

CHEM 115

Temperature and Heat Energy in Chemical Systems

Lecture 13
Prof. Sevian



Note: If we do not get all the way through these lecture slides in one lecture, we will continue after spring break where we leave off.

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Agenda

- Relevance of the chemistry
- Heat vs. temperature
- Kinetic vs. potential energy
- Kinetic and potential energy changes as heat energy is added to a pure substance
- Transfer of energy and the Law of Conservation of Energy
- Calorimetry example
- Hess's law

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Conservation of Matter: A Real Consequence

- Energy
 - How much?
 - From where?
 - At what cost?
 - To whom?
- CO₂ emissions
 - Where does the CO₂ come from?
 - Who is responsible?
 - How bad is the problem?
- Mitigating the problem
 - Reducing CO₂ production (e.g., biofuels, energy conservation)
 - Capturing and storing CO₂

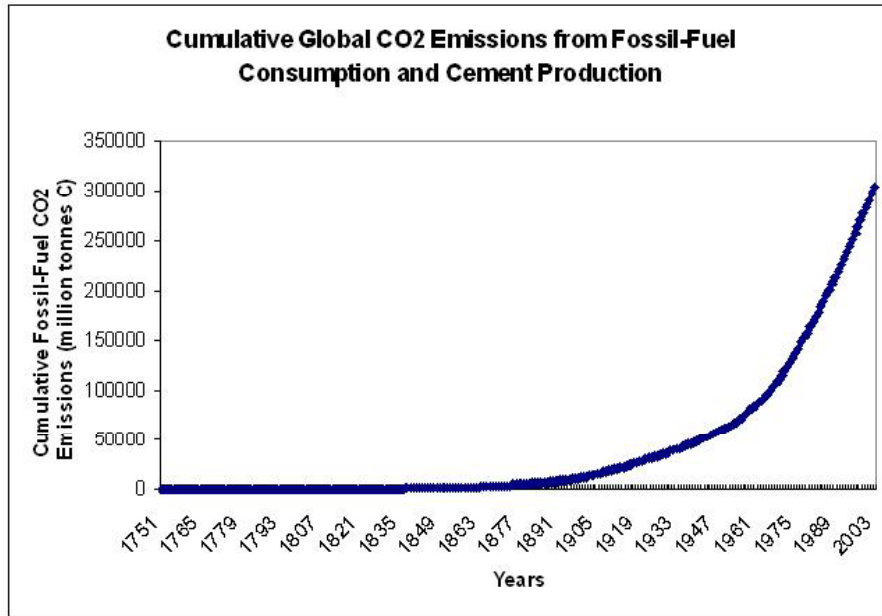
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CO₂ emissions

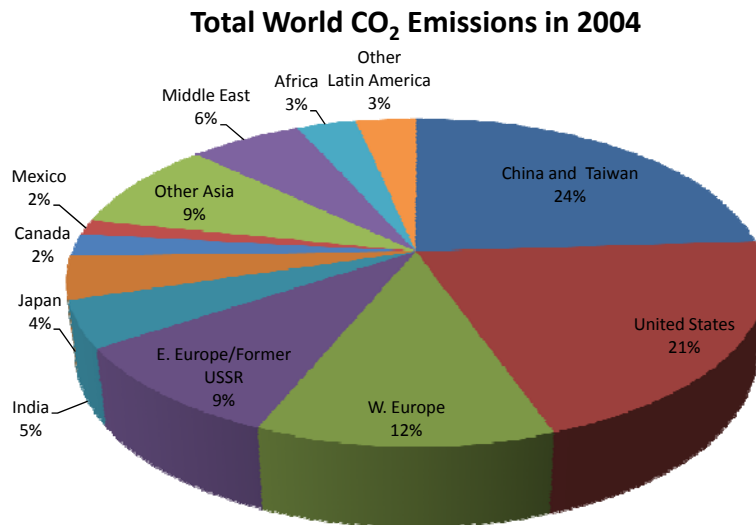
- Since 1751 roughly 305 billion tons of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production. Half of these emissions have occurred since the mid 1970s. The 2003 global fossil-fuel CO₂ emission estimate, 7303 million metric tons of carbon, represents an all-time high and a 4.5% increase from 2002.

Source: Oak Ridge National Laboratory (http://cdiac.ornl.gov/trends/emis/tre_glob.htm)

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Source: Oak Ridge National Laboratory (http://cdiac.ornl.gov/trends/emis/tre_glob.htm)

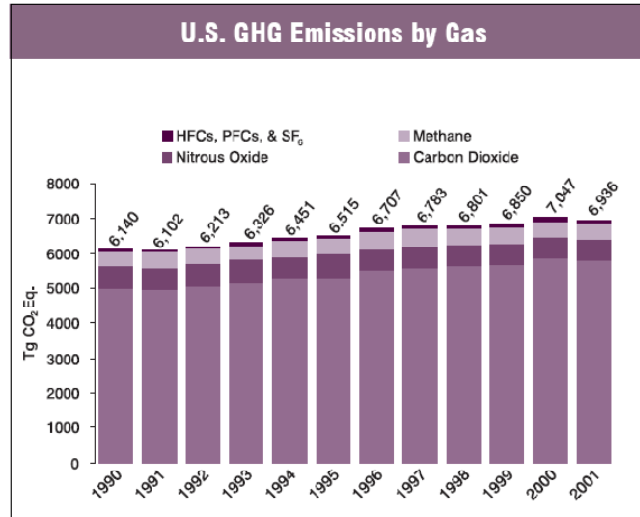


- Sovereign states by carbon dioxide emissions due to human activity
- Data considers only carbon dioxide emissions from the burning of fossil fuels, but not emissions from deforestation, and fossil fuel exporters
- Source: Carbon Dioxide Information Analysis Center, United Nations (data collected in 2007 about CO₂ emissions in 2004)

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Why are CO₂ emissions important?

