

Thermochemistry – Chapter 5

The study of chemical reactions and energy changes that involve

heat



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Nature of Energy

- Chemistry is the study of matter. Energy affects matter.
- * • Energy is anything that has the capacity to do work.
- * • Work is a force acting over a distance.
 - ✓ energy = work = force × distance
- Energy can be exchanged between objects through contact.
 - ✓ collisions

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Energy, Heat, and Work

- You can think of energy as a quantity an object can possess.
 - ✓ or collection of objects
- * • You can think of heat and work as the two different ways that an object can exchange energy with other objects.
 - ✓ The energy can flow either out of the object or into the object.

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Energy

–Chemists define work as directed energy change resulting from a

process. → $F \times d$

–Energy used to cause the temperature of an object to rise is called heat.

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Energy

- Chemists are interested in different kind of energies:
 1. Kinetic Energy
 2. Radiant Energy
 3. Thermal Energy
 4. Chemical Energy
 5. Potential Energy

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Kinetic Energy, E_K KE

The energy associated with an object by virtue of its motion.

$$E_K = \frac{1}{2}mv^2$$

m = mass (kg)

v = velocity (m/s)

Temperature is directly related to the average kinetic energy of a system.

$$KE = \frac{3}{2}nRT \quad (R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

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Radiant Energy

- It's solar energy and comes from sun
- It's the primary Energy source for Earth
- It heats the atmosphere and surface of earth
- Vegetation through photosynthesis

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* Thermal Energy

- Thermal energy is the energy that is associated with the random motion of atoms and molecules.
- Temperature is not the measurement of the thermal energy. mass
- Thermal energy depends on quantity: it is an extensive property.
- Thermal energy is a kind of kinetic energy.

KE →

* →

Bucket of water at 30°C → Cup of water at 30°C

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Heat

- **Heat** and Thermal energy are different
- **Heat** is the transfer of thermal energy between two bodies that are at ~~the~~ different temperatures.
- Heat flows from warmer objects to cooler objects.
- **Thermochemistry** is the study of heat changes in chemical reactions.

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Chemical Energy

- Chemical energy is stored within the structural units of chemical substances. (It's a kind of potential energy) position
- When substances participate in chemical reactions chemical energy is released, stored, or converted to other form of energies.

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- * Energy is released when chemical bonds form results in stability
- * Energy is consumed when chemical bonds are broken

• particles are moved farther apart → requires energy

Simplified Chemical Energy Graph

$$2 \text{ H}_2 + \text{ O}_2 \longrightarrow 2 \text{ H}_2\text{O}$$

reactants products

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Potential Energy, E_p PE

- * The energy an object has by virtue of its position in a field of force, such as gravitational, electric, or magnetic field.

Gravitational potential energy is given by the equation

$$E_p = mgh$$

m = mass (kg)
 g = gravitational constant (9.80 m/s²)
 h = height (m)

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electrostatic P.E.

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

$N \rightarrow$ SI unit of force

$$F = m \times a$$

$$\frac{\text{kg} \cdot \text{m}}{\text{s}^2} = \text{kg} \times \frac{\text{m}}{\text{s}^2}$$

The SI unit of energy is the joule, J, pronounced "jewel."

$$E = F \times d \quad J = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = \text{Nm}$$

The calorie is a non-SI unit of energy commonly used by chemists. It was originally defined as the amount of energy required to raise the temperature of one gram of water by one degree Celsius.

The exact definition is given by the equation:

$$* 1 \text{ cal} = 4.184 \text{ J (exact)}$$

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$$1000 \text{ calories} = 1 \text{ Kcal} =$$

cal

Food / 1 Calorie
calorie / 1 Cal

?

