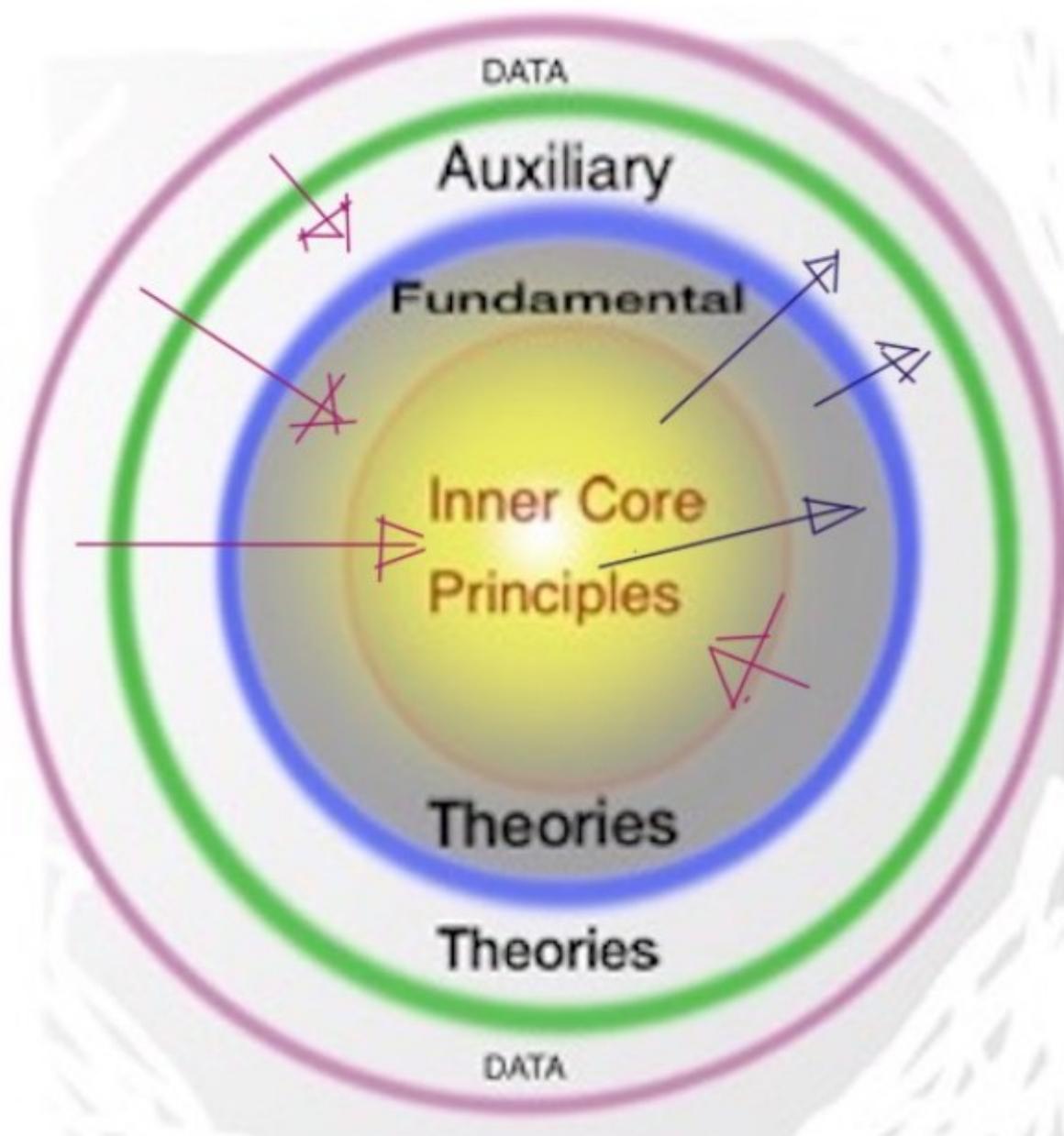


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Lakatos "Scientific Research Programme"

black arrows indicate direction of foundation information flow; red arrows indicate

direction of feedback information flow.

(Diagram made by RJK)

]

“To develop a complete mind: Study the art of science; study the science of art. Learn how to see. Realize that everything connects to everything else”

—Leonardo DaVinci

SECTION 1: Elements of the Physics of Motion

1.1 INTRODUCTION

This section is for those students who don't remember (or perhaps never were taught) elementary physics. I hope to give qualitative notions of some basic concepts in physics and to do so with a minimum of mathematics, using pictures, animations and links to available explanations on the web. So, dear reader, imagine you're living in pre-Renaissance Europe, and are listening to those Medieval monks explain what they think about motion, and how it differs from what Aristotle had to say.

1.2 DISTANCE, VELOCITY, ACCELERATION

First, let's consider **distance**. I believe you readers have an intuitive notion of what distance is: you draw a straight line between point A and point B and the length of that line is the distance between points A and B.¹

What is **velocity**, then? Velocity is a rate, distance per time. (And, to be fussy, velocity has direction; “speed” is the magnitude of velocity; you don't care what the direction is; velocity is “speed” plus direction.)

Now I ask your pardon, dear reader to bear with me while I inject just a little math to make the concept clear. Suppose it's four miles to the nearest rest stop on the thruway and you must get there in five minutes (or less-I won't ask why). How fast do you have to travel or what should your car's velocity be? Your rate of travel, speed, must be four miles in five minutes, or 4miles/ 5 minutes, or as it would be written conventionally, 4/5 miles/minute; in other words, distance divided by time. Since there are 60 minutes in an hour, a little arithmetic shows you would have to travel 60x (4/5) miles/hour or 48 mph². And here's an equation (again, pardon)

