Introduction to Thermodynamics

Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.1-2.2 of Atkins (7th, 8th and 9th editions)

Basic Concepts

Work
Heat
Energy

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

Last updated: Sept. 18, 2012, minor edit slide 1.

Introduction to Thermodynamics

Thermodynamics: Study of static (i.e., stationary) states of matter and how they differ from one another in terms of energetic quantities.

Thermodynamics gives us a set of rules which applies to any object or set of objects independent of what those objects are, what they were previously, or what they will be in the future.

There are some (relatively) simple assumptions and definitions, and a mathematical framework available, which allow scientists and engineers to take very complex situations and reduce them to relatively simple problems.

Food

Energy

Waste

Applications:
Heating and cooling buildings   Engine efficiency
Batteries (chemical work)   Biological energy transfer
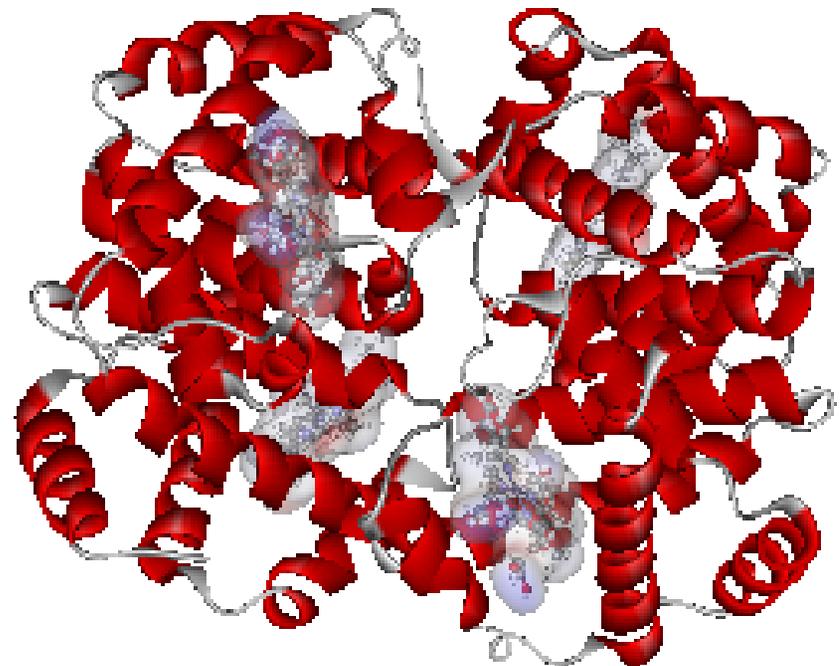Plant/factory design   Insulators and conductors
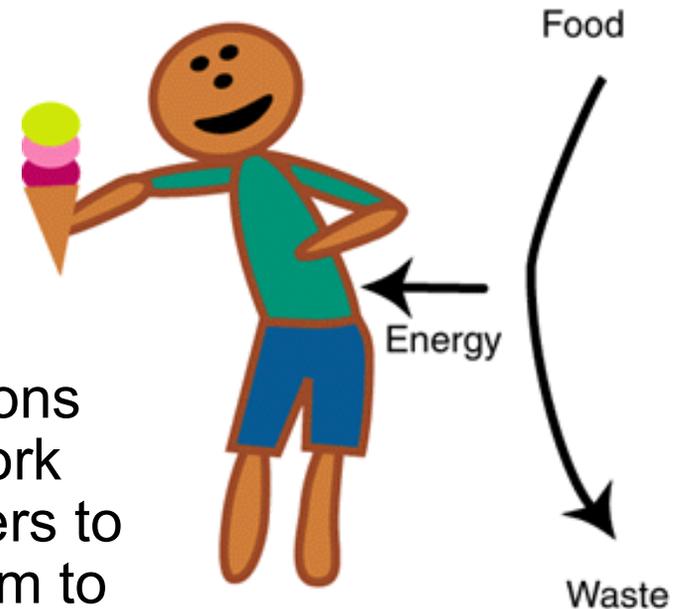
Introduction to Thermodynamics

Thermodynamics: The study of patterns of energy change, where *thermo* refers to heat, and *dynamics* refers to patterns of change

