With the exception of the energy that comes from the sun, most energy is created via chemical processes. The combustion of gasoline, production of energy from burning coal, the heating of homes through the use of natural gas and the use of batteries to power electronic are all examples of the use of chemical energy in our lives. What exactly is energy, though, and what principles are involved in its production, consumption and transformation from one form to another? The study of energy and its transformation is known as thermodynamics (from the Greek therme meaning heat and dy’namis meaning power).

5.1 – NATURE OF ENERGY

The concept of matter is easy to grasp because it can be seen and manipulated. By contrast energy is familiar but much more challenging to describe. Energy is defined as the capacity to work or transfer heat. Work is the energy used to cause an object to move against a force. Heat is the energy used to cause the temperature of an object to rise.

KINETIC AND POTENTIAL ENERGY

- Objects, regardless of size, have energy associated with movement. Kinetic energy is the energy of motion.
- The amount of energy in this kinetic energy depends on its mass and speed which can be described using the following formula:

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

DISCUSSION

- Which would have more energy?
  - Sedan travelling at 80 km/h or 100 km/h? Why?
  - Sedan travelling at 100 km/h or semi at 100 km/h?

- Why is it possible to throw a baseball faster than a bowling ball?
POTENTIAL ENERGY

- All other kinds of energy – the energy stored in a stretched spring, in a weight held above your head, or in a chemical bond, for example – are potential energy.
- An object has potential energy due to its relative position to others.
- Potential energy essentially is stored energy due to the attractive or repulsive forces objects experience in relation to one another.

POTENTIAL ENERGY

- We are all familiar in which potential energy is converted into kinetic energy. For example we can consider a biker at the top of a hill.
- As the bike moves down the hill due to gravitational forces, the potential energy decreases while the kinetic energy increases as the speed increases.
- The conversion of one form of energy into the next is a essential tenant of thermodynamics.
- While gravity acts on large objects in an apparent manner, it has a minimal impact on objects at an atomic scale. Instead, electrical charges influence potential energy.

ELECTROSTATIC POTENTIAL ENERGY

- Electrostatic potential energy, $E_{el}$, is the energy associated with interactions of charged particles.
- This energy is proportional to the electrical charges on the two interacting objects, $Q_1$ and $Q_2$, and inversely proportional to the distance, $d$, separating them:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

- $\kappa$ is a constant of proportionality, $8.99 \times 10^9$ J-m/C$^2$. [C is the coulomb, a unit of electrical charge, and J is joule, a unit of energy].
- At the molecular level, the electrical charges of $Q_1$ and $Q_2$ are typically on the order of magnitude of the charge of the electron ($1.60 \times 10^{-19}$ C)
- This equation shows the electrical electrostatic potential energy goes to zero as the object reach infinite distance.
- When the particles are separated by a sufficient distance, there is no potential energy.

ELECTROSTATIC POTENTIAL ENERGY

- When $Q_1$ and $Q_2$ have the same charge there a repulsive force and pushes the particles apart. In this case, $E_{el}$ is positive, and the potential energy decreases as the particles move farther and farther apart.
- When $Q_1$ and $Q_2$ have opposite signs, the particles attract each other, and an attractive force pulls them together. In this case, $E_{el}$ is negative, and the potential energy increases (becomes less negative) as the particles move apart.
A positively charged particle and a negatively charged particle are initially far apart. What happens to their electrostatic potential as they are brought closer?

**UNITS OF ENERGY**

- The SI unit for energy is the Joule (J) in honor of James Joule, a notable scientist for his work in heat related fields.
- His work revealed that a Joule is the equivalent energy of a 2 kg mass moving at a speed of 1 meter per second.

\[ E_k = \frac{1}{2} mv^2 = \frac{1}{2} (2 \text{ kg})(1 \text{ m/s})^2 = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ J} \]

**SYSTEMS**

- Systems may be open, closed or isolated.
  - An open system is one in which matter and energy can be exchanged with the surroundings.
  - A closed system is one that is able to exchange energy but no matter.
  - An isolated system is one in which neither matter nor energy is exchanged with the surroundings.

**SYSTEM AND SURROUNDINGS**

- When analyzing energy changes, we need to focus on a limited and well defined part of the universe to keep track of the energy changes that occur.
  - The portion we single out for study is called the system.
  - Everything else is called the surroundings.
  - A system could be as an atom, beaker, classroom or universe.