A person weighing 75.0 kg (165 lbs) runs a course at 1.78 m/s (4.00 mph). What is the person's kinetic energy?

$$m = 75.0 \text{ kg}$$

$$v = 1.78 \text{ m/s}$$

$$E_k = \frac{1}{2} mv^2$$

$$E_k = \frac{1}{2} (75.0 \text{ kg}) \left(1.78 \frac{\text{m}}{\text{s}} \right)^2$$

$$E_k = 119 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = 119 \text{ J}$$

(3 significant figures)

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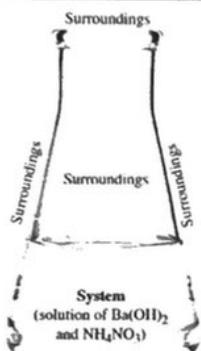
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Thermodynamic System

The substance under study in which a change occurs is called the thermodynamic system (or just system).

Thermodynamic Surroundings

Everything else in the vicinity is called the thermodynamic surroundings (or just the surroundings).



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THREE TYPES OF SYSTEMS

1. Open System: e.g. water in an open container. Can exchange mass and energy (in the form of heat) with the surroundings.
2. Closed System: e.g. water in a closed containers. Only transfer of energy, not mass.
3. ~~Isolated~~ Insulated System: e.g. water in a insulated container. No transfer of mass or energy

*

calorimeter

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Exchanging Energy

- Energy cannot be created or destroyed.
- Energy can be exchanged between objects.
- Energy can also be transformed from one form to another.



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* The First Law of Thermodynamics: Law of Conservation of Energy

- When energy is exchanged between objects or transformed into another form, all the energy is still there.
- The total amount of energy in the universe before the change has to be equal to the total amount of energy in the universe after.
- You can, therefore, never design a system that will continue to produce energy without some source of energy.

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Stop 3rd per
Stop 7th per

Internal Energy

- * The internal energy is the total amount of kinetic and potential energy a system possesses.
- * The change in the internal energy of a system depends only on the amount of energy in the system at the beginning and end.
- * A state function is a mathematical function whose result depends only on the initial and final conditions, not on the process used.
- * $\Delta E = E_{\text{final}} - E_{\text{initial}}$
- * $\Delta E_{\text{reaction}} = E_{\text{products}} - E_{\text{reactants}}$

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State Functions

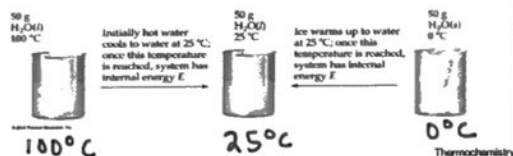
- * State functions are the properties that are determined by the state of system, regardless of how that condition was achieved.
- * Energy, pressure, volume, and temperature are the examples of state functions.

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State Functions

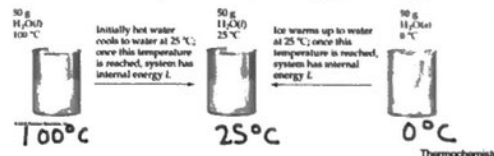
- * The internal energy of a system is independent of the path by which the system achieved that state.
 - In the system depicted in this figure, the water could have reached room temperature from either direction.



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State Functions

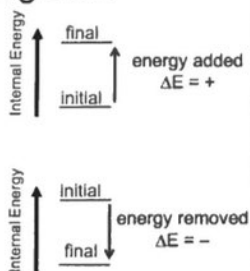
- * Therefore, internal energy is a state function.
- * It depends only on the present state of the system, not on the path by which the system arrived at that state.
- * And so, ΔE depends only on E_{initial} and E_{final} .



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Energy Diagrams

- * Energy diagrams are a "graphical" way of showing the direction of energy flow during a process.
- * If the final condition has a larger amount of internal energy than the initial condition, the change in the internal energy will be +.
- * If the final condition has a smaller amount of internal energy than the initial condition, the change in the internal energy will be -.