Other gases also contribute to climate change, but CO₂ is by far the greatest contributor.



Source: US Environmental Protection Agency
<http://yosemite.epa.gov/oar/globalwarming.nsf/content/ResourceCenterPublicationsGHGEmissionsUSEmissionsInventory2003.html>

What part comes from the US?

- The United States continues to be the largest single national source of fossil fuel-related CO₂ emissions.
- In 2003, U.S. fossil-fuel emissions were 28% higher than those of the world's second largest emitter, the People's Republic of China, but China has now surpassed the U.S.
- Emissions in 2003 were down slightly (0.1%) from 2002 but have doubled since the mid-1950s.
- The U.S. share of global emissions declined from 44% to 23% between the mid-1950s and now because of higher growth rates in other countries.
- In 2003, 42.3% of U.S. fossil-fuel emissions come from the consumption of petroleum products.

Source: Oak Ridge National Laboratory (http://cdiac.ornl.gov/trends/emis/tre_usa.htm)

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Worldwide CO₂ emissions

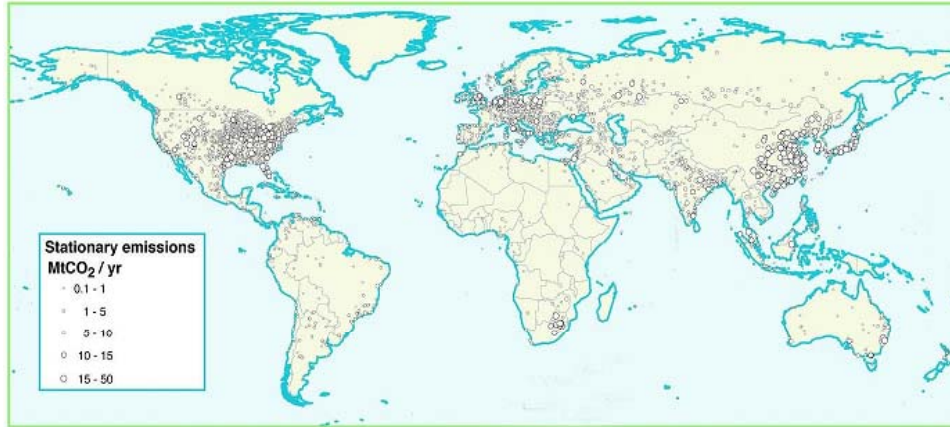


Fig. SRCCS-2a. Global distribution of large stationary sources of CO₂ from IPCC Special Report on CO₂ Capture and Storage (2003)
<http://www.ipcc.ch/pub/reports.htm>

In the US, what part comes from fossil fuel combustion?

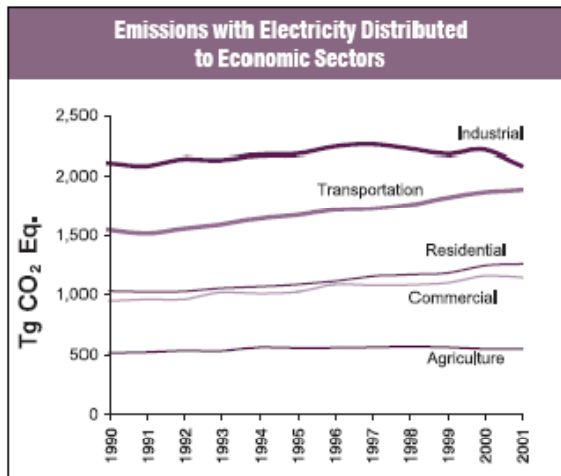
The vast majority (more than 95%) of CO₂ emissions come from fossil fuel combustion.

Table ES-1: Recent Trends in U.S. Greenhouse Gas Emissions and Sinks (Tg CO₂ Eq.)

Gas/Source	1990	1995	1996	1997	1998	1999	2000	2001
CO₂	5,003.7	5,334.4	5,514.8	5,595.4	5,614.2	5,680.7	5,883.1	5,794.8
Fossil Fuel Combustion	4,814.8	5,141.5	5,325.8	5,400.0	5,420.5	5,488.8	5,692.2	5,614.9
Iron and Steel Production	85.4	74.4	68.3	71.9	67.4	64.4	65.8	59.1
Cement Manufacture	33.3	36.8	37.1	38.3	39.2	40.0	41.2	41.4
Waste Combustion	14.1	18.5	19.4	21.2	22.5	23.9	25.4	26.9
Ammonia Manufacture & Urea Application	19.3	20.5	20.3	20.7	21.9	20.6	19.6	16.6
Lime Manufacture	11.2	12.8	13.5	13.7	13.9	13.5	13.3	12.9
Natural Gas Flaring	5.5	8.7	8.2	7.6	6.3	6.7	5.5	5.2
Limestone and Dolomite Use	5.5	7.0	7.6	7.1	7.3	7.7	5.8	5.3
Aluminum Production	6.3	5.3	5.6	5.6	5.8	5.9	5.4	4.1
Soda Ash Manufacture and Consumption	4.1	4.3	4.2	4.4	4.3	4.2	4.2	4.1
Titanium Dioxide Production	1.3	1.7	1.7	1.8	1.8	1.9	1.9	1.9
Carbon Dioxide Consumption	0.9	1.1	1.1	1.2	1.2	1.2	1.2	1.3
Ferroalloys	2.0	1.9	2.0	2.0	2.0	2.0	1.7	1.3

Source: US Environmental Protection Agency
<http://yosemite.epa.gov/oar/globalwarming.nsf/content/ResourceCenterPublicationsGHGEmissionsUSEmissionsInventory2003.html>

Who in the US uses the fossil fuels that generate CO₂?