(a)   energy conversion
(b)   directions of change and molecular stability

(a) $U_p = mgh$

$U_p + U_e$

heat, sound, light upon impact

U_e
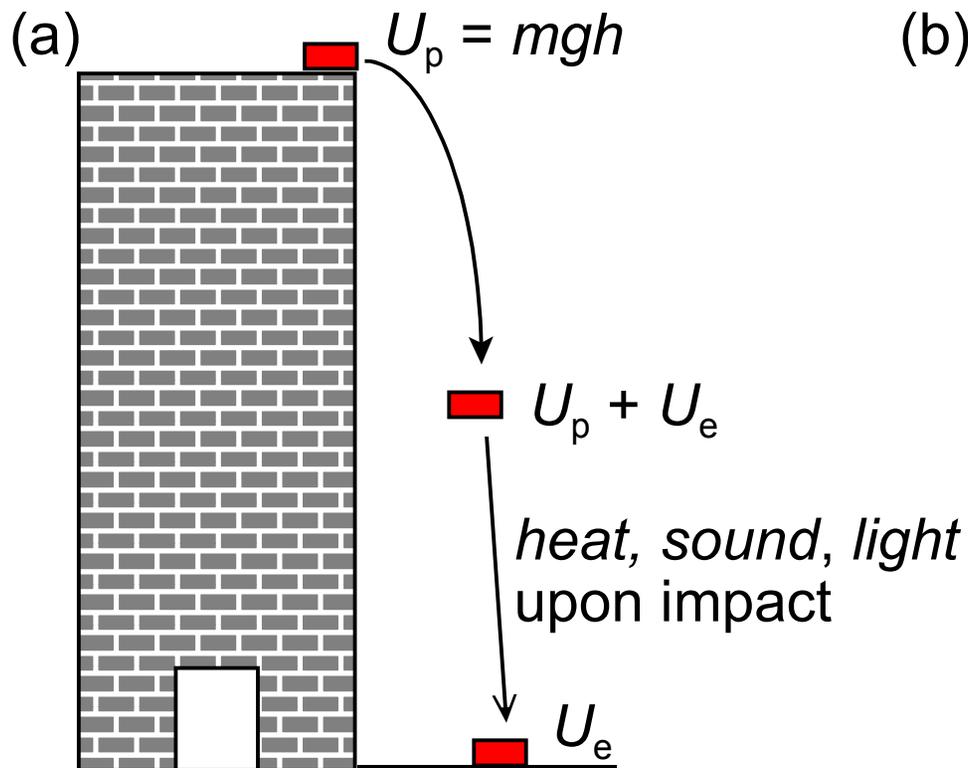
(b) *Protein structure and folding*

Systems and Surroundings

System: The object or region of interest

Surroundings: Everything outside of the system (we do our measuring in the surroundings)

The definition of the system is very dependent upon the **boundaries** which separate the system the the surroundings - i.e., can **energy**, which is the capacity to do work, be transferred between the system and surroundings
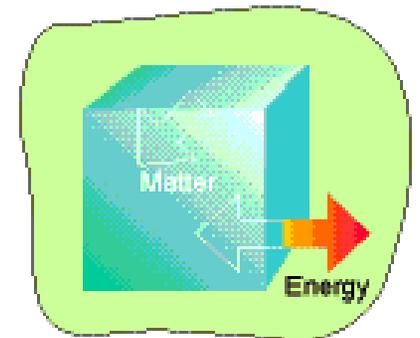
Open: Matter can go in and out of the system

Closed: Matter cannot go in and out of the system

Isolated System: Closed system with no thermal or mechanical contact with the outside world (this is an **ideal system**)
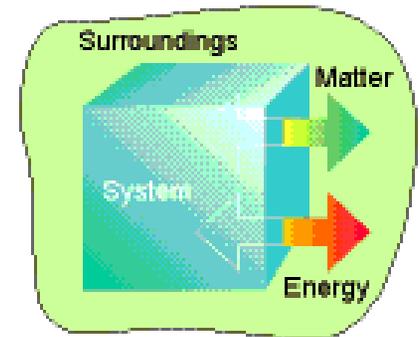