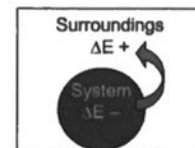


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Energy Flow

- * When energy flows out of a system, it must all flow into the surroundings.
- * When energy flows out of a system, ΔE_{system} is -.
- * When energy flows into the surroundings, $\Delta E_{\text{surroundings}}$ is +.
- * therefore:



System → Surroundings

Energy flow

$\Delta E_{\text{sys}} < 0$ (negative) $\Delta E_{\text{sur}} > 0$ (positive)

$$-\Delta E_{\text{system}} = \Delta E_{\text{surroundings}}$$

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Energy Flow

- When energy flows into a system, it must all come from the surroundings.
- When energy flows into a system, ΔE_{system} is +.
- When energy flows out of the surroundings, $\Delta E_{\text{surroundings}}$ is -.
- therefore: $\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$

$\Delta E_{\text{surroundings}} > 0$ (positive) $\Delta E_{\text{surroundings}} < 0$ (negative)

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stop 2nd

Energy Exchange

- Energy is exchanged between the system and surroundings through heat and work.
- q = heat (thermal) energy
- w = work energy
- q and w are NOT state functions; their value depends on the process.

$\Delta E = q + w$

q (heat)	system gains heat energy +	system releases heat energy -
w (work)	system gains energy from work +	system releases energy by doing work -
ΔE	system gains internal energy +	system loses some of its internal energy -

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ΔE
 Internal
 E is a
 state fun.

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Energy Exchange

- Energy is exchanged between the system and surroundings through either heat exchange or work being done.

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Endothermic Process

A chemical reaction or process in which heat is absorbed by the system (q is positive). The reaction vessel will feel cool.

Exothermic Process

A chemical reaction or process in which heat is evolved by the system (q is negative). The reaction vessel will feel warm.

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In an **endothermic** reaction:

The reaction vessel cools.

Heat is absorbed.

Energy is added to the system.

q is positive.

Feels cold *

In an **exothermic** reaction:

The reaction vessel warms.

Heat is evolved.

Energy is subtracted from the system.

q is negative.

Feels warm *

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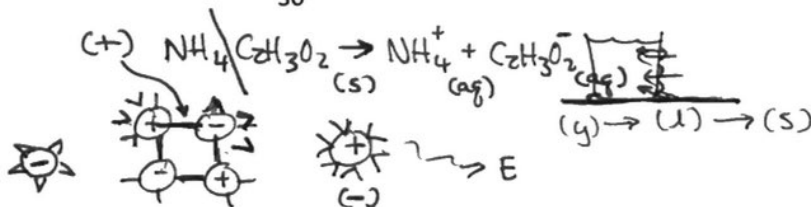
Endothermic and Exothermic Reactions

Examples:

- Chemical heat packs contain iron filings that are oxidized in an exothermic reaction. Your hands get warm because the released heat of the reaction is absorbed by your hands.
- Chemical cold packs contain NH_4NO_3 that dissolves in water in an endothermic process. Your hands get cold because they are giving away your heat to the reaction.

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Pressure–Volume Work

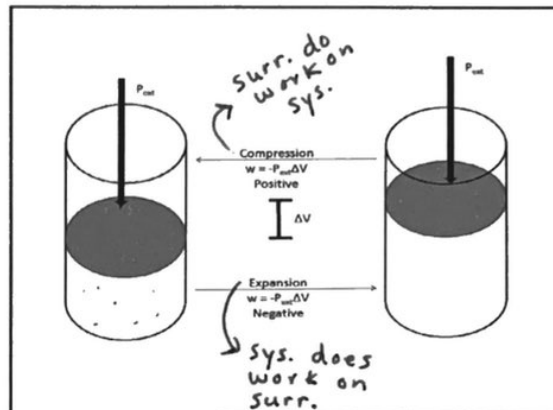
- PV work is work that is the result of a volume change against an external pressure.
- When gases expand, ΔV is +, but the system is doing work on the surroundings, so w_{gas} is -.
- When gases contract, ΔV is -, and the surroundings are doing work on the system, so w_{gas} is +.
- As long as the external pressure is kept constant, $w = -P\Delta V$

✓ To convert the units to joules, use $101.3 \text{ J} = 1 \text{ atm}\cdot\text{L}$.