Residential usages and transportation accounted for 43% of CO₂ emissions from fossil fuels in 2001.

Source: US Environmental Protection Agency

(<http://yosemite.epa.gov/oar/globalwarming.nsf/content/ResourceCenterPublicationsGHGEmissionsUSEmissionsInventory2003.html>)

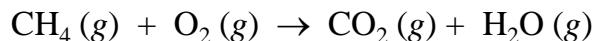
Conservation of Matter, Getting Energy from Fuel: How is CO₂ produced by the combustion of fossil fuels?

U.S. energy sources*

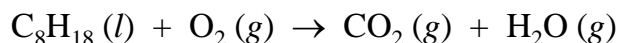
Coal (solid carbon) 23%



Natural gas (methane) 24%



Petroleum (octane shown here) 39%



A chemical reaction is when you break bonds in reactants (requires input of energy) and then atoms rearrange and form new bonds in products (releases energy). If the energy released (when new bonds form) is more than the energy input (to break bonds in the reactants), then there is a net output of energy.

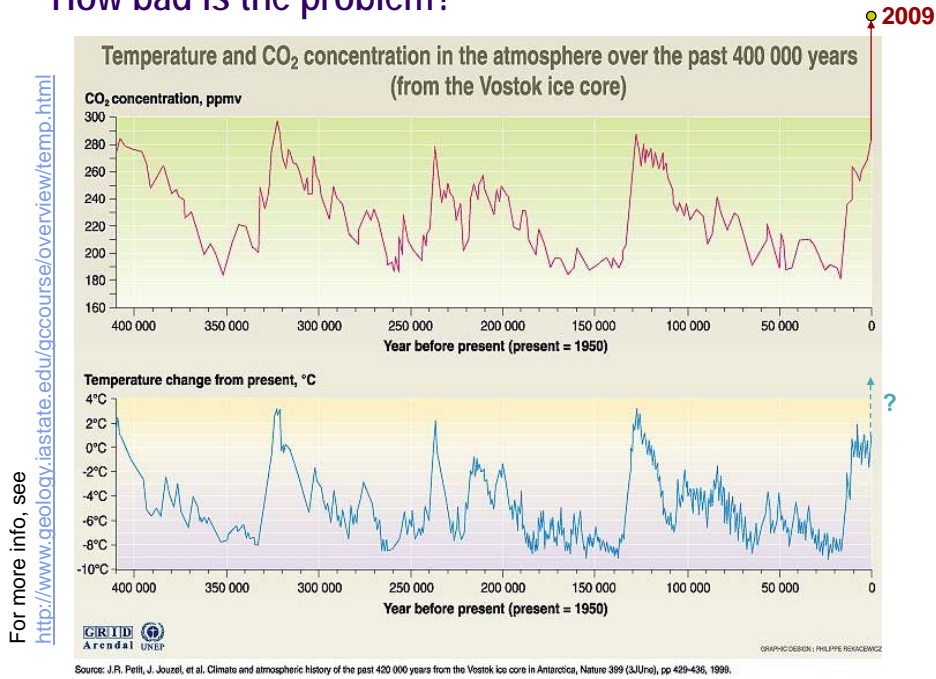
Tinier portions:

- Nuclear 8%
- Hydroelectric 3%
- Other 3%

Coming soon (when we get to the later parts of ch. 5): Which of these fuels is the worst pollutant (produces the greatest mass of CO₂ per unit of energy)? To do this problem, you'll need to use stoichiometry with properly balanced chemical reactions.

*Source: U.S. Department of Energy (2002 data)

How bad is the problem?



How can we get rid of CO₂?

- Reduce usage of fossil fuels (biofuels, energy conservation, etc.)
- Capture and store CO₂

(conservation of matter argument drives this idea)

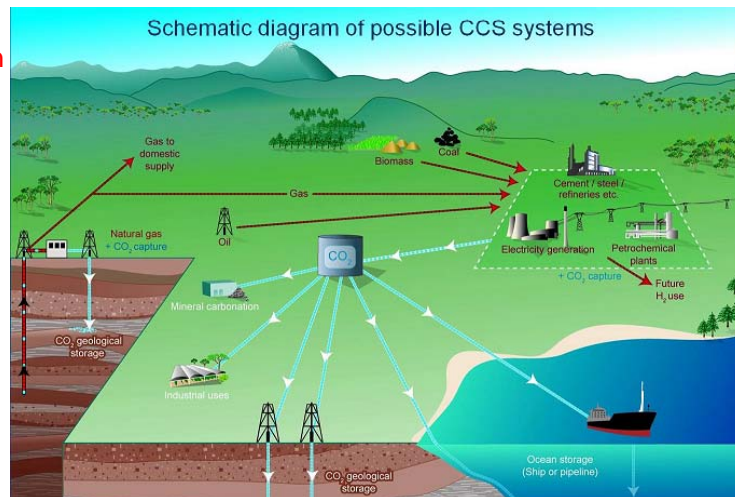


Fig. SRCCS-TS1 from IPCC Special Report on CO₂ Capture and Storage <http://www.ipcc.ch/pub/reports.htm>

Where can you learn more?