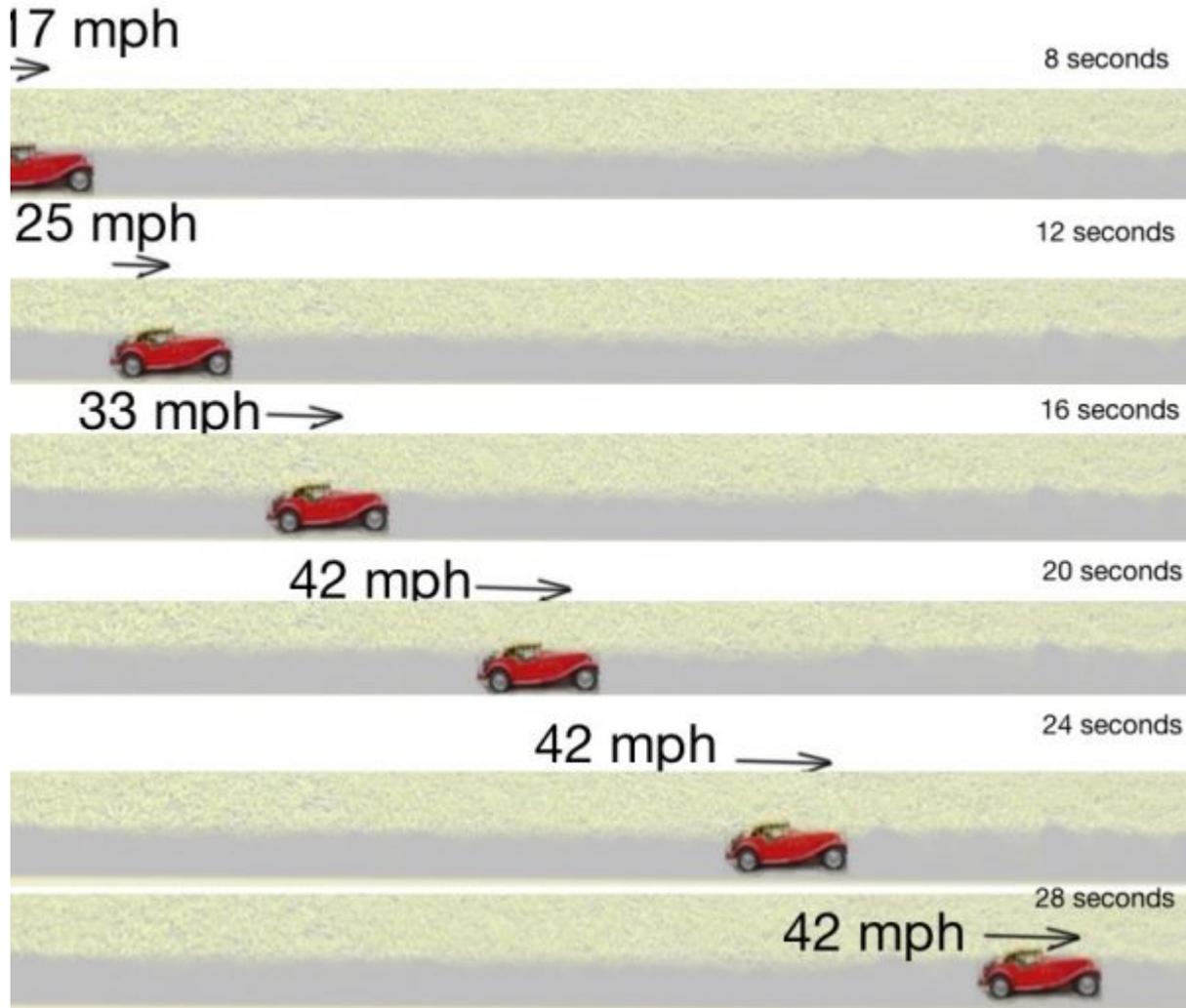
$$v = d/t \quad \text{where } v \text{ is velocity, } d \text{ is distance and } t \text{ is time to travel that distance}$$

What is **acceleration**? It's also a rate, the change in velocity divided by the corresponding change in time. Let's turn again to an example with some numbers. Fresh out of grad school I bought a MG TD (red, no less!). The MG was not, to use my grandson's lingo, "zippy." From a standing start, it could get to a speed of 42 mph in about 20 seconds (real sports cars take only about 5 seconds to get to 60 mph). This acceleration rate corresponds happily (for nice numbers) to about 1 (m/s)/s or 1 m/s². So we have **acceleration, a**, given by the gain in velocity over the time, t, it takes to achieve that change:

$$\mathbf{a = (change\ in\ v) / t}$$

Here's an illustration to give you some notion of what acceleration and velocity look like. It's the MG TD performing as above, going from 0 to 42 mph in 20 s and thereafter at the constant speed of 42 mph. The shots correspond to 4 s intervals from 8s to 28 s.

Velocity Profile for Acceleration, $a = 1 \text{ m/s}^2$

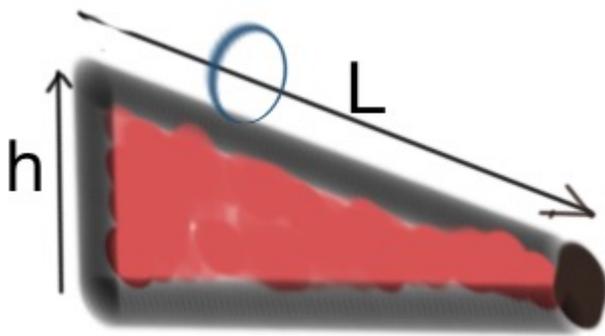


Velocities at 4 second intervals from 8s to 28 s. Acceleration is 1 m/s^2 , to get to 42 mph in 20 s. Acceleration ceases at 20 seconds, so velocity is constant from 20 seconds to 28 seconds; the speed is listed above each car image; the arrow length corresponds (roughly) to the velocity:

An easy way to think about constant acceleration is that the distance covered in a given time is average velocity multiplied by the time. The average velocity is just $(1/2)(v_{\text{beginning}} +$

v_{end}).³

As pointed out in ESSAY 1, SECTION 3.2, Nicolas Oresme had derived these relations between velocity, distance and acceleration by a graphical analysis, 100 years before Galileo. However, it was Galileo who did the science: confirmed the theory by experiment.



Inclined Plane used by Galileo to measure relation between distance, velocity and acceleration

How did Galileo set up an experiment where the motion would be slow enough for him to measure time, distances and speed?

Acceleration of falling bodies would be too fast.

Here's the experiment, done in elementary physics lab classes. An inclined plane, as in the illustration below, length L , is set up so that the top end of the plane is a height h above the ground. A ball or cylinder rolls down the plane and you measure distance traveled in given times. Now if the plane were to be vertical ($h=L$), the ball would fall with an acceleration that of gravity (9.8 m/s^2) and that would be too fast. If the plane is flat ($h=0$), the ball would not roll at all (hey! that's poetry?).

