CHEM 103
Energy in Chemical Systems

Lecture Notes
March 21, 2006
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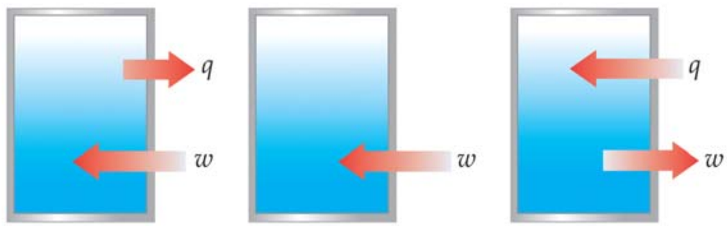
Map of this chapter

- 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

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)
  - When work (w) is done on the system (by the surroundings)

For the systems below, describe what is happening to ΔE



(i) (ii) (iii)

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), $\Delta H = q$
- 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

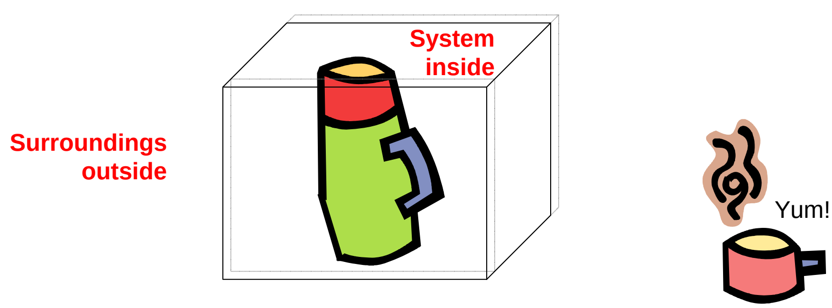
For the systems in the previous diagram, determine whether each one is endothermic or exothermic

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 energy transfers, it must transfer *from* something *to* something else
- Involves being able to draw imaginary boundaries around a “system”

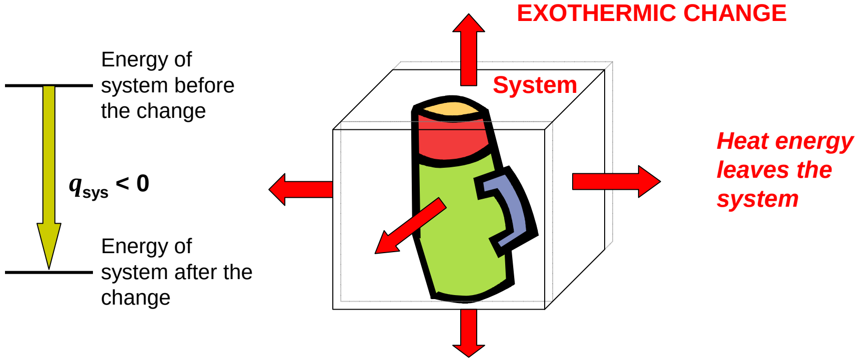
What is a System?

- A “system” is 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.



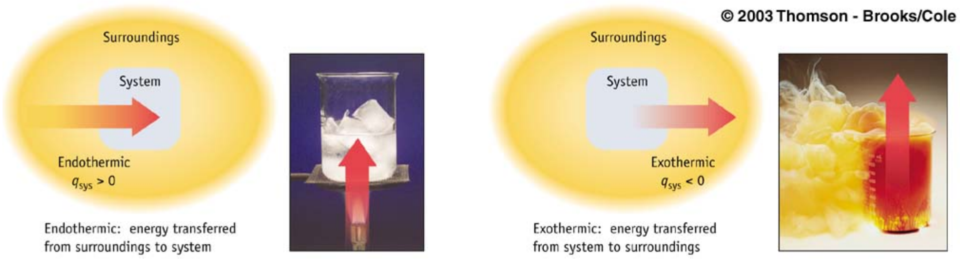
Conservation of Energy

- When heat energy 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

Endothermic vs. Exothermic

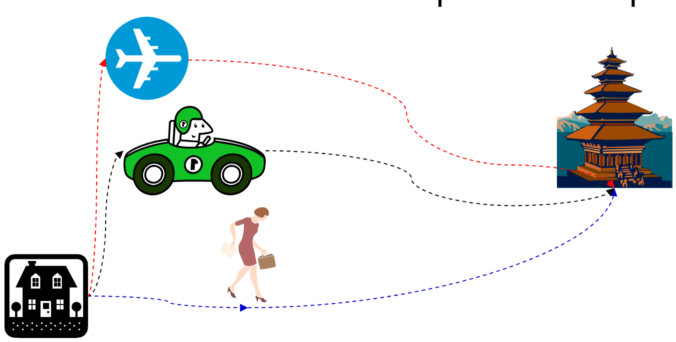
Endothermic
Example: ice melting
Heat enters system
System gains energy
$q_{sys} > 0$

Exothermic
Example: fire burning
Heat exits system
System loses energy
$q_{sys} < 0$



