto H \square=-2803 \mathrm{~kJ}
$$

- Fats, for example tristearin, react with $\mathrm{O}_{2}$ as follows:

$$
2 \mathrm{C}_{57} \mathrm{H}_{110} \mathrm{O}_{6}(s)+163 \mathrm{O}_{2}(g) \square 114 \mathrm{CO}_{2}(g)+110 \mathrm{H}_{2} \mathrm{O}(l) \quad \infty H \square=-75,250 \mathrm{~kJ} .
$$

- Fats contain more energy than carbohydrates. Fats are not water soluble. Therefore, fats are good for energy storage.


## Fuels

- In the United States we use about $1.03 \times 10^{17} \mathrm{~kJ} /$ year $\left(1.0 \times 10^{6} \mathrm{~kJ}\right.$ of fuel per person per day $)$.
- Most of this energy comes from petroleum and natural gas.
- The remainder of the energy comes from coal, nuclear, and hydroelectric sources.
- Coal, petroleum, and natural gas are fossil fuels. They are not renewable.
- Natural gas consists largely of carbon and hydrogen. Compounds such as $\mathrm{CH}_{4}, \mathrm{C}_{2} \mathrm{H}_{6}, \mathrm{C}_{3} \mathrm{H}_{8}$ and $\mathrm{C}_{4} \mathrm{H}_{10}$ are typical constituents.
- Petroleum is a liquid consisting of hundreds of compounds. Impurities include S, N, and O compounds.
- Coal contains high molecular weight compounds of C and H . In addition, compounds containing $\mathrm{S}, \mathrm{O}$, and N are present as impurities that form air pollutants when burned in air.
- Syngas (synthesis gas): a gaseous mixture of hydrocarbons produced from coal by coal gasification.


## Other Energy Sources

- Nuclear energy is the energy released in the splitting or fusion of nuclei of atoms.
- Fossil fuels and nuclear energy are nonrenewable sources of energy.
- Renewable energy sources include:
- solar energy.
- wind energy.
- geothermal energy.
- hydroelectric energy.
- biomass energy.
- These are virtually inexhaustible and will become increasingly important as fossil fuels are depleted.