Clearly the acceleration is going to vary as the height h changes. It turns out that the acceleration is proportional to h/L . It will be the same—independent of size or material—for a given shape sliding or rolling down the plane.

1.3 MOMENTUM

How do objects acquire velocity, that is accelerate? Buridan in the 14th Century had ideas about velocity that anticipated Galileo and Newton centuries later. He said that a moving body had "impetus," the heavier the body moving at a given velocity, the more impetus it had. If you threw a ball, the motion of your arm gave the ball its impetus. "Impetus" is what we now call "momentum" and define as

$$\text{momentum} = \text{mass} \times \text{velocity}$$

Mass is what we ordinarily think of as weight, but to be fussy, weight is really mass times the force of gravity. You can think of mass as resistance to change in motion, what would technically be termed "inertia."

Here's an example to give you some intuitive notion about momentum: the MG TD referred to above is a very light car, weighing only about 1/2 ton (1000 pounds); a late model Cadillac is much heavier, weighing about two tons. Accordingly, the mass of the Caddy is about four times greater than that of the MG. So, if the MG were traveling at 40 mph and the Caddy at $(1/4) \times 40 \text{ mph} = 10 \text{ mph}$, they would have equal momentum (if they were traveling in the same direction—remember, velocity has direction, speed does not). This is illustrated below.



Caddy (top) is moving 1/4 as fast as MG(below) but has 4 times the mass; so the momentum of the Caddy and the MG are the same.

1.4 FORCE

What causes a body to accelerate, acquire velocity? Again, Buridan had the right qualitative notion: the body acquired impetus because of an action by an agent, you, throwing the ball with your arm. In this notion there is an implied notion of force, which Newton (17th century) made explicit by his [Second Law of Motion](#):

$$\text{Force} = \text{mass} \times \text{acceleration}$$

more generally if mass doesn't stay constant (think of an example involving liquids!)

Force = change of momentum/change of time

For the first definition, go back to the example of the accelerating MG: the force is provided by friction between the tires and the road, the tires—wheels—are made to go round by the engine turning a drive-shaft.

For the second definition, think of a pitcher winding up and releasing a baseball moving at 90 mph as depicted in [this video](#). The baseball has a mass of about 0.15 kg (or about 0.3 lbs) If you go frame by frame in the video, you'll see that it takes less than 10 ms (0.01 s) for the pitcher to start his windup and release the ball; that's the change in time for the baseball to acquire its velocity of 90 mph (we'll neglect air friction slowing the ball down). So, fussing with units—I don't need for you all to mess with the arithmetic—you get a force of about 650 Newtons required.

For comparison, the force of gravity on the baseball is about 1.5 Newtons. If air friction is neglected, from what height would the ball have to fall to get this 90 mph velocity? About 100 yards. Why the greater force to throw the ball this fast? Because the force of the throw is acting for only a short period of time, during the pitcher's windup, whereas gravity will be acting all during the fall.

1.5 KINDS OF ENERGY; CONSERVATION OF ENERGY

1.5.1 Kinds of Energy: Examples

There are two other physics concepts that bear on motion; these are energy and work. I'll talk about "Work" in Section 1.6, below, but here are some ideas about the different kinds of energy. To get an intuitive idea of this, let's discuss how the MG acquires velocity.

fuel is burnt in the cylinders to move the pistons up and down; this is done by the expansion of combustion gases in the piston;

the pistons moving up and down rotates the shaft that turns the rear wheels around; there is friction between the rubber on the tires and the road; this friction makes the car move forward when the wheels rotate.

Thus chemical energy from the gasoline combining with oxygen (burning) is converted to mechanical energy. There are various kinds of energy: motion, chemical, light, sound, heat, electrical. [This video](#) shows how different forms of energy can be transformed.

1.5.2 Kinetic Energy: Energy of Motion

The energy of motion is called “**kinetic energy**” and is given by the formula

$$\text{Kinetic Energy} = (1/2) \text{ mass} \times \text{velocity}^2 \text{ (the “}^2\text{” means “squared”)}$$

1.5.3 Potential Energy: Energy due to Position; Change of Potential to Kinetic Energy

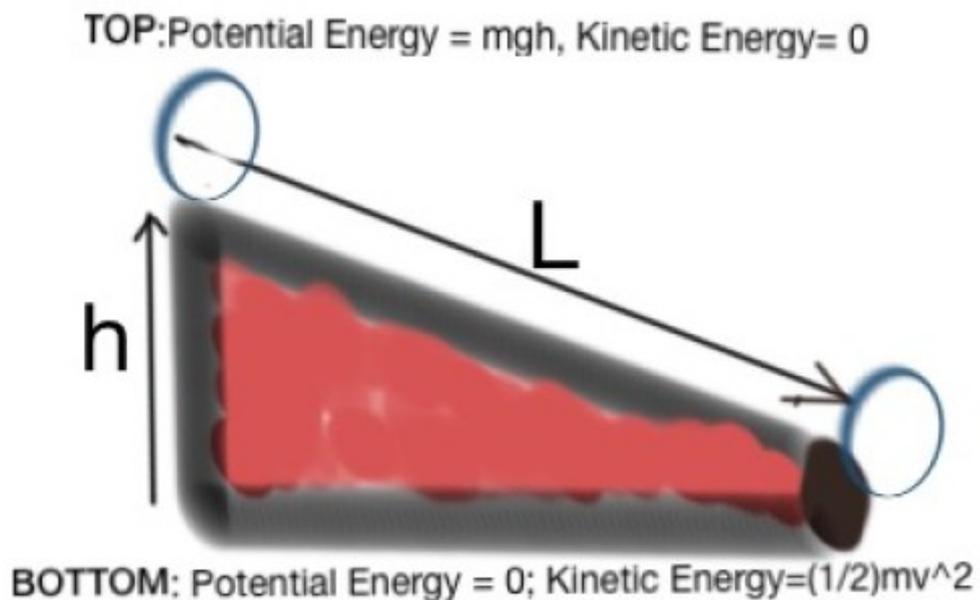
Another important form of energy is “**potential energy**,” energy a body has by virtue of its position. Let’s think about what this means. When you let a ball roll down an inclined plane it has zero kinetic energy at the top and kinetic energy at the bottom after it has accelerated due to gravity and thus acquired velocity. So where does that kinetic energy come from? To balance the energy books we say the ball at the top of the plane has potential energy that can be converted to kinetic energy. This potential energy is given (for gravity at the surface of the earth) by

$$\text{Potential Energy} = \text{mass} \times g \times h = mgh$$

where g is the acceleration due to gravity (9.8 m/s^2), h is the

height above the bottom

This is illustrated below:



Potential Energy Changed to Kinetic Energy as Ball Rolls down the Inclined Plane.