Alternative Pathways

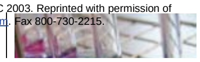
"State function" doesn't depend on the path taken

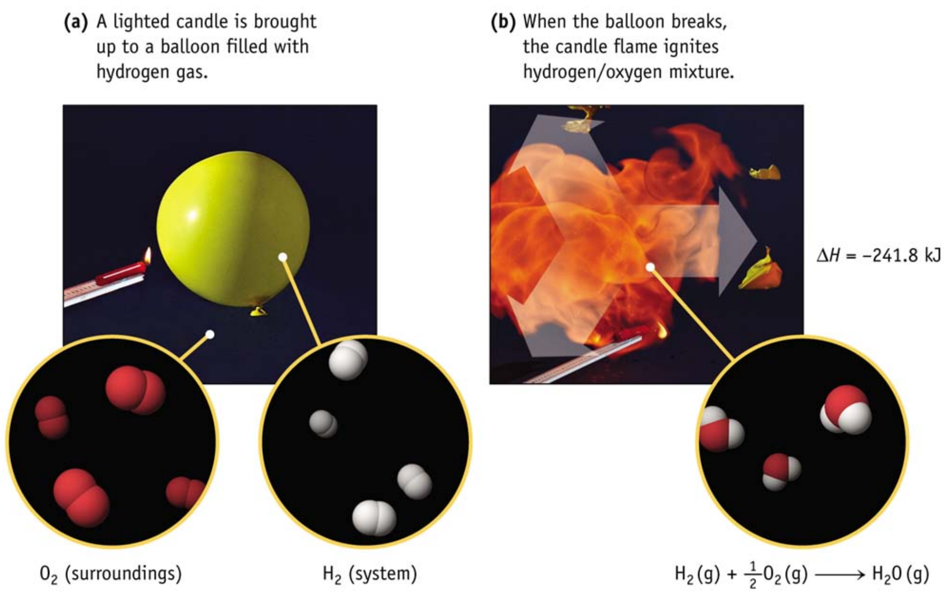


Distance traveled is not a state function

Displacement (vector along straight line) is a state function

Altitude is a state function

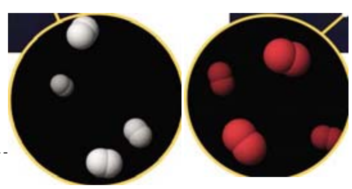




http://jws-edcv.wiley.com/college/bcs/redesign/student/resource/0,12264,_0471150584_BKS_1907__10615_3446__,00.html

Enthalpy Change

Enthalpy axis



Reactants

$\Delta H_{rxn} < 0$

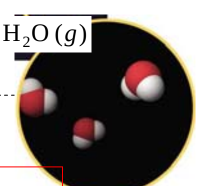
$$H_2\,(g) + \frac{1}{2}\,O_2\,(g)$$

1) Stoichiometry

2) What if you double the amounts of reactants?

3) What if you reverse the rxn?

$H_2O\,(g)$



Products

Two ways to write the reaction so that it includes enthalpy information

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g) + 241.8\,kJ$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g) \qquad \Delta H = -241.8\,kJ$$

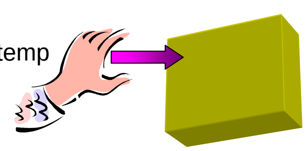
Important things to know about state functions like Δ*H* and Δ*E*

1. The delta (Δ) always means change from initial to final, calculated as "final minus initial."
   - $\Delta H_{rxn} = H\text{ (products)} - H\text{ (reactants)}$
   - Therefore, when Δ*H* is positive, it means the products were higher than the reactants
2. Reversing a reaction means changing the sign of the state function, since products and reactants are switched.
3. 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.
4. The physical states of the chemicals in the reaction matter.
   - $2\ H_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2\ H_2O\ (l)$ $\Delta H_{rxn} = -571.66$ kJ
   - $2\ H_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2\ H_2O\ (g)$ $\Delta H_{rxn} = -483.64$ kJ

Quantitatively

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

Body temp 37ºC



Object at room temp 25ºC

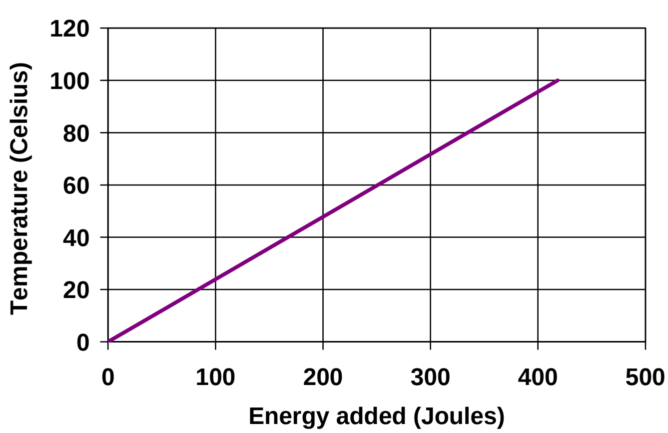
- What does the quantity of heat transferred depend on?
  - Quantity of material in the object
  - Size of temperature change
  - Identity of the material the object is made from

$$q = m\ C\ \Delta T$$

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 1ºC)
  - 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.