**UNITS OF ENERGY**

- In terms of chemical reactions the joule is not large, we often use kilojoules (kJ) to describe changes in energy.
- A non-SI unit that was common was a calorie (cal) which was defined as the amount of energy required to raise 1 g of water from 14.5 to 15.5 C. Now the calorie is defined in terms of joules (1 cal = 4.184 J).
- Calorie (Cal) is equal to 1000 cal and is often used in nutritional labels.
DISCUSSION

Is a perfectly isolated system possible?

What type of system is a human?

PRACTICE PROBLEMS

Section 5.1 – The Nature of Energy

#5.13 – 5.15 & 5.16, 5.18-5.20

5.2  
THE FIRST LAW OF THERMODYNAMICS

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THE FIRST LAW OF THERMODYNAMICS

- We have seen that the potential energy of a system can be converted into kinetic energy, and vice versa. We have also seen that energy can be transferred back and forth between a system and its surroundings in the form of work and heat.
- This observation is perhaps one of the most central understandings of science:
  - Energy is neither created nor destroyed.
  - Any energy lost by a system is gained by the surroundings.
- This important observation, that energy is conserved, is known as the first law of thermodynamics.

INTERNAL ENERGY

- Internal Energy, \(E\), of a system is the sum of all kinetic and potential energies of the components of a system.
- This includes the kinetic energy of the atomic motion of but also the interaction between molecule and even the energy associated with the nuclei or electronic interactions.
- We generally do not know the numerical value of a system's internal energy – instead we focus on the measurable change in \(E\) which accompanies a change in the energy of a system.

\[
\Delta E = E_{\text{final}} - E_{\text{initial}}
\]
INTERNAL ENERGY

- It is difficult to get actual values for $E_{\text{initial}}$ and $E_{\text{final}}$ but we can apply the law based on three parts:
  - (1) Unit (2) magnitude, which with unit, gives a magnitude of the change and, (3) a sign that gives the direction.
- A positive $E (E_{\text{final}} > E_{\text{initial}})$ indicates the system gained energy from the surroundings.
- A negative $E (E_{\text{final}} < E_{\text{initial}})$ indicates a system lost energy to the surroundings.

EXAMPLE

(1) In a chemical reaction, the initial state of the system refers to the reactants and the final state refers to the products. In the following reaction, energy is lost to the surroundings in the form of heat. Sketch a diagram that shows how the internal energy changes.

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\ell)$$

(2) The decomposition of magnesium chloride into its constituent elements requires heat. Write the chemical equation for this reaction, then sketch an energy diagram.

RELATING $\Delta E$ TO HEAT AND WORK

- As previously mentioned systems can interact with the surroundings by either doing work, or transferring heat.
- The magnitude of internal energy can change as heat is added or removed from a system or as work is done on or done by a system.
- If we think of internal energy as the system’s bank account of energy, we see that deposits of withdrawals, can be made in either increments of heat or in increments of work.
- Deposits increase $E$, while withdrawals decrease $E$. 

INTERNAL ENERGY

[Diagram showing energy changes in a chemical reaction and the relationship between work, heat, and internal energy changes.]
DISCUSSION

If work is done on a system, but heat is transferred out, can we determine the sign of $\Delta E$ for this process?

INTERNAL ENERGY

- As internal energy is directed affect by both heat and work, we can write a simple equation that describes this relationship.
- When a system undergoes and chemical or physical change, the accompanying change in internal energy, $\Delta E$, is the sum of the heat liberated from the system, $q$, and the work done on or by the system, $w$:

$$\Delta E = q + w$$

SIGN CONVENTIONS

- When heat is added, or work is done on a system the internal energy of the system increases.

| TABLE 6.1: Sign Conventions for $q$, $w$, and $\Delta E$ |
|-----------------|------------------|
| $q$             | $w$              |
| $+$ means system gains heat | $+$ means work done on system |
| $-$ means system loses heat | $-$ means work done by system |
| $\Delta E$      | $\Delta E$      |
| $+$ means net gain of energy by system | $-$ means net loss of energy by system |

EXAMPLE

Gases $A(g)$ and $B(g)$ are confined in an cylinder-and-piston arrangement and react to form a solid product $C(s)$: $A(g) + B(g) \rightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in internal energy of the system?