The Intergovernmental Panel on Climate Change (IPCC)

<http://www.ipcc.ch/index.html>

- See the Summary for Policymakers in the recently released report on CO₂ capture and storage
- http://arch.rivm.nl/env/int/ipcc/pages_media/SRCCS-final/IPCCSpecialReportonCarbondioxideCaptureandStorage.htm

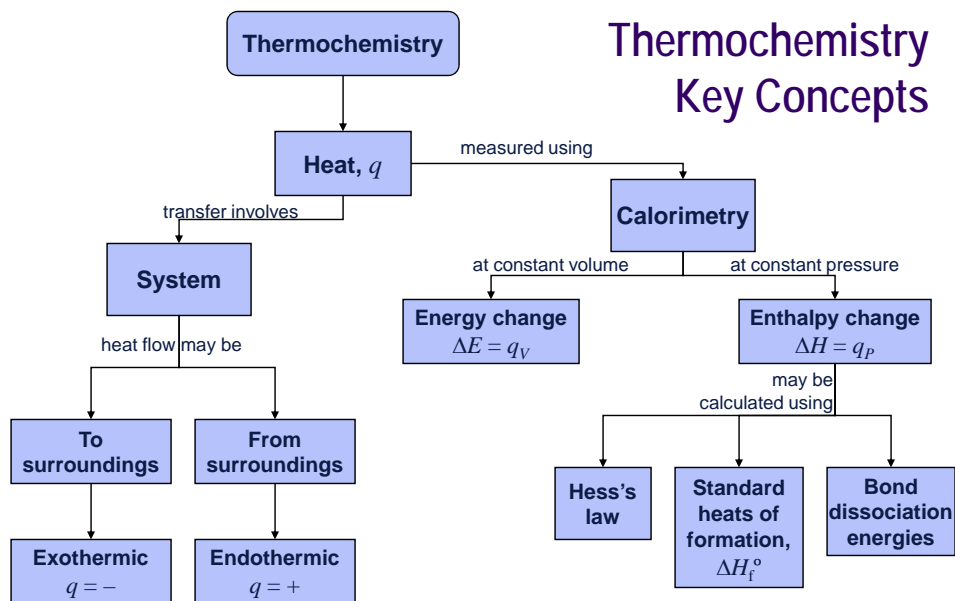
US Environmental Protection Agency

- What you can do
- <http://epa.gov/climatechange/wycd/index.html>

General resources

- *An Inconvenient Truth*, movie and book by Al Gore
website: www.climatecrisis.org
- USA Today resource page on climate change science
<http://www.usatoday.com/weather/resources/climate/climate-sci-resources.htm>
- United Nations Environment Programme
<http://www.gcric.org/ipcc/qa/index.htm>

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Adapted from McMurray & Fay, 2001

More to come: entropy (S), entropy change (ΔS), free energy change (ΔG), spontaneity, etc.

Map of chapter 5

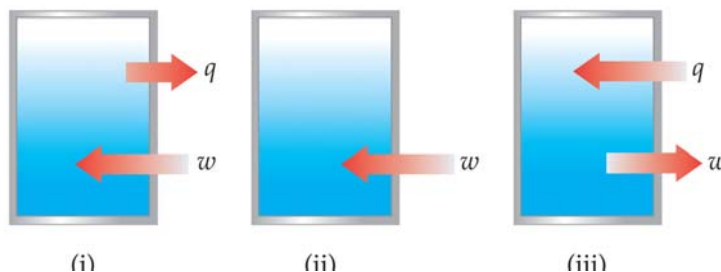
- Energy in chemistry
 - Kinetic and potential energy changes as heat energy is added to a pure substance
- First law of thermodynamics
 - Transfer of energy and the Law of Conservation of Energy
 - Endothermic vs. exothermic changes
 - Enthalpy
- Measuring heat energy (enthalpy) changes (ΔH) in the laboratory
 - Heat energy and heat capacity of a material
 - Calorimetry technique
- Using laboratory measurements to calculate ΔH for reactions we can't measure in the lab

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Energy content or Internal energy, E

- Sum of the kinetic and potential energies of all the particles in the system
- Can change in only two ways:
 - When **heat** (q) is transferred to the system (from the surroundings) or vice versa
 - When work (w) is done on the system (by the surroundings) or vice versa

For the systems below, describe what is happening to $\Delta E = q + w$



Heat is only part of E , work is the rest

- In most chemistry systems, we are concerned with enthalpy (H), not internal energy (E)
- In systems where the pressure is constant (i.e., most laboratory experiments and most of real life), $\Delta H = q$
- Endothermic and exothermic designations refer ONLY to the sign of the heat transfer (q)
- Fortunately, it simplifies matters to talk about ΔH instead of ΔE

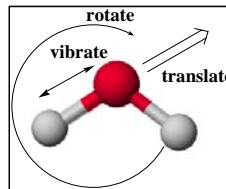
For the systems in the previous diagram, determine whether each one is endothermic or exothermic