(a) Open

(b) Closed

(c) Isolated

Work, Heat and Energy

Energy: Capacity to do work - the energy of a system can be changed by work and heat **Units**: joules (J) or for molar energy kJ mol^{-1}

Work: A form of energy which can transfer in and out of a system, that is stored in the *organized motion* of molecules. Work is done when an object is moved against some opposing force

Heat: A form of energy which can transfer in and out of a system, that is stored in the *random motion* (**thermal motion**) of molecules. If an energy difference of a system results from a temperature difference between it and its surroundings, energy has been transferred as heat
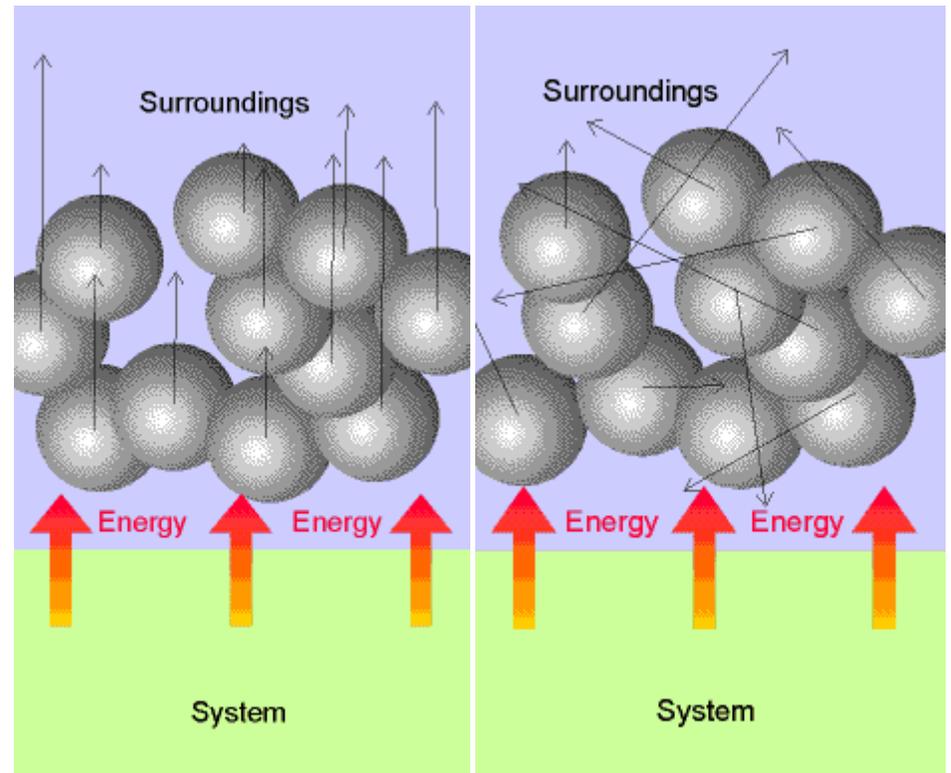
Thermodynamic Definitions of Work & Heat

Work: Work (w) is energy which is transferred across the boundary of a thermodynamic system during a change in its state and which could be converted completely into the "lifting of a weight" in the surroundings (i.e., motion of a mass against opposing force).

Sign conventions for work:

$w_{system} < 0$ Work is done by the system on the surroundings.
$w_{system} > 0$ Work is done on the system by the surroundings.

Heat: Heat (q) is energy which is transferred across the boundary of a thermodynamic system during a change in its state by virtue of a difference in temperature between the system and its surroundings.

Sign conventions for heat:

$q_{system} < 0$ Heat transferred from the system to the surroundings.
$q_{system} > 0$ Heat transferred to the system from the surroundings.