An important principle of physics is that **energy is conserved**. What does that mean? It means that energy doesn't disappear into nowhere, for example:

If kinetic energy, energy of motion, is lost due to friction, it is converted to the same amount of heat energy;

If kinetic energy, energy of motion, is lost due to making an increase in potential energy, for example, an MG moves up a hill without using its engine, the gain in potential energy is equal to the loss of potential energy.

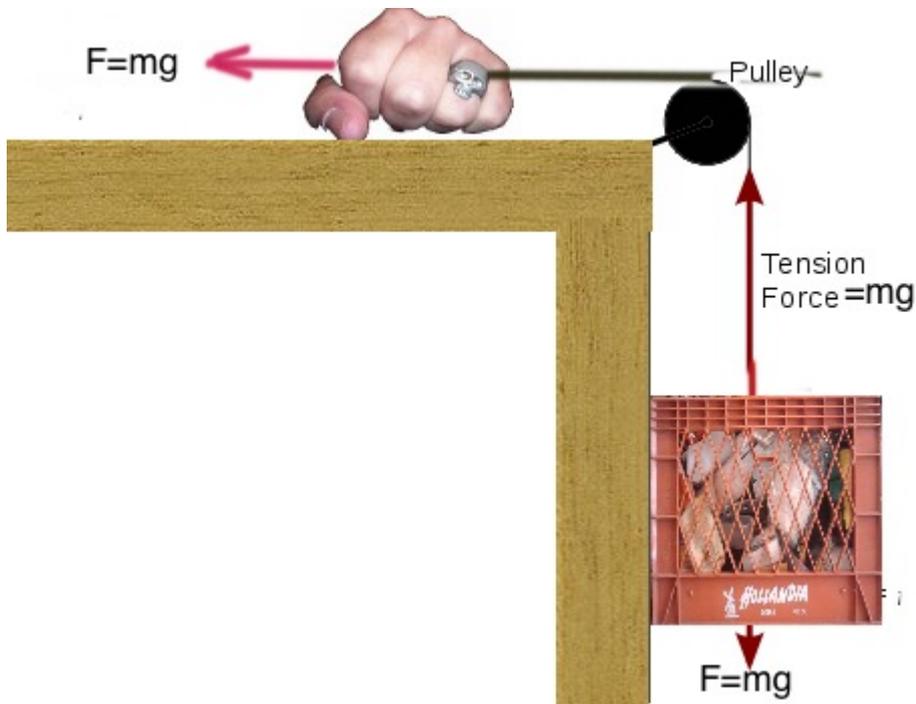
chemical energy of the gasoline is converted to kinetic energy less friction losses in the engine, drive shaft, and on the road, as the MG moves along a level road.

Accordingly, the energy bank account balances: input (at the beginning) of chemical energy, gasoline in the fuel tank = kinetic energy at the end of the drive, when the fuel tank is empty + energy lost due to friction of the tires with the road, engine and drive shaft friction + work done due to a net change in height level at the end or gain in potential energy. One important concept that deals with how energy is lost or gained is “Work,” discussed next.

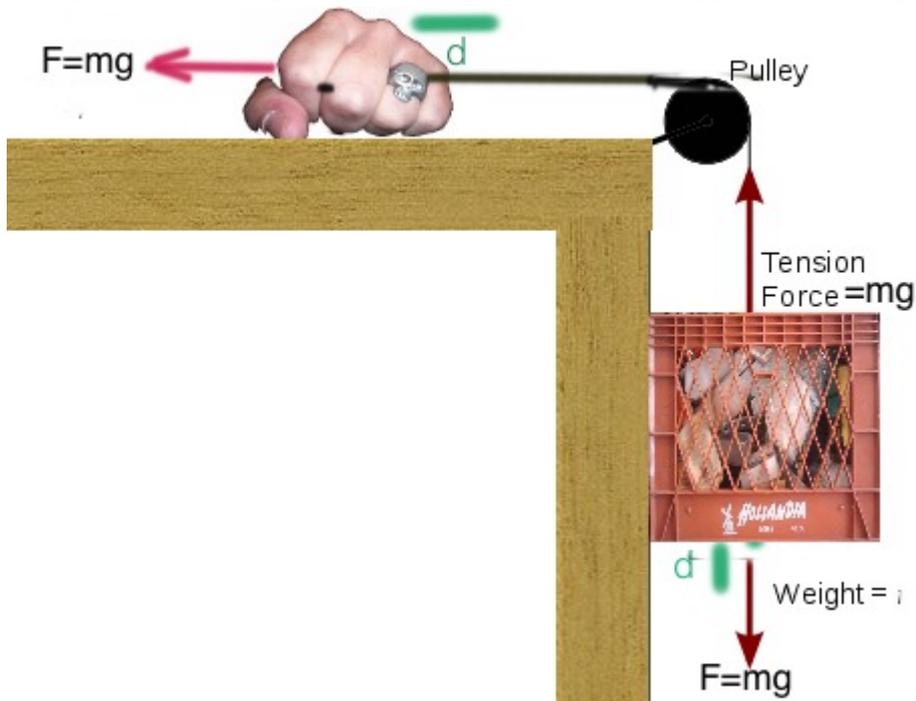
1.6 WORK

What do we mean in physics by the term “work”? It means applied force times distance moved. If you apply a force—push against a stone wall—but don’t move the wall, you may work up a sweat, but you haven’t done any work. These ideas are illustrated below. In the two diagrams below, a basket is moved up a distance d . The force applied is the weight, mg , due to gravity: $F=mg$; the distance moved is “ d .” So the work W is given by