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• cylinder is the system



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Enthalpy

- If a process takes place at constant pressure (as the majority of processes we study do) and the only work done is this pressure–volume work, we can account for heat flow during the process by measuring the *enthalpy* of the system.
- Enthalpy** is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

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internal energy

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Enthalpy

- When the system changes at constant pressure, the change in enthalpy, ΔH , is

$$\Delta H = \Delta(E + PV)$$

- This can be written

$$\Delta H = \Delta E + P\Delta V$$

\downarrow \downarrow
 $q + w$ $-w$

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Enthalpy

- Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = (q + w) - w$$

$$\star \Delta H = q \text{ at constant } P$$

- So, at constant pressure, the change in enthalpy is the heat gained or lost.

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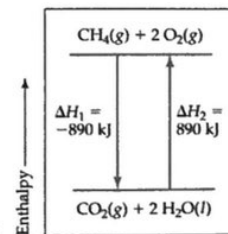
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Enthalpy of Reaction

The *change* in enthalpy, ΔH , is the enthalpy of the products minus the enthalpy of the reactants:

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



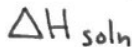
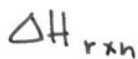
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Enthalpy of Reaction

This quantity, ΔH or ΔH_r , is called the **enthalpy of reaction**, or the **heat of reaction**.



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The Truth about Enthalpy

1. Enthalpy is an extensive property.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.

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Sample Exercise 5.3 Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH , in these processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic: (a) A 1 g ice cube melts, (b) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O .

Solution

Analyze Our goal is to determine whether ΔH is positive or negative for each process. Because each process occurs at constant pressure, the enthalpy change equals the quantity of heat absorbed or released, $\Delta H = q_p$.

Plan We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for ΔH ; those in which heat is released are exothermic and have a negative sign for ΔH .

Solve In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is endothermic.

In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is exothermic.

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Sample Exercise 5.4 Relating ΔH to Quantities of Reactants and Products

How much heat is released when 4.50 g of methane gas is burned in a constant pressure system? (Use the information given in Equation 5.18.)

Solution

Analyze Our goal is to use a thermochemical equation to calculate the heat produced when a specific amount of methane gas is combusted. According to Equation 5.18, 890 kJ is released by the system when 1 mol CH_4 is burned at constant pressure.

Plan Equation 5.18 provides us with a stoichiometric conversion factor (1 mol CH_4 = 890 kJ). Thus, we can convert moles of CH_4 to kJ of energy. First, however, we must convert grams of CH_4 to moles of CH_4 . Thus, the conversion sequence is grams CH_4 (given) \rightarrow moles CH_4 \rightarrow kJ (unknown to be found).

Solve By adding the atomic weights of C and 4 H, we have 1 mol CH_4 = 16.0 CH_4 . We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 to kilojoules.

$$\text{Heat} = (4.50 \text{ g } CH_4) \left(\frac{1 \text{ mol } CH_4}{16.0 \text{ g } CH_4} \right) \left(\frac{-890 \text{ kJ}}{1 \text{ mol } CH_4} \right) = -250 \text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

$$\frac{890 \text{ kJ}}{1 \text{ mol } CH_4}$$

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Part 1 Steps Here!

Calorimetry

Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.

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Quantity of Heat Energy Absorbed Heat Capacity

- When a system absorbs heat, its temperature increases.
- The increase in temperature is directly proportional to the amount of heat absorbed.
- The proportionality constant is called the heat capacity, C .
✓ Units of C are $J/^\circ C$ or J/K .

$$q = C \times \Delta T$$

- * The heat capacity of an object depends on its mass. \rightarrow extensive property
✓ 200 g of water requires twice as much heat to raise its temperature by $1^\circ C$ as does 100 g of water.
- * The heat capacity of an object depends on the type of material.
✓ 1000 J of heat energy will raise the temperature of 100 g of sand $12^\circ C$, but only raise the temperature of 100 g of water by $2.4^\circ C$.

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