ENDOTHERMIC/EXOTHERMIC PROCESSES

- Because the transfer of heat is central to the understanding of thermodynamics there are special terminology used to describe the direction of heat flow
  - Endothermic indicates energy has moved from the surroundings to the system (e.g., melting ice)
  - Exothermic indicates energy has moved from the system to the surroundings (e.g., combustion of methane)

STATE FUNCTIONS

- Any state function depends only on the present state (e.g., temperature, pressure, volume) of the system, and not on the path by which the system by which the system arrived at that state.
- The total internal energy of water at 25°C would be the same if a system was cooled from 100°C or was raised from 0°C.
STATE FUNCTIONS

- While internal energy is a state function, it is important to note both work and heat are not state functions.
- Consider the mountaineer’s possible paths. While the elevation change will be the same for both paths, the amount of work required will be different.

DISCUSSION

Explain how the two cases, a wire shorting out, and a fan blowing demonstrate that internal energy is a state function while heat and work are not.

PRACTICE PROBLEMS

Section 5.2 – First Law of Thermodynamics

#5.25 – 5.27 & 5.30 – 5.32

ENTHALPY

- The chemical and physical changes that occur around us, such as the photosynthesis in the leaves of a plant, or the evaporation of water from a lake or beaker in the lab, occur under the essentially constant pressure* of the atmosphere.
- A system that consists of a gas can be characterised (described) by both pressure and volume.
- Like internal energy, these are state functions and can be combined to describe and new state function called enthalpy.

ENTHALPY

- Enthalpy is useful for discussing heat flow in processes that occur under constant pressure.
- Enthalpy, we is denoted by H, is defined as the internal energy plus the product of pressure and volume of the system:

\[ H = E + PV \]
The work in the expansion of gases in a constant pressure system (e.g., atmospheric conditions can be represented by the following equation).

Pressure is represented by P while volume is shown by V.

Pressure will always be positive, or zero as negative pressures cannot exist.

If the volume increases, the overall term will be negative as the system will do work on the surroundings. If the volume decreases, the work term will be positive as work is being completed on the system.

\[ w = -P \Delta V \]

When a change occurs at constant pressure, the change in enthalpy, \( \Delta H \), is given by the relationship between the change in internal energy plus the product of the constant pressure times the change in volume.

\[ \Delta H = \Delta (E + PV) = \Delta E + P \Delta V \quad \text{(constant pressure)} \]

Through this substitution we can see that under constant pressure conditions, the change in enthalpy is equal to the amount of heat gained or lost \( (q_p) \).

Because \( q_p \) is easily measured, and because so many physical and chemical reactions of interest occur at constant pressure, enthalpy is a much more useful function for most reactions than it internal energy.

Recall that \( \Delta E = q + w \) and that the work involved in the expansion or compression of a gas is \( w = -P \Delta V \) (at constant pressure).

\[ \Delta H = \Delta E + P \Delta V = (q_p + w) - w = q_p \]

ENDOTHERMIC AND EXOTHERMIC
EXAMPLE

Indicate the sign of the enthalpy change, $\Delta H$, in these processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic: (a) An ice cube melts; (b) 1 g of butane is combusted in sufficient oxygen to give complete combustion to carbon dioxide and water; (c) molten gold cools and begins to solidify.

5.4

ENTHALPY OF REACTIONS

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ENTHALPIES OF REACTION

The enthalpy of a reaction is determined by the change in enthalpy as given by:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

This sometimes is called the enthalpy or heat of reaction, symbolized by $\Delta H_{\text{rxn}}$.

When we give a numerical value for $\Delta H_{\text{rxn}}$, we must give the equation involved.

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

ENTHALPY UNDERSTANDINGS

1. Enthalpy is an extensive property:
   - The magnitude of $\Delta H$ depends on the amount of material involved.
   - 1 mol. of methane produces 890 kJ of energy, while 2 mol. produces 1780 kJ.

2. The enthalpy for a reverse reaction is opposite:
   - Melting 1 mol. of water needs about 6.07 kJ, 6.07 is released when it freezes.

3. Enthalpy is state dependent:
   - The phase change of substances during a chemical reaction can increase or decrease the amount of change.
ENTHALPY UNDERSTANDINGS

CH₄(g) + 2 O₂(g) → CO₂(g) + 2 H₂O(l) \[ \Delta H = -890 \text{ kJ} \]

CO₂(g) + 2 H₂O(l) → CH₄(g) + 2 O₂(g) \[ \Delta H = +890 \text{ kJ} \]

2 H₂O(l) → 2 H₂O(g) \[ \Delta H = +88 \text{ kJ} \]

EXAMPLE

How much heat is released when 4.50 g of methane is burned in a constant-pressure system?

