Einstein on Thermodynamics:

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me."

"It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, *it will never be overthrown.*"

--Albert Einstein

http://www.eoht.info/page/Thermodynamics+humor

In one episode of the *The Simpsons*, after Lisa constructs a perpetual motion machine whose energy increases with time, Homer scolds her with:

"In this house, we obey the laws of thermodynamics!"

****

In the late 1940s, German theoretical physicist Arnold Sommerfeld, having previously written a series of books in physics: mechanics (1943), electrodynamics (1948), optics (1950), etc., was asked why he had never written a book on thermodynamics? The following is his humorous (but fairly accurate) and frequently quoted answer:

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all.

The second time you go through it, you think you understand it, except for one or two small points.

The third time you go through it, *you know you don't understand it*, but by that time you are so used to it, it doesn't bother you anymore."

3 LAWS of THERMODYNAMICS

1st Law: The Energy (of the Universe) is conserved.

2ndLaw: The Entropy (disorder) of the *Universe* increases during all natural processes!!!

3rd Law: Entropy of a perfect crystal at zero Kelvin = 0.

(Note the EMPHASIS on 2nd Law)

(The 3rd Law is nice, but not needed)

What is a Law of Nature (or Scientific Law)?

“A scientific Law is a regularity observed in nature and formulated after a very large number of observations”

[by many, many people in many different laboratories at many different times]

“Because they are solidly grounded in experimental observations, scientific laws are sometimes modified after further experience, but they are rarely refuted”

from Page 13 of our Textbook.

There is another law of thermodynamics that is sometimes stated explicitly in textbooks and sometimes not: **all the people of the world are constantly doing the experiments that check this Law for its validity:**

The Zeroth Law of Thermodynamics:

Heat does not flow spontaneously from a cold object to a warmer object.

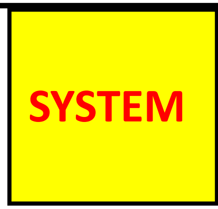
This law was invoked in establishing the all-important 2nd Law.

Next: Language and definitions of Thermodynamics

Very important definitions: “system” and “surroundings”

System: whatever you want it to be

Surroundings: everything else



surroundings = (what is ***NOT*** system)

System is anything you can define with a boundary

e.g., a cell, beaker of water, a cat, earth + atmosphere, solar system, etc.

System + Surroundings = “universe”

What do we mean by “universe”?

Even if we enclosed our GALAXY (or even the Solar System) with an insulating, impenetrable shield, we would not notice a difference in our lifetime.

Types of systems (boundaries)

Isolated: Exchanges no energy and no matter
(sealed, insulated, no mechanical connection)
i.e., **a little "universe"**

Closed: Exchanges energy but no matter
(sealed balloon of gas)

Open: Exchanges energy ***and*** matter
(hen's egg, a cell)

More Language (vocabulary) for Thermodynamics

First Law: The ENERGY (U) of the "universe" is constant (conserved)

First Law: $U_{syst} + U_{surr} = U_{universe} = \text{constant}$

notation: $U \quad + \; U_{surr} = \text{constant}$

(Note: **no subscript** means **system** ;

But, can only know ***CHANGES*** (no such thing as absolute energy)

"Process" means the system changes state: state 1--> state 2

(*different temperature, volume, pressure, chemical nature, etc.*)

state 2: $U_2 \; + \; U_{surr2} = U_{univ}$

state 1: $U_1 \; + \; U_{surr1} = U_{univ}$

Difference = $(U_2 - U_1) + (U_{surr2} - U_{surr1}) = 0$

$\Delta U + \Delta U_{surr} = 0$ therefore: $\Delta U = -\Delta U_{surr}$

$\Delta U = -\Delta U_{surr}$ is a statement of the 1st Law

In 1850: The System was a black box (an engine, a cat, ...)
(They did not know what goes on in the system. Today we do know much more, typically, but should pretend it is a black box when working problems in thermodynamics.)

WE are in the surroundings; **we** observe energy going in or out of the system.