The Physics of Energy

- There are two kinds of energy
 - Kinetic energy: the energy associated with motion
 - Potential energy: stored energy
- These show up in chemical systems in various ways

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Energy



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

1. Kinetic energy

- Energy of motion, mechanical energy
- The faster the velocity, the higher the kinetic energy
- Particle level energy
 - Thermal energy*: particles in motion in a material
 - Electrical energy: electrons moving through a conductor
 - Sound energy: orchestrated vibration of particles in a material such that spaces between the particles compress and expand
 - Light energy: photons of various energies
- Macroscopic level mechanical energy
 - Moving objects

*Thermal energy and "heat" are synonyms

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Energy

2. Potential energy

- Energy of relative separation (because there are forces of attraction/repulsion between objects)
- "Chemical" potential energy and electrostatic energy are associated with the arrangements of charged particles within and between atoms, according to predictions of Coulomb force

$$F = \frac{k Q_1 Q_2}{r^2} \quad \text{and} \quad P.E. = -\int F dr$$

- Gravitational potential energy is associated with arrangements of objects with mass, according to predictions of gravitational force

$$F = \frac{G m_1 m_2}{R^2} \quad \text{which simplifies to } F = mg$$

$$\text{and } P.E. = -\int F dr$$

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The Chemistry of Energy

- Energy can be converted from one form to another:
 - Kinetic (motion): thermal (heat), electricity, light
 - Potential (stored): bonds, configurations
- Energy transfer occurs in such a way that the total energy of the universe remains constant
(**First Law of Thermodynamics**)
- Energy transfer occurs in such a way that matter and energy become more dispersed, that is, more spread out
(**Second Law of Thermodynamics**)
- Let's consider how energy transfer happens when we are concerned only with thermal energy (a.k.a., heat)

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Heat Transfer

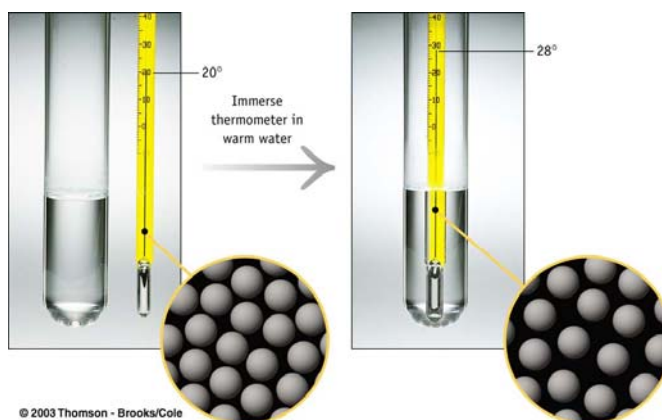
- Thermal energy
<http://www.colorado.edu/physics/2000/bec/temperature.html>
- Transfer of thermal energy from one location to another
<http://jersey.uoregon.edu/vlab/Thermodynamics/therm1a.html>

When thermal energy is transferred, it always transfers from a location with more thermal energy to a location with less thermal energy. Energy continues to transfer until thermal equilibrium is established. (Energy gets more spread out.)
Simply: hot to cold.
- To understand more about thermodynamic equilibrium, try all 7 “thought experiments” at
<http://jersey.uoregon.edu/vlab/Thermodynamics/index.html>

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Temperature

- A measurement made using an instrument called a thermometer
- How it works:



- So, what does temperature measure?

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Relative vs. Absolute Temperature Scales

- Relative temperature (linear) scale measures temperature of an object relative to two points
 - Coldest and warmest temperatures at which humans can typically survive → Fahrenheit scale is relative
 - Freezing and boiling points of water → Celsius scale is relative
- Absolute temperature (linear) scale measures absolute motion of particles → Kelvin scale is absolute
 - Absolute zero temperature is a point of reference for disorder: there is no disorder at zero (**Third Law of Thermodynamics**)
 - Convenience: the size of 1 °C is equal to the size of 1 K

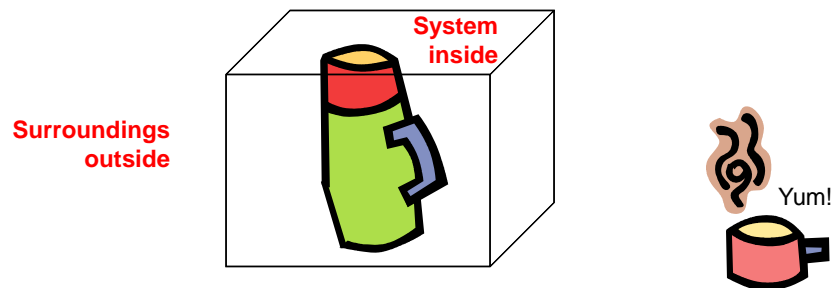
Thermodynamics

- The study of heat (a.k.a., thermal energy)
- Theoretical model is built on taking averages (using statistics) of multiple possible arrangements of particles
- The most important question:
What could the particles do?
- If heat transfers, it must transfer *from* something to something else
- Involves being able to draw imaginary boundaries around a “system”

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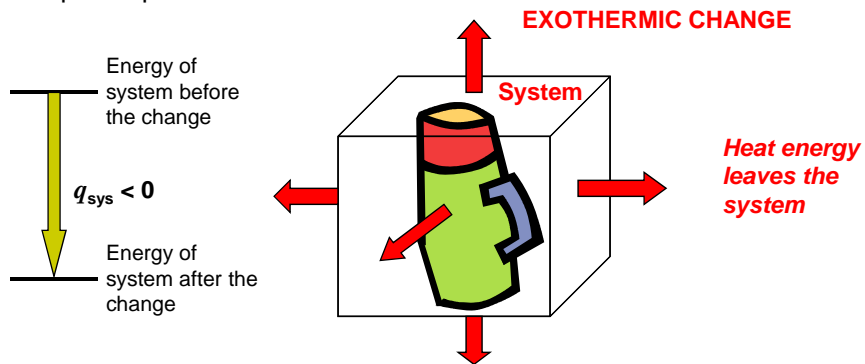
What is a System?