Work = applied force times distance moved or $W = mg \times d$

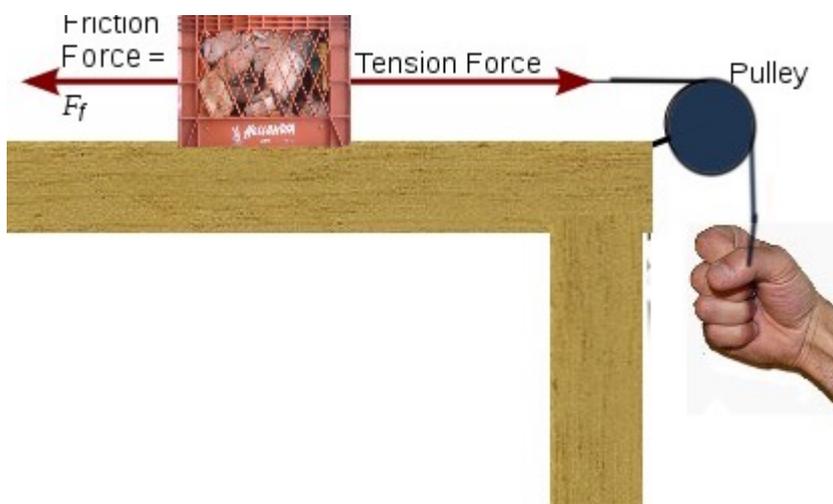


weight (basket) before being lifted. The basket is at height h above ground. The potential energy is then mgh .

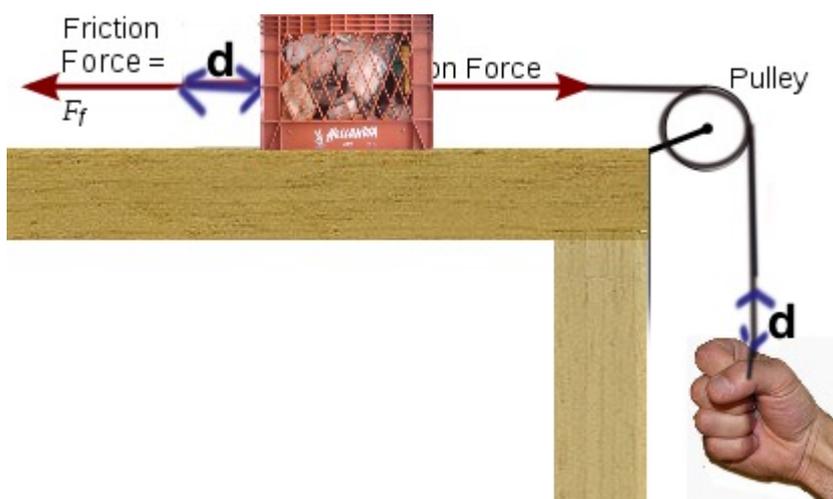


basket after being lifted a distance d . the basket is now a height $h+d$ above the ground and the potential energy is $mg(h+d)$

In the next two diagrams the basket is moved across a table against a resisting frictional force, F_r . Again the basket moves a distance d , so the Work done on the basket is $W=FrXd$.



Basket before being moved.



Basket after being moved a distance d against a

frictional force F_r .

I should emphasize that the examples given are for “mechanical work. I also want to emphasize again that doing work is more than exerting a force. Work is force times distance force moved.

1.7 WORK, HEAT AND ENERGY

To repeat: there are many kinds of energy: for example, *mechanical (motion); electrical; magnetic, chemical, heat*. All these forms of energy can be converted to work and work can be changed into these several forms of energy. (See [this interesting video](#) about conversion of different forms of energy and the conservation of energy.)

In the first example above, a basket is pulled up a distance d against the force of gravity, mg .

before the lift the potential energy was mgh ;

after the lift the potential energy was $mg(h+d)$ (the height above the ground of the basket has increased to $h+d$)

so the difference (after – before) is just mgd , is the increase in potential energy;

but this is just the *work done*, mgd , force \times distance, done in lifting the basket.

In the second example the work done does not increase the potential energy of the basket—it’s still at the same height. Where has the energy which should have been produced by the work gone? Recall that the basket moved against a frictional force. What form of energy is produced by friction? Heat! An account of Joule’s experiment on the conversion of work to heat: is given in Section 2.2

In SECTION 2, I’ll have more to say about the science of energy, “Thermodynamics,” particularly these two important laws: **The First and Second Laws of Thermodynamics.**

1.7 NOTES

¹Let me add a cautionary note physicswise: if you are traveling between A and B (home and the local fast-food place, let's say) and you wander around, make side-trips, the distance is still the length of the line between beginning and ending points. If you want to get total mileage traveled, then you have to draw straight lines between each of the intermediate starting and stopping points and add the lengths up.

² Since each hour contains 60 minutes, you would have to go $60 \text{ (minutes/hour)} \times (4/5) \text{ (miles/minute)}$ or $60 \times (4/5) \text{ (miles/hour)} = 48 \text{ (miles/hour)}$.

³For our example, the distance covered by the accelerating MG between 12 seconds ($v_{\text{beginning}} = 25 \text{ mph}$) and 16 seconds ($v_{\text{end}} = 33 \text{ mph}$) is just

$(1/2) (25+33) \text{ (miles/hour)} \times (1 \text{ hour} / (3600 \text{ seconds})) \times (16-12) \text{ seconds}$ or about 56 yards

SECTION 2: Thermodynamics, the Science of Energy

"It looks full of hard words and signs and numbers, not very entertaining or understandable looking, and I wonder whether it will make people wiser or better." So wrote a cousin of Josiah Willard Gibbs when she happened onto a copy of his most famous paper on thermodynamics lying on his desk."

—As quoted from [Order and Chaos](#), by Stanley Angrist and Loren Hepler.

2.1 INTRODUCTION

From the uncoiling energetics of DNA to the information lost into black holes, thermodynamics enters into every field of science. The Second Law of Thermodynamics, all

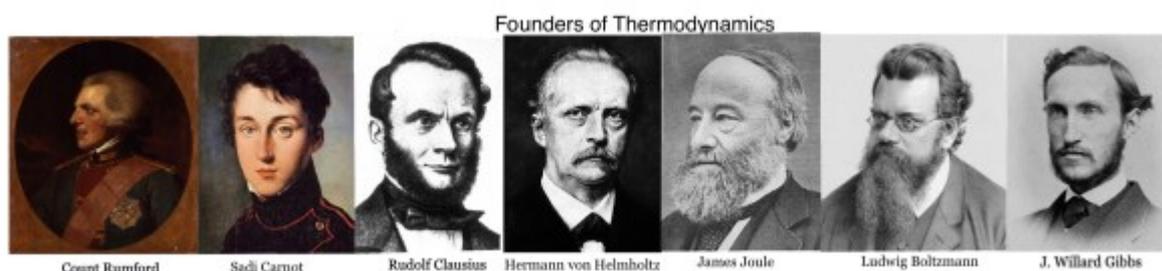
about order and disorder—you can't (realistically) unscramble eggs—is perhaps the most fundamental of those principles at the inner core of the Lakatos sphere. Einstein's comment about thermodynamics says it all:

“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. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.”