PRACTICE

Hydrogen peroxide can decompose to water and oxygen by the reaction:

2 H₂O₂(ℓ) → 2 H₂O(l) + O₂(g) \[ \Delta H = -196 \text{ kJ} \]

Calculate the quantity of heat released when 5.00 grams decomposes at constant pressure.

-14.4 kJ

PRACTICE PROBLEMS

Section 5.3 & 5.4 – Enthalpy*

#5.33 – 5.36, 5.39, 5.41, 5.43, 5.45 & 5.47

CALORIMETRY

- Calorimetry is an experimental method to determine enthalpy through heat flow.
- A calorimeter is a device that measures heat flow.
HEAT CAPACITY

- The more heat an object gains, the hotter it becomes.
- Not all objects will increase by the same amount when heated equally.
- The ability of a substance to be heated is called the heat capacity (C).
- Heat capacity is defined as the amount of heat required to raise the temperature by 1°C or 1K.
- The amount of heat one mole of substance by 1°C is the molar heat capacity (C_m).
- The specific heat is the amount of heat required to raise 1 gram of substance by 1°C (C_s).

DISCUSSION

Which substance would have the largest temperature change if the mass and amount of heat absorbed was the same?

CALORIMETRY EQUATION

- Rearranging the values we can get the calorimetry equation, which shows how heat is transferred between two objects.

\[ q = C \times m \times \Delta T \]

- Heat Transfer (q) measured in joules, (+) indicates heat flows out, (+) heat flows in.
- m - mass measured in grams usually.
- C_s or C_m - heat capacity - units shown previously.
- \( \Delta T \) - change in temperature (\( T_f - T_i \)) in Celsius or kelvin.

EXAMPLE

(a) How much heat is needed to warm 250.0 grams of water (C_s 4.18 J/g°C) from 22°C to 98°C. (b) what is the molar heat capacity of water?

PRACTICE

(a) Large beds of rock are used in some solar-heated homes to store heat. Assume the specific heat capacity of the rocks is 0.82 J/g-K. Calculate the heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0°C. (b) what temperature change would these rocks undergo if they emitted 450 kJ of heat?

CONSTANT PRESSURE CALORIMETRY

- Imagine mixing two aqueous solutions which react to form a product. The solutions, made of substances [system], are in direct contact with water and calorimeter (system).
- Assuming a perfect calorimeter (no heat lost to the environment) the enthalpy of reaction can be calculated using the first law of thermodynamics.
- \( q_{\text{soln}} = q_{\text{rxn}} \)

\[ q_{\text{soln}} = \text{(specific heat of solution)} \times \text{(grams of solution)} \times \Delta T = -q_{\text{rxn}} \]
CONSTANT PRESSURE CALORIMETRY

- For dilute aqueous solutions, it can be assumed the specific heat capacity of the solution is equal to that of water (because the solute changes the property of water so little).
- A change in temperature of greater than 0 indicates an exothermic reaction. Endothermic reactions will have a negative temperature change.

EXAMPLE

When a student mixed 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming the calorimeter loses only a negligible amount of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL and that its specific heat is 4.18 J/g °C.

PRACTICE

When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:

\[
\text{AgNO}_3(aq) + \text{HCl}(aq) \rightarrow \text{AgCl}(s) + \text{HNO}_3(aq)
\]

Calculate the ΔH for this reaction in kJ/mol AgNO₃, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g °C.

BOMB CALORIMETERS

- Bomb calorimeters are used to determine the enthalpy of combustion reactions in a more accurate way.
- Samples are placed into an oxygen-rich environment and then ignited using wire leads.
- The calorimeter is built to withstand the blast and rapid temperature change.
- The calorimeter itself heats up according to the equation \( C_{cal} \), which is the combination of the water and components.
- The enthalpy of reaction can be calculated using the following formula:

\[
q_{rxn} = -C_{cal} \times \Delta T
\]

EXAMPLE

The combustion of methylhydrazine (CH₆N₂), a liquid rocket fuel, produces N₂(g), CO₂(g) and H₂O(l):

\[
2 \text{CH}_6\text{N}_2(l) + 5 \text{O}_2(g) \rightarrow 2 \text{N}_2(g) + 2 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l)
\]

When 4.00 grams of methylhydrazine is combusted in a bomb calorimeter, the temperature rises from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH₆N₂.
PRACTICE

A 0.5865-g sample of lactic acid (HC$_3$H$_5$O$_3$) is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 °C to 24.95 °C. Calculate the heat of combustion of lactic acid. (a) per gram and (b) per mole.