- For our purposes, we will define a “system” to be a 3-dimensional space, surrounded by an imaginary surface boundary, such that no matter passes through the boundary, but heat energy can transfer freely across the boundary



What happens to the SYSTEM when heat transfer occurs?

- As coffee eventually cools, heat energy is transferred to the air around the thermos and the counter beneath it.
- System: Particles in the coffee slow down their motion.
- Surroundings: Particles in the air, and particles in the counter, speed up their motion.



Conservation of Energy

- When heat enters or leaves matter, energy is conserved.
- This means energy has to come from somewhere, and it has to go somewhere. It can be accounted for.
- Particle level: energy can go into or come out of the system, thereby increasing or decreasing the energy in the particles
 - Kinetic energy: motion of particles (translation, vibration, rotation) in solid, liquid and gas states
 - Potential energy: electron states in atoms or within bonds
- Sometimes, it's easier to measure how much heat (which is energy) goes into or comes from the surroundings around a system
 - If heat goes into the surroundings, then it must have come out of the system
 - If the surroundings lose heat, then it must have gone into the system

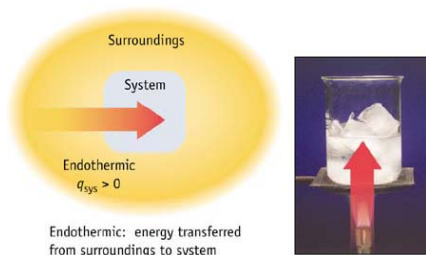
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Endothermic vs. Exothermic

Endothermic

Example: ice melting
Heat enters system
System gains energy

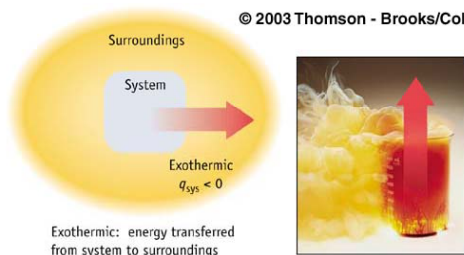
$$q_{\text{sys}} > 0$$



Exothermic

Example: fire burning
Heat exits system
System loses energy

$$q_{\text{sys}} < 0$$

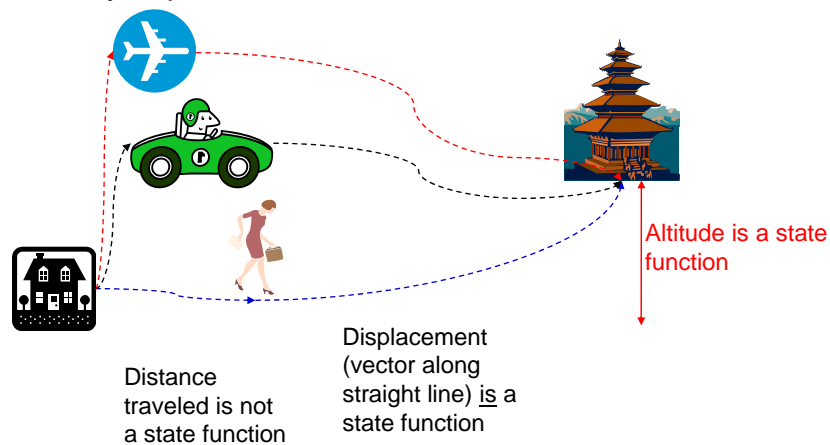


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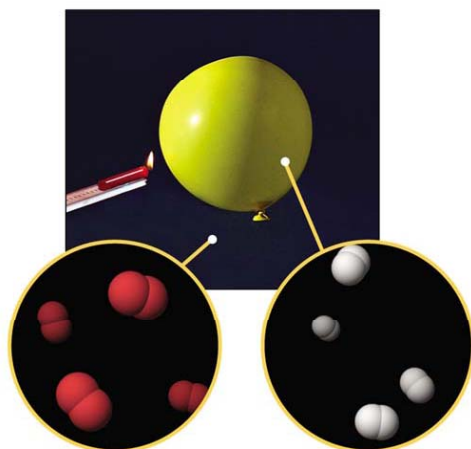
Alternative Pathways

“State function” doesn’t depend on the path taken
- Only depends on the condition the state is in



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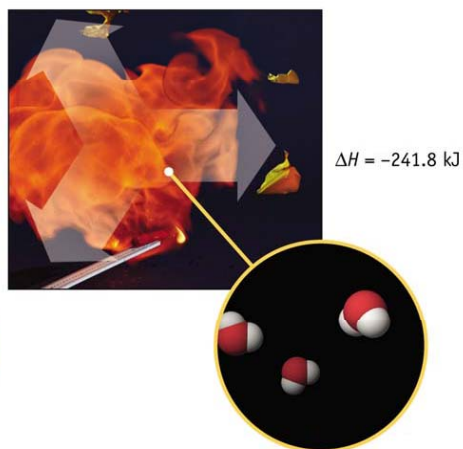
(a) A lighted candle is brought up to a balloon filled with hydrogen gas.