More About Heat

Diathermic (Diabatic) System: A system in which energy is allowed in and out in the form of heat - system in **thermal contact** with surroundings
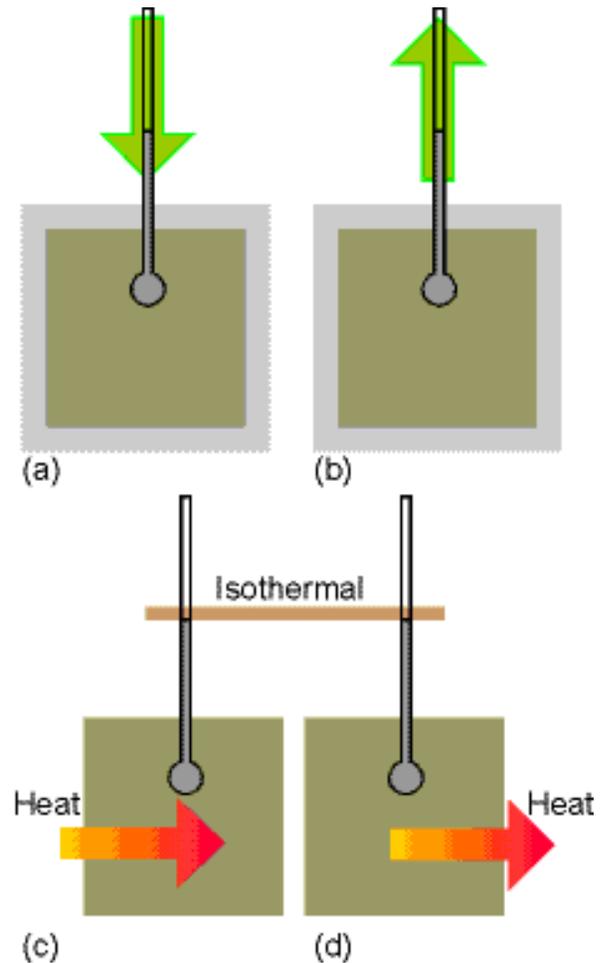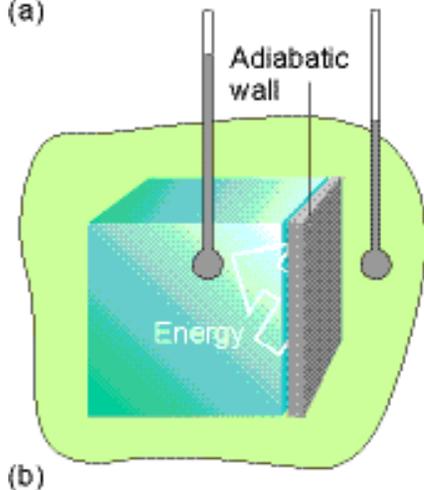**Adiabatic System**: A system in which heat is not allowed in or out
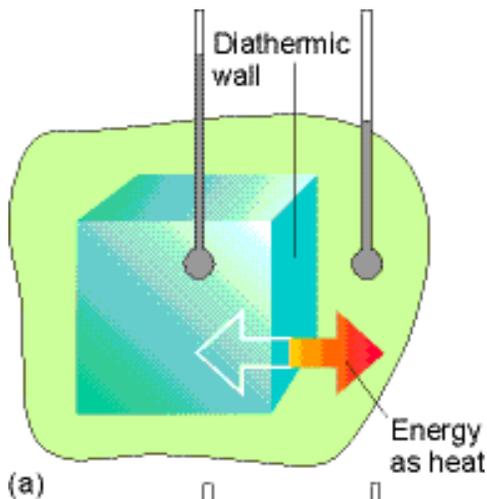
(a) Endothermic Process: Process that absorbs heat

(b) Exothermic Process: Process that releases heat

(c) Endothermic process in a diathermic container: decreases temperature of surroundings

(d) Exothermic process in a diathermic container: increases temperature of surroundings

Internal Energy

Internal Energy (U): total energy of a *system* at any given time - it comes from the total kinetic and potential energy of molecules which compose the system

Change in Energy (ΔU): Change in U as system goes from an initial state with energy U_i to final state with U_f

$$\Delta U = U_f - U_i$$

Internal energy is:

a state function: only depends on the current state, not on preparation of the state.

an extensive property: is dependent upon the amount of matter Properties whose values are increased/decreased in direct proportion to the enlargement/reduction of the system

Recall that an ***intensive property*** is independent of the amount of matter - all of the thermodynamic driving forces are selected from among properties of this type.