WE measure two kinds of energy exchange as observed in the **SURROUNDINGS**.

Heat = q (measured by **temperature** change
Work = w (measured by ***mechanical*** change

NEVER decide q and w by what you think is going on in the system

The First Law in its most-used form:

$\Delta U =$ q + w (eq. 2.26, p. 24)

$\Delta U =$ heat + work

Energy change of system during process

Energy absorbed by system because of temperature difference between system and surroundings.

Something in the surroundings *must get colder or hotter,* or else q = 0

Energy absorbed by system because of a *force acting in surroundings*.

Something in surroundings must *move* (or some mechanical happening that could cause something to move, e.g., charging a battery.)

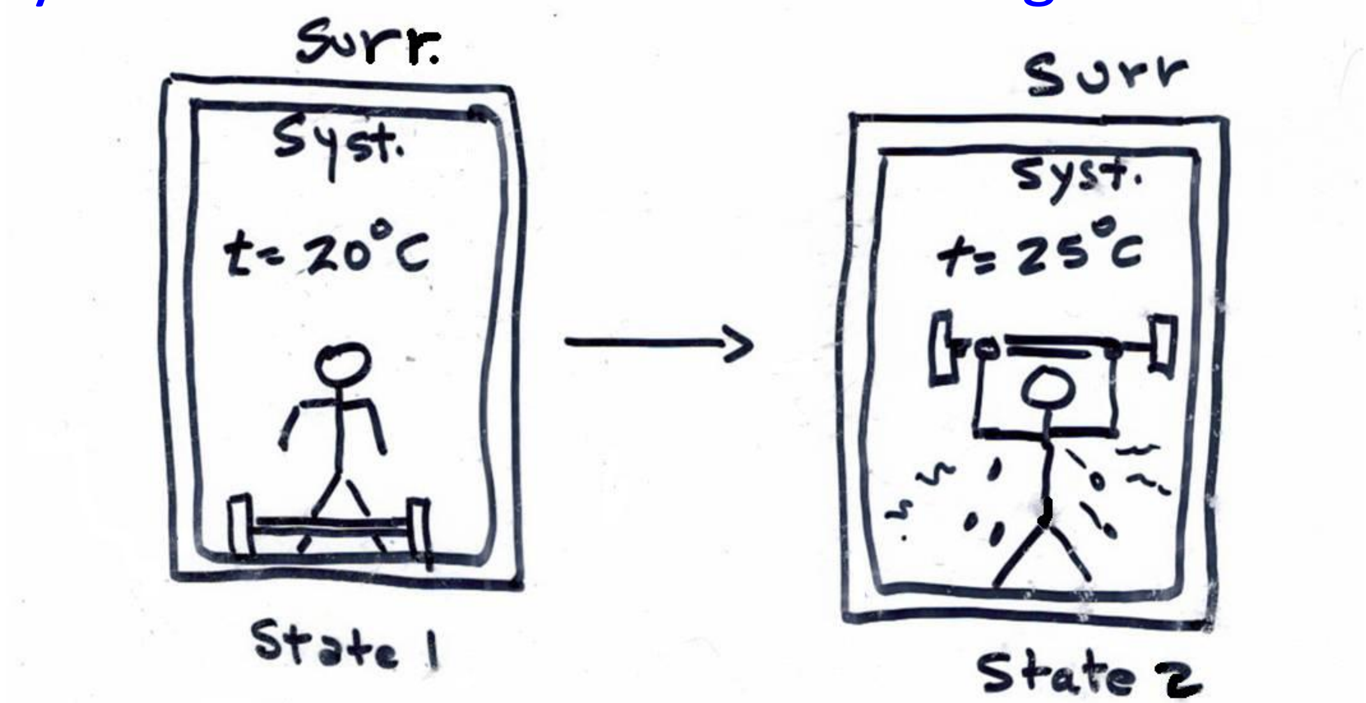
<u>FOR ANY PROCESS:</u>

If q = + we say it is **ENDO**thermic
If q = - we say it is **EXO**thermic

If w = + we say work is done **ON** the system
If w = - we say work is done **BY** the system