O₂ (surroundings)

H₂ (system)

(b) When the balloon breaks, the candle flame ignites hydrogen/oxygen mixture.

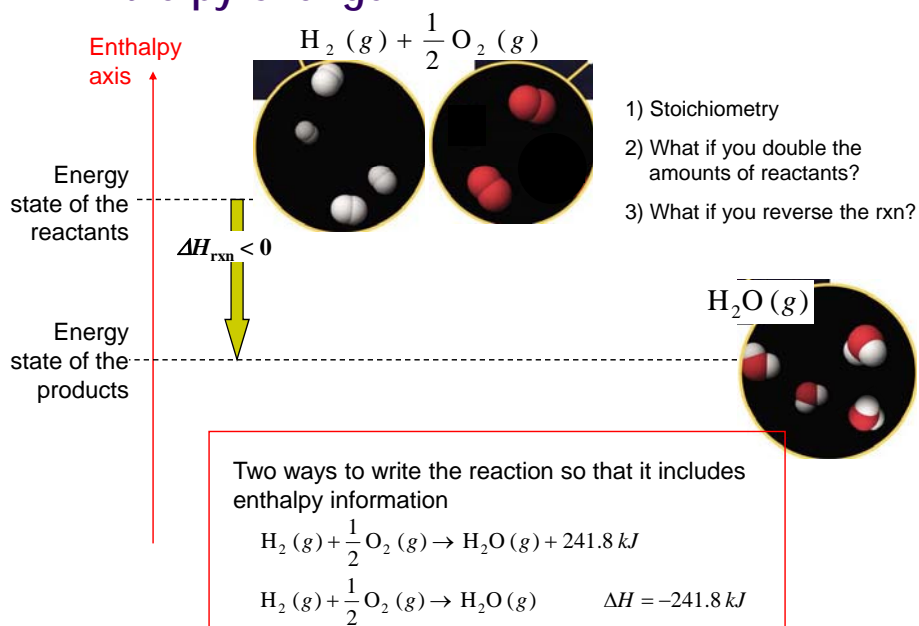


H₂(g) + $\frac{1}{2}$ O₂(g) → H₂O(g)

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http://iws-edcv.wiley.com/college/bcs/redesign/student/resource/0.12264_0471150584_BKS_1907_10615_3446_00.html

Enthalpy Change



Important things to know about state functions like ΔH and ΔE

- The delta (Δ) always means change from initial to final, calculated as “final minus initial.”

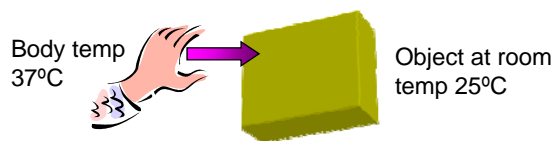
$$\Delta H_{\text{rxn}} = H(\text{products}) - H(\text{reactants})$$
 Therefore, when ΔH is positive, it means the products were higher than the reactants
- Reversing a reaction means changing the sign of the state function, since products and reactants are switched.
- ΔH_{rxn} can be given in two ways: as kJ or as kJ/mol. If it is given in kJ, then it depends on the amount of reactant.
- The physical states of the chemicals in the reaction matter.

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \quad \Delta H_{\text{rxn}} = -571.66 \text{ kJ}$$

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H_{\text{rxn}} = -483.64 \text{ kJ}$$
- State functions don't depend on the path***

Quantitatively

- How do we measure heat lost or gained by a system?



- What does the **quantity of heat transferred** depend on?
 - Quantity of material in the object
 - Size of temperature change
 - Identity of the material the object is made from

$$q = m C \Delta T$$

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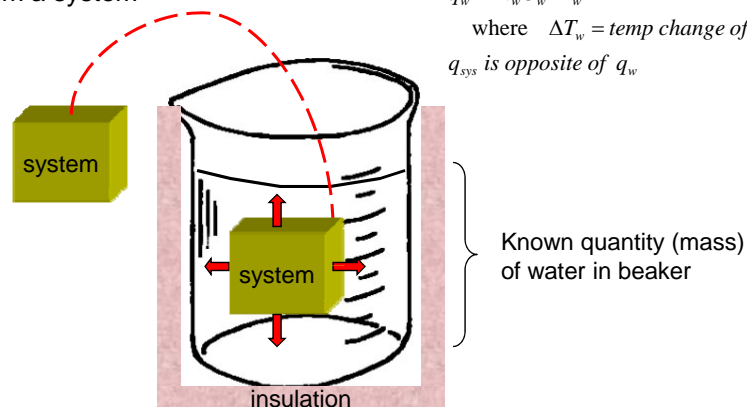
Water: A Useful Substance

- Liquid water's capacity to absorb heat (C) is enormous compared to most materials
- Heat capacity of water is very accurately known: 4.184 Joules per gram per degree Kelvin
- What this means:
 - If you have one gram of liquid water
 - To raise its temperature by 1 Kelvin (equal to 1°C)
 - Takes 4.184 Joules of energy (equal to 1 calorie)
- Since $q = m C \Delta T$, if you are working with water then you know C . Therefore, if you have a specific quantity of water, and you measure the temperature it changes by, you can calculate the heat that transferred.