(a) -15.21 kJ/g (b) -1370 kJ/mol

PRACTICE PROBLEMS

Section 5.5

#5.49, 5.53, 5.55 – 5.58

HESS’S LAW

Because enthalpy is a state function it is possible to calculate the enthalpy of reaction using tabulated values. Hess’s Law states if a reaction is carried out in a series of steps, ∆H for the overall reaction will be the sum of the enthalpy changes for the individual steps.

ΔH = ΔH$_1$ + ΔH$_2$ + ΔH$_3$ + ...

HESS’S LAW

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HESS’S LAW

CH$_4$(g) + 2 O$_2$(g) → CO$_2$(g) + 2 H$_2$O(l) $\Delta H = -890$ kJ

Example

The enthalpy of reaction for the combustion of C to CO$_2$ is -393.5 kJ/mol C, and enthalpy for the combustion of CO to CO$_2$ is -283.0 kJ/mol CO:

(1) C(s) + O$_2$(g) → CO$_2$(g) $\Delta H = -393.5$ kJ

(2) CO(g) + $\frac{1}{2}$O$_2$(g) → CO$_2$(g) $\Delta H = -283.0$ kJ

Using these data, calculate the enthalpy for the combustion of C to CO:

(3) C(s) + $\frac{1}{2}$O$_2$(g) → CO(g) $\Delta H = ?$
# ENTHALPY OF FORMATION

We can calculate the enthalpy changes for many reactions using these tabulated values. For example, extensive tables exist of enthalpies of vaporization (ΔH for converting liquids to gases), enthalpies of fusion (ΔH for melting solids), enthalpies of combustion (ΔH for combusting a substance in oxygen), and so forth.

This is useful to determine the enthalpy change for a more complex product from its constituent elements. This is called the **enthalpy of formation** (or heat of formation) and denoted by ΔH_f.

### STANDARD ENTHALPY CHANGE

- The magnitude of the enthalpy change depends on the temperature, pressure, and state of the reactants and products.
- To compare enthalpies of different reactions there is a standard state which the values have been calculated.
- The standard state of a substance is its pure form, at atmospheric pressure (1 atm) and the temperature of interest which is usually 25 °C.
- The standard enthalpy change of a reaction is defined as the enthalpy change when all reactants and products are in their standard states – this is shown by ΔH_f where ° indicates standard-state conditions.

### EXAMPLE

For which of these reactions at 25 °C does the enthalpy change represent standard enthalpy for formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

1. 2 Na(s) + 1/2 O_2(g) → Na_2O(s)
2. 2 K(l) + Cl_2(g) → 2KCl(s)
3. C_6H_{12}O_6(s) → 6C(diamond) + 6H_2(g) + 3O_2(g)

### EXPLANATION

- **2 Na(s) + 1/2 O_2(g) → Na_2O(s)**: This reaction is a single substance reacting to form another substance. Its reaction is endothermic, which turns the signs in the table.
- **2 K(l) + Cl_2(g) → 2KCl(s)**: This reaction follows rule 1, so is an enthalpy of formation.
- **C_6H_{12}O_6(s) → 6C(diamond) + 6H_2(g) + 3O_2(g)**: This reaction does not follow rule 1, so it is **not** an enthalpy of formation.
**EXAMPLE**

Using standard enthalpy of formation determine the heat of combustion for propane \( \text{C}_3\text{H}_8 \).

\[ \Delta H_{\text{rxn}} = -2043.93 \text{ kJ/mol} \]

**ENTHALPY OF FORMATION**

We can break down any reaction into formation reactions as we have done previously. When we do, we obtain the general result that the standard enthalpy of a reaction is the sum of the standard enthalpies of formation of the products minus the standard enthalpies of formation of the reactants.

\[ \Delta H_{\text{rxn}}^\circ = \Sigma n \Delta H_f^\circ (\text{products}) - \Sigma m \Delta H_f^\circ (\text{reactants}) \]

**EXAMPLE**

(a) Calculate the standard enthalpy change for the combustion of 1 mol of benzene, \( \text{C}_6\text{H}_6(l) \), to \( \text{CO}_2(g) \) and \( \text{H}_2\text{O}(l) \).

**PRACTICE PROBLEMS**

Section 5.7

#5.69, 5.71, 5.73, 5.75, 5.77