For a 1.00-gram sample of liquid water



What happens if you add more heat energy to liquid water at 100ºC?

- It boils
- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase

Heating Curve of 1.00-gram Sample of Some Substance (not H_2O) at Standard Pressure

A = solid below melting*

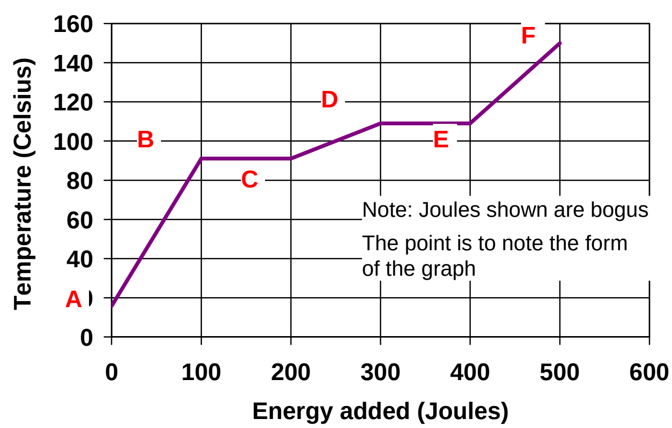
B = solid has reached melting temperature, and is beginning to melt*

C = liquid at melting temperature, has just completed melting

D = liquid has reached boiling temperature, and is beginning to boil*

E = gas at boiling temperature, has just completed boiling*

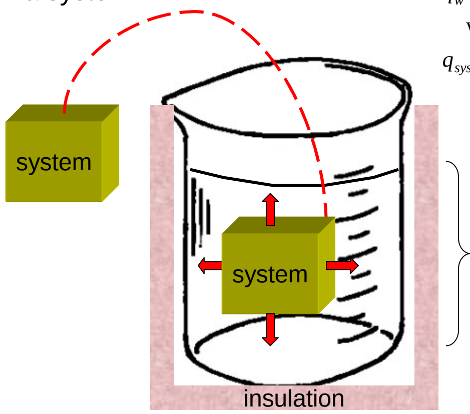
F = gas above boiling temperature



See http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/

Back to Liquid Water's Capacity to Absorb Heat Energy

Measuring heat transferred
from a system



Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

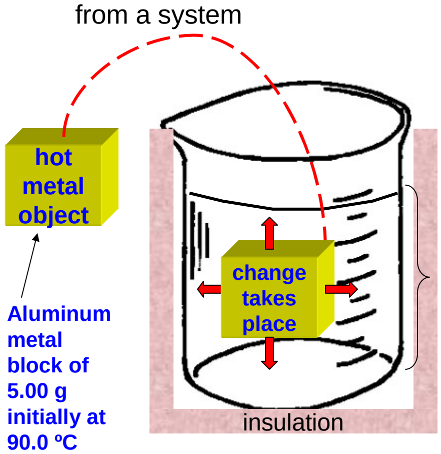
where $\Delta T_w = \textit{temp change of } \mathrm{H_2O}$

q_{sys} *is opposite of* q_w

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

A hot metal block placed in cold water

Measuring heat transferred
from a system



Given information

Initial temperature of Al block = 90.00ºC

Mass of Al block = 5.00 g

Mass of water = 100.0 g

Temperature of water before = 23.00ºC

Temperature of both after = 23.71ºC

C_{water} = 4.184 J/g·K

Question: What is the heat capacity of Al?

Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

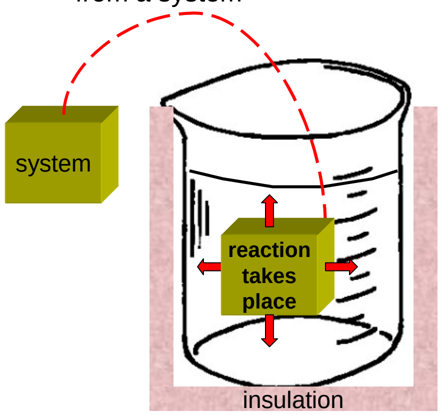
where $\Delta T_w = \textit{temp change of } \mathrm{H_2O}$

q_{sys} *is opposite of* q_w

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

Calorimetry is the same idea

Measuring heat transferred from a system



Problem Solving Strategy

$q_w = m_w C_w \Delta T_w$

where $\Delta T_w = temp\ change\ of\ \mathrm{H_2O}$

q_{sys} *is opposite of* q_w

Given information

Mass of water = 100.0 g

Temperature of water before = 23.3ºC

Temperature of water after = 47.3ºC

C_{water} = 4.184 J/g·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

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

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

Heat Changes More Generally