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Liquid Water has a Large and Very Well Known (quantitatively) Capacity to Absorb Heat Energy

Measuring heat transferred from a system



Problem Solving Strategy

$$q_w = m_w C_w \Delta T_w$$

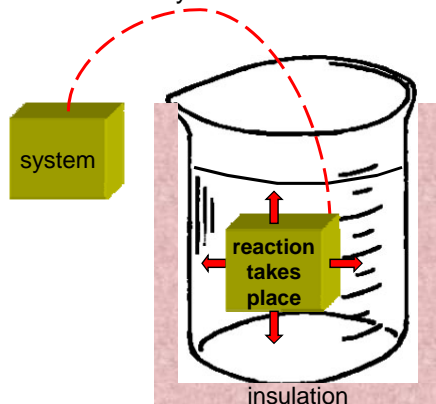
where $\Delta T_w = \text{temp change of H}_2\text{O}$

q_{sys} is opposite of q_w

Beaker image: core.ecu.edu/chem/chemlab/equipment/ebeaker.htm

Calorimetry

Measuring heat transferred from a system



Problem Solving Strategy

$$q_w = m_w C_w \Delta T_w$$

where $\Delta T_w = \text{temp change of H}_2\text{O}$

q_{sys} is opposite of q_w

Given information

Mass of water = 100.0 g

Temperature of water before = 23.3°C

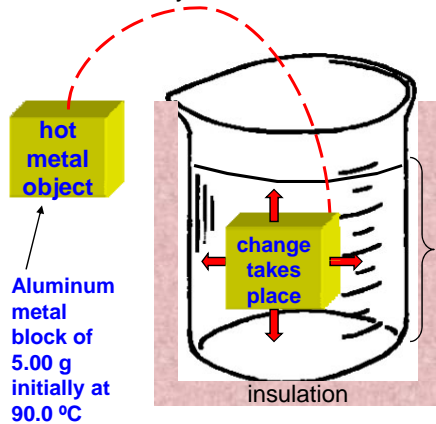
Temperature of water after = 47.3°C

$C_{\text{water}} = 4.184 \text{ J/g}\cdot\text{K}$

100.0 g
of H₂O

A hot metal block placed in cold water

Measuring heat transferred from a system



Aluminum metal block of 5.00 g initially at 90.0 °C

Given information

Initial temperature of Al block = 90.00°C

Mass of Al block = 5.00 g

Mass of water = 100.0 g

Temperature of water before = 23.00°C

Temperature of both after = 23.71°C

$C_{\text{water}} = 4.184 \text{ J/g}\cdot\text{K}$

Question:

What is the heat capacity of Al?

Problem Solving Strategy

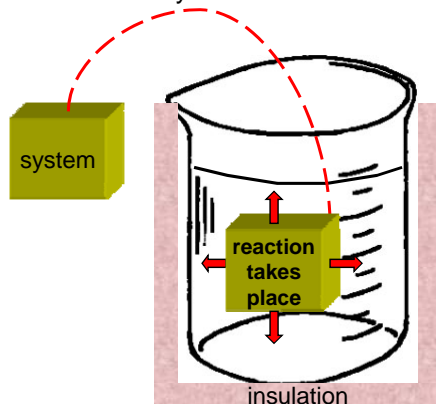
$$q_w = m_w C_w \Delta T_w$$

where $\Delta T_w = \text{temp change of H}_2\text{O}$

q_{sys} is opposite of q_w

Calorimetry is the same idea

Measuring heat transferred from a system



Problem Solving Strategy

$$q_w = m_w C_w \Delta T_w$$

where $\Delta T_w = \text{temp change of H}_2\text{O}$

q_{sys} is opposite of q_w

Given information

Mass of water = 100.0 g

Temperature of water before = 23.3°C

Temperature of water after = 47.3°C

$C_{\text{water}} = 4.184 \text{ J/g}\cdot\text{K}$

100.0 g
of H_2O

The confusing part is that once the change takes place, the system and the water are mixed together, and the heat energy gets distributed throughout the mixture

Calorimetry problems

- Water is something we know a lot of very accurate data about
- Measure heat changes that get transferred to water by a (reaction) system
- Calculate amount of heat that water received from or gave to a system
- If the calorimeter is insulated, then all heat that enters (or leaves) the water must have come from (or gone to) the system being studied
- Figure out things about the system that you didn't know before

What we've learned so far

- Systems can either lose or gain heat during a change
 - Exothermic: heat flows out to surroundings
 - Endothermic: heat flows in to system
- Heat changes can be measured using calorimetry
 - Typical calorimetry uses liquid water as the surroundings
 - Liquid water either absorbs heat from the system (T_{water} increases) or gives heat to the system (T_{water} decreases)
 - If calorimeter is well insulated then
 - $q_{\text{water}} = -q_{\text{system}}$, and
 - $q_{\text{water}} = m_{\text{water}} C_{\text{water}} \Delta T_{\text{water}}$ (where C_{water} is slope of line for liquid region)
- Under typical laboratory conditions (constant pressure), heat change is equal to enthalpy change
- Enthalpy change is a state function (path independent)

What's next: Because of its path independence, enthalpy change can be calculated by several methods:

- Hess's law
- Standard heats of formation
- Bond dissociation energies (second semester general chem)