—[Albert Einstein](#) (author), Paul Arthur, Schilpp (editor). Autobiographical Notes. A Centennial Edition. Open Court Publishing Company.

In this section I'll try to explain some fundamental concepts in thermodynamics and to explore what the First and Second Laws of thermodynamics tell us about the world. Before doing that a brief account of how thermodynamics developed is in order.

2.2 A BRIEF HISTORY OF THERMODYNAMICS

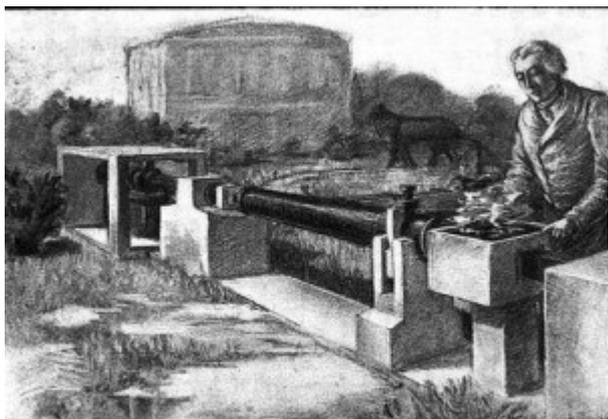


The pictures above are of scientists who developed thermodynamics in the 19th century: beginning with the American (but a Loyalist) Benjamin Thompson, Count Rumford, who showed by his cannon-boring experiments that heat was not a substance (the “caloric”) but

something else, not conserved; and ending with the American, Josiah Willard Gibbs, who developed a theory, statistical mechanics, that explained thermodynamics in terms of molecular motions and probability (capping theories by Maxwell and Boltzmann). Gibbs also developed an elegant mathematical form for the laws of thermodynamics.

I'll discuss briefly how each of these scientists contributed to the development of thermodynamics.

History of Thermodynamics: Count Rumford: Cannon Boring → Heat Not Conserved.



*From Elmer Burns' illustrated 1910 book
"The Story of the Great Inventions"
(See Project Gutenberg .)*

Count Rumford's Cannon-Boring Experiment-Making Water Boil

In 1798 Benjamin Thompson, Count Rumford, submitted a paper to the Royal Society about his experiments in which boring a cannon could make water boil, and boring with a blunt instrument produced more heat than with a sharp one (more friction with the blunt). The experiments showed that repeated boring on the same cannon continued to produce heat, so clearly heat was not conserved and therefore could not be a material substance.

This experiment disproved the then prevalent theory of heat, that it was a fluid transmitted from one thing to another, "the caloric." The results validated another theory of heat, [the kinetic theory](#), in which heat was due to the motion of atoms and molecules. However the kinetic theory, despite Rumford's groundbreaking

experiment, still did not hold sway until years later, after James Joule showed in 1845 that work could be quantitatively converted into heat.

History of Thermodynamics: James Joule: Work—>Heat

As the weight falls, the potential energy of the weight is converted into work done (a paddle stirs the water in the container against a frictional force due to water viscosity). The temperature rise corresponding to a given fall of weights (work done) yields the amount of heat rise (in calories) of the known mass of water.¹ Since the temperature rise is very small, the measurements have to be very accurate.

It took 30 to 50 years after Joule's definitive experiment (and subsequent refinements and repetitions) for the kinetic theory of heat—heat caused by random, irregular motion of atoms and molecules—to be fully accepted by the scientific community. James Clerk Maxwell published in 1871 a paper, ["Theory of Heat"](#). This comprehensive treatise and advances in thermodynamics convinced scientists finally to accept that heat was a form of energy related to the kinetic energy (the energy of motion) of the atoms and molecules in a substance.

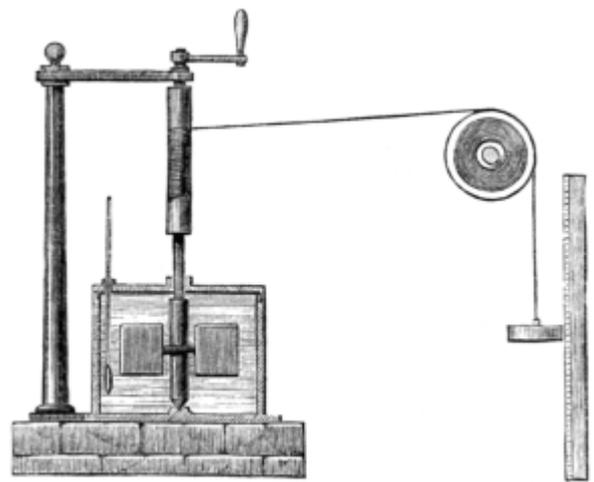


Diagram of Joule's Apparatus for Measuring the Mechanical Equivalent of Heat
from [Wikimedia Commons](#)

2.3 CONSERVATION OF ENERGY—THE FIRST LAW OF THERMODYNAMICS

The conservation of mechanical energy was discussed in Section 1: the potential energy of a body a height h above the ground is equal to its kinetic energy just before it hits the ground, where the potential energy is zero. The First Law of Thermodynamics states the conservation of energy in a more general way:

$$\Delta E = Q + W$$

We focus here on a “system.” The system might be a container of water, it might be the earth, or anything of interest with some boundaries that are closed (by “closed” we mean that no matter crosses the boundaries of the system). “ Q ” is the heat absorbed by the system; “ W ” is the work done on the system; “ ΔE ” is the change in energy of the system.² (The “ Δ ” is a symbol for “change of.”)