Conservation of Energy

Internal energy of a system can be changed by:
  1.   Doing work to the system (w)
  2.   Energy transferred as heat to the system (q)

$$\Delta U \;=\; q \;+\; w$$

Heat and work are equivalent ways of changing the energy of a system

System is like a bank, where currencies can be deposited or withdrawn

If a system is completely isolated from its surroundings: no change in the internal energy takes place: $\Delta U = 0$ (no **perpetual motion**)

Recall:

If heat or work are transferred to the system:
$$q > 0, \; w > 0 \qquad \text{(acquires energy)}$$

If heat or work are transferred from the system:
$$q < 0, \; w < 0 \qquad \text{(releases energy)}$$

James Prescott Joule

James Prescott Joule is the scientist credited with establishing the First Law of Thermodynamics. He was born on December 24, 1818 in Salford, England. As a child, Joule was educated at home, and he never received a formal education. When Joule was fourteen, his father began sending him to weekly chemistry lessons with the famous scientist John Dalton. By 1838, Joule had begun performing his own experiments, and his first paper was published that year. Throughout his life, Joule performed many experiments in the area of thermodynamics, and his determination of the principle of conservation of energy (essentially the First Law of Thermodynamics) is considered to be the chief contribution of the nineteenth century to physical science.

In the past, there was some belief in conservation of matter (except for combustion), and Lavoisier demonstrated this in chemical reactions

The ancient biblical affirmation, "*What so ever a man sows, that shall he also reap*" is, in a sense, a conservation law.

First Law of Thermodynamics

The equation $\Delta U = q + w$ is a mathematical statement of the **First Law of Thermodynamics**, stating that

(i) Heat and work are equivalent forms of energy, and are the only ways to change the internal energy of a system

(ii) Internal energy is conserved in any thermodynamic process in an isolated system, ΔU, since q and w must be zero

Alternative Statement of the First Law of Thermodynamics:

In any thermodynamic process, the internal energy of the universe is conserved, as energy is neither created nor destroyed:

$$\Delta U_{universe} \quad = \quad \Delta U_{system} \quad + \quad \Delta U_{surroundings} \quad = \quad 0$$

This follows from the law above, since the universe can be considered an isolated system.

First Law of Thermodynamics, 2

Energy is a property of any system, and changes in this property can be deduced from the *conservation-of-energy* principle. The work needed to change an *adiabatic system* from one specified state to another **is the same however the work is done** (*mountain climbing analogy*)

So, internal energy can be measured by measuring work needed to bring about change in an adiabatic system

If 1 kJ (kilojoule = 1000 J) of work is done by stirring a system, or 1 kJ of electrical work is done by passing current through a heater, the same increase in energy (and therefore rise in temperature) is produced
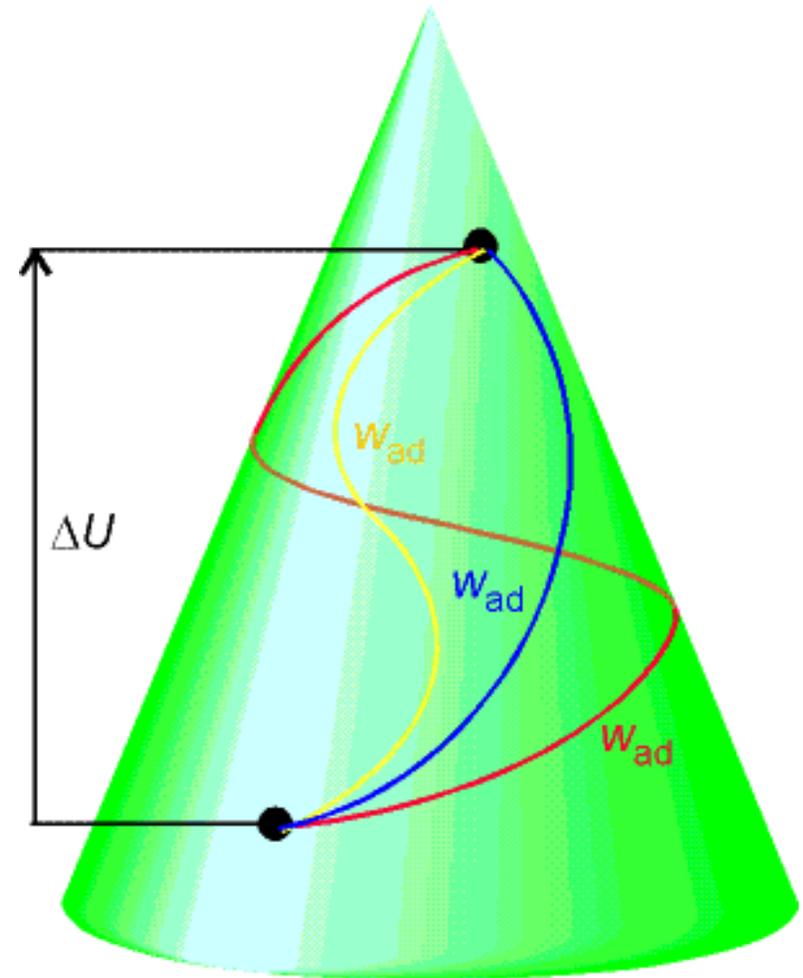
Mechanical Definition of Heat