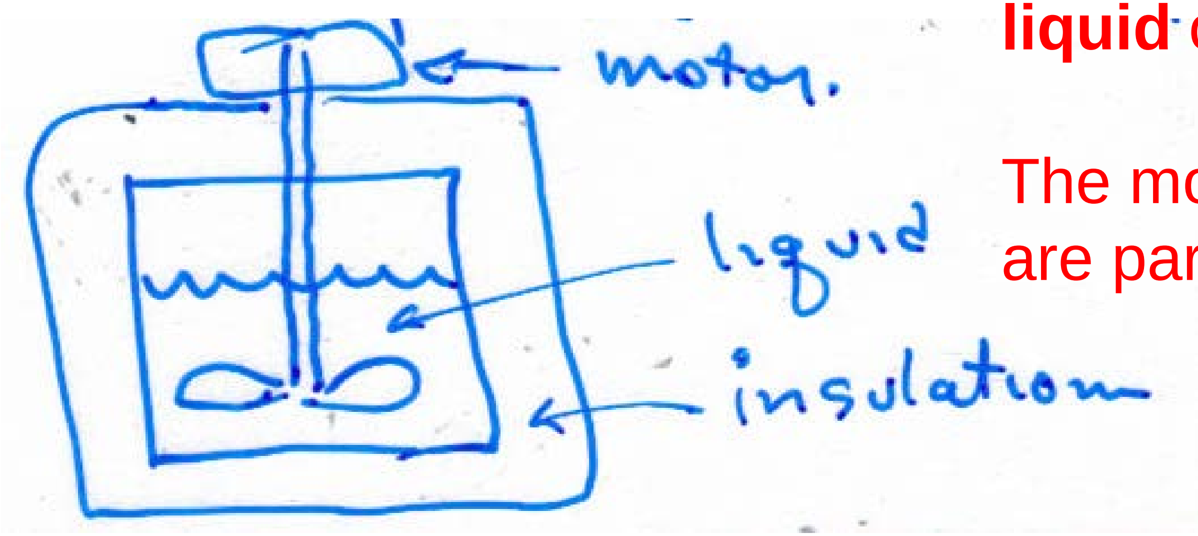
A little quiz

System = **insulated** room with weight lifter



Weight lifter **works** out and the room **heats** up from 20° C to 25° C

Are ΔU, q, w positive, zero, or negative?



The system is the **liquid** only.

The motor and propeller are part of surroundings

Liquid in a thermally insulated container is stirred vigorously and its temperature is found to increase by 10 ^{o}C due to friction.

Tell whether q,w, and ΔU are +,-, or zero

Now consider the **same system** of water, but **NOT insulated**, in contact with a hot iron until the temperature rises by 10 ^{o}C.
The water is the system and the iron is in the surroundings

Tell whether q,w, and ΔU are +,-, or zero

Work was **originally** defined as positive when done **BY** the system
In old chemistry books and in most engineering texts one sees:

$$\Delta U = q - w$$

Is this wrong?

What is the definition of w in this case?

w is defined as work obtained FROM the system if we use the above equation.

$$\Delta U = q + w$$

is now the accepted convention

Calculating Work

work = w = external force x distance

(if the force is constant)

between the system and surroundings

displacement in the system

The ***sign*** depends on whether system expands or contracts in response to the force.

What if the force is NOT constant?

$$\text{a very small amount of work} = dw = f_{ext}(x)dx$$

where *dw* and *dx* mean infinitesimally small (but we can think of this as just meaning really, really, really, small);

***$f_{ext}(x)$* means the force is NOT CONSTANT, but depends on x.**

Now just add up all the small bits:

$$w = \int_{x_1}^{x_2} f_{ext}(x)dx$$

Constant Force Case

$$w = f_{ext}\int_{x_1}^{x_2} dx = f_{ext}(x_2 - x_1) = f_{ext}\Delta x$$