Let’s see how the First Law applies to the Joule Experiment:

a weight (mass m) drops a distance h and has no velocity at the end of the drop (it moves very slowly);

the weight has lost potential energy mgh but has not gained kinetic energy;

where has the potential energy of the weight gone? into work moving the rotors in the liquid;

the rotors have negligible mass, so the work done on them is not converted into kinetic energy but into heat, because they’re moving against the friction imposed by the liquid in which they’re immersed.

This heat, Q , is then equal to $Q = mgh$

Now, let’s look at the liquid as the system of interest. The liquid absorbs an amount of heat Q ; no work is done on the liquid itself since no force has moved the liquid any distance (the rotors are moving some liquid around but the liquid comes back to its original position so the net distance moved is zero).

The change of energy of the liquid is then $\Delta E = Q = mgh$. The heat, Q , absorbed by the liquid is related to its [heat capacity](#), C , whereby the expected temperature change can be calculated (see Note 1 below).

An early statement (1850) of the First Law was given by the German physicist Rudolf Clausius:

"In all cases in which work is produced by the agency of heat, a quantity of heat is consumed which is proportional to the work done; and conversely, by the expenditure of an equal quantity of work an equal quantity of heat is produced."

Clausius also gave a definitive statement for the Second Law, but before discussing that I'd like to talk about how the Second Law developed and the concept of entropy came to be.

2.4 THE SECOND LAW: HEAT ENGINES AND ENTROPY

The diagram below illustrates how steam engines work. Water is heated in the boiler to make steam, gaseous water. The steam passes through a pipe into a cylinder and expanding, moves a piston up, doing mechanical work. The steam then passes through a pipe and is cooled by condensing water to form liquid water. The water is pumped back into the boiler by a pump. Less work is used to pump the water from the condenser into the boiler than is done by the expanding steam in the engine cylinder.

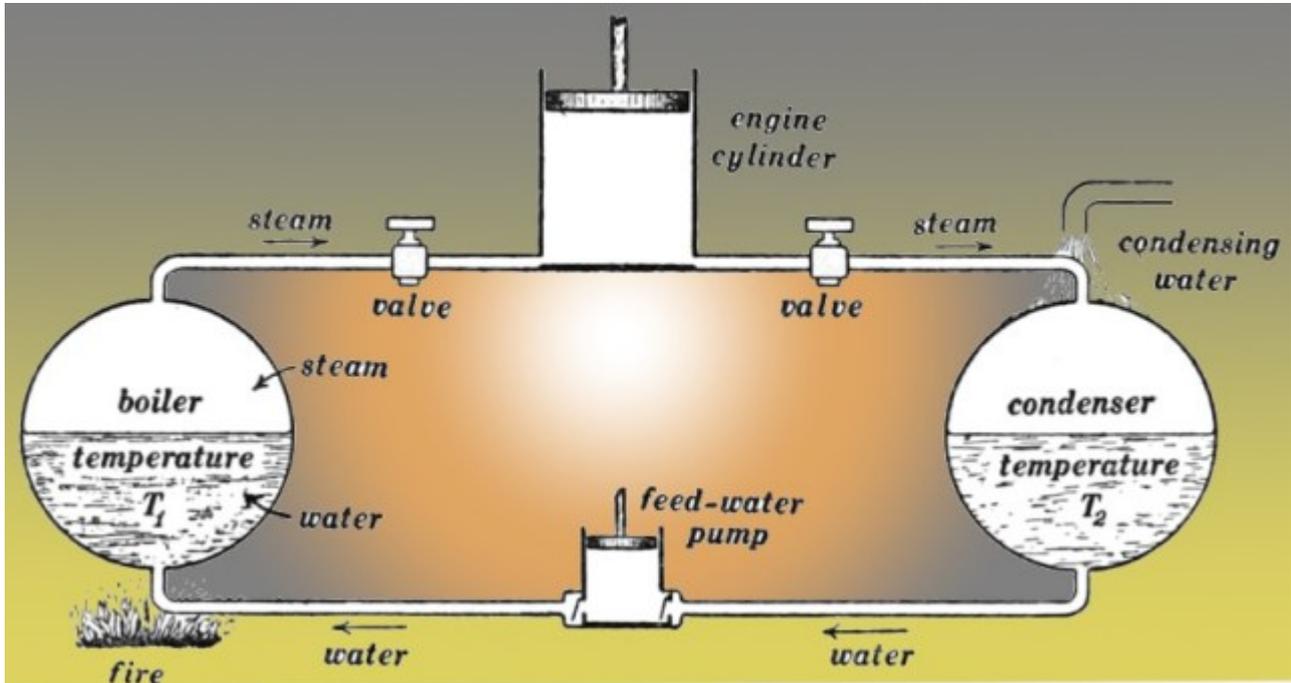
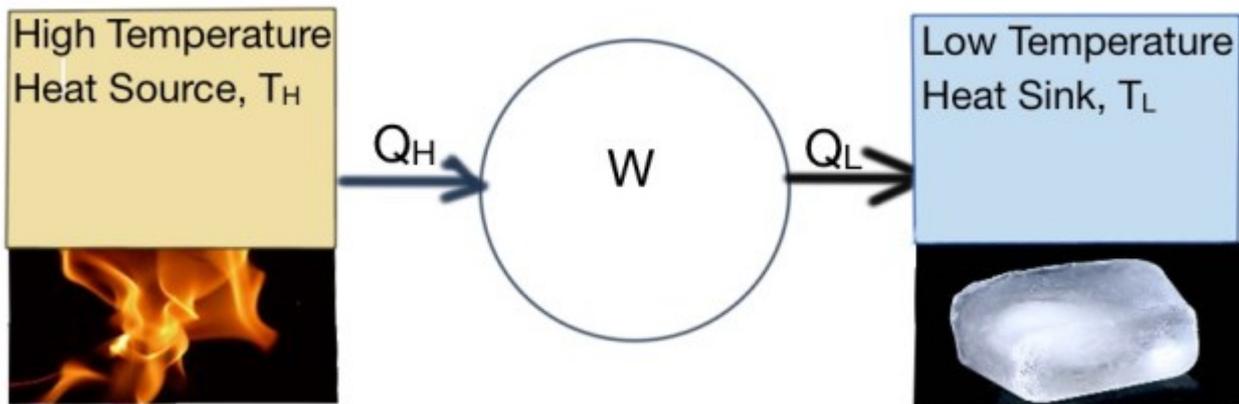


Diagram of the Second Law of Thermodynamics for a Heat Engine;
 adapted from [Wikimedia Commons](#)

History of Thermodynamics: Carnot's Cycle

Carnot devised an abstract scheme for the working of a heat engine (for example, the steam engine) that laid the foundation for the later development of thermodynamics in his book "[Reflections on the Motive Power of Heat.](#)" This scheme was the "Carnot Cycle," which set discrete stages for what happened to the water as it went from the boiler to the piston to the condenser and then back to the boiler.