Imagine that our system is not purely adiabatic (thermal insulation is not very good). The change in U, the internal energy, may be the same before (state function), but *more work* is required to make the same kind of change in energy:

> e.g., 42 kJ of work is done in an adiabatic container; however, to achieve the same change of state in a diathermic container: 50 kJ of work is required

The system is absorbing heat if $q > 0$ $\qquad q = w_{ad} - w$

q = 42 kJ - 50 kJ = -8 kJ   (8 kJ is lost from the system as heat)

Since ΔU is by definition equal to w_{ad}, the expression for energy transferred to a system as heat is

$$q = \Delta U - w$$

which is the same as the expression for the First Law, $\Delta U = q + w$

Applications/Processes of Thermodynamics

The *First Law* works differently for a process in which the volume stays constant than for a process in which the pressure stays constant

Isochoric Process
The volume of the system remains constant ($\Delta V = 0$). On a pV diagram, this type of process would be represented by a vertical line. Therefore, there is no area under the curve.

Since there is no change in volume, $w = 0$. So the internal energy of the system depends only on heat transfer.

$$\Delta U = q_V$$

Isobaric Process
The system's pressure is fixed ($\Delta p = 0$). It is represented by a horizontal line on a pV diagram.

Both w and q will still exist for this process.

$$\Delta U = q + w$$

Applications/Processes of Thermodynamics

Adiabatic Process
There is no transfer of heat to or from the system, $\Delta q = 0$, though other characteristics such as the pressure, volume, and temperature of the system may vary. The curve of an adiabatic process on a pV diagram depends on the changes in the system.

$$\Delta U = w_{ad}$$

Isothermal Process
The system's temperature is fixed ($\Delta T = 0$). It is represented by a pV diagram and energy stays constant ($\Delta U = 0$)

$$q = -w$$

Cyclic Process
Certain processes have the same initial and final states (e.g., engines). This is represented by a closed path and $\Delta U = 0$

$$q = -w$$

Molecular Interpretation of Energy

Energy of one atom of a monatomic perfect gas at temperature T:

$$E_K = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

According to Boltzmann, average energy of each term is $\frac{1}{2}kT$; mean energy of atoms is three times this, with total energy $(3/2)NkT = (3/2)nRT$

$$U_m = U_m(0) + \frac{3}{2}RT$$

here $U_m(0)$ is the **internal molar energy** at $T = 0$ (no translation) - so energy can also come from internal structure of atoms

If gas has polyatomic molecules, they can rotate about 3 axes as well, for an additional energy contribution of $(3/2)RT$ (E inc. 2x as rapid as above)

$$U_m = U_m(0) + 3RT$$

Vibration cannot be treated classically - separations between energy levels are very wide - can derive, with the Boltzmann distribution:

$$U_m = U_m(0) + \frac{N_A h\nu}{e^{h\nu/kT} - 1}$$

The right term inc. with temperature, and approaches RT when $kT >> h\nu$.
T is increased: internal energy increases: various modes of motion are excited