Here's how it works:



Heat Engine Cycle

Heat (Q_H) is transferred from the high temperature source, the boiler, at temperature T_H , to the water. (T is the symbol used for absolute temperature.) The water vaporizes (steam) and goes into the piston expanding and doing work (W); the steam is condensed to liquid water in the condenser at temperature T_L , and gives off heat (Q_L) to the condenser and is then pumped back into the boiler. That's the cycle.

History of Thermodynamics: State Functions (Gibbs)

So, in this cycle the water goes back into the boiler at the same temperature, pressure, etc. as when it started to heat up and boil off. It's like someone making a trip around the city from his home and coming back to the home. In 1876 Willard Gibbs set forth the concepts of states and state functions (see Note 3, below) to yield the following important and useful relation:

if a system starts off in some initial state and ends up in some final state, then the value for a change in state function depends ONLY on what the initial and final states were, not on the path taken to get from initial to final state.

Thus, if the initial and final states are the same—if you're dealing with a "cycle"—then the

change in the state function is zero, since the state function has the same value for the initial and final states—they are the same state.

Then we can say that since the initial and final states of the water (the system) in this heat engine cycle are the same, and since the Energy E of the system is a state function, the change in energy for this cycle is zero: $\Delta E_{\text{CYCLE}} = 0$. (Recall, the “ Δ ” is a symbol for “change of.”) What is this change in E for the cycle in terms of the heat transferred and net work done? It’s net heat input minus work done by the system:

$$\Delta E = Q_H - Q_L - W = 0 \quad (1)$$

Notice that there’s a minus sign in front of Q_L because the system (the water) is transferring energy in the form of heat to its environment, the condenser. Notice also the minus sign in front of W ; W is work done BY the system against the environment (pushing the piston against a resisting pressure) so the system has to lose energy if W is positive. (We’re treating Q ’s and W as positive numbers.) So we get a relation between work done in the cycle, W , and the net heat transferred to the system, $Q_H - Q_L$:

$$W = Q_H - Q_L \quad (2)$$

Is there any more information we can get about this? Yes, but we have to learn about entropy and the 2nd Law of thermodynamics in order to do so.

History of Thermodynamics: Clausius’s Definition of Entropy

In the early part of the 19th Century Rudolf Clausius noticed something very important about heat: it flows spontaneously from a high temperature to a lower temperature, as, for example, if you drop an ice cube into a cup of hot coffee, heat will flow from the hot liquid to the cold ice cube and melt it. The greater the difference in temperature, the faster the heat flows from hot to cold.

So, here's how Clausius might have thought about this: "Ach, so! (heavy German accent here, please!). Vat can I write that vill have heat and temperature in it? Let's call this new function "entropy" from the Greek 'εν τροπε, 'in trope' or 'in change' or 'transformation.' And I'll denote it by the letter S." (Why S? I don't know.) "So, if we have a little bit of heat, and a high temperature, the transformation would be small, so let's say that a little bit of S equals a little bit of heat transferred divided by temperature." Actually, Clausius used arguments from calculus to arrive at his definition. See the [1867 English translation of the work](#) in which he defined entropy.

Then what we get the relation below for the change in entropy, ΔS , for some change of state:

$$\Delta S = \text{adding up (little bits of heat/T)} \quad (3)$$

If the temperature stays constant (what's called an "isothermal process") you can add up the little bits of heat separately to have Q, total heat transferred to the system (+Q) or from the system (-Q) to get

$$\Delta S = Q/T \text{ or } -Q/T \quad (Q \text{ a positive number}) \quad (4)$$

Entropy is a State Function

Clausius stipulated, and this is important, that entropy, S, is a state function. That means that the entropy change for a cyclic process (beginning and end states the same) is zero:

$$\Delta S(\text{cycle}) = S(\text{end state}) - S(\text{beginning state}) = 0$$

since the beginning and end states are the same. What does this tell you about the heat engine? Well, the entropy change when the liquid is heated is Q_H/T_H ; when the liquid is cooled the entropy change is $-Q_L/T_L$; So we get for the total cycle

$$\Delta S = 0 = Q_H/T_H - Q_L/T_L \quad (5)$$

Thermodynamic Efficiency of a Heat Engine

A reasonable definition for the efficiency of a heat engine is the ratio of the energy input to the work output, or more specifically, the ratio of the heat input at the high temperature to the work output:

$$\text{thermodynamic efficiency} = W / Q_H \quad (6)$$

Using the relations above (1-6) and some algebraic manipulation³ (see Note 3), one finds that this thermodynamic efficiency depends ONLY on the difference in temperature difference between hot and cold temperature reservoirs, $\Delta T = T_H - T_L$ and the temperature of the hot reservoir, T_H :

$$\text{thermodynamic efficiency} = \Delta T / T_H; \quad (7)$$

Here are some important things to notice about this definition of thermodynamic efficiency.

First, the engine is operating ideally, that is, reversibly—everything is at equilibrium at all points (see the section on reversibility and equilibrium below);
second, the thermodynamic efficiency of this ideal heat engine depends only on the high and low temperatures; it doesn't depend on the liquid being vaporized, how it's heat or cooled or any practical details;
third, the thermodynamic efficiency of real heat engines will generally be less than that of the ideal heat engine, and never greater.

To explain items 1-3, let's discuss reversible and irreversible processes and equilibrium.

Reversible and Irreversible Processes; Equilibrium

Let's try to get a clearer notion of reversible and irreversible processes by some examples.

Here's a billiard ball on a pool table: you can give the ball a tiny push to the left and it'll move to the left; you can give it a tiny push to the right and it'll move to the right. The ball is in mechanical equilibrium and your pushes are reversible. Now suppose you hit the ball so hard that it jumps over the rim of the table and falls to the floor. That is an irreversible process.

Here's one way to think about reversible and irreversible processes. Suppose you take a video of what's happening. If you can clearly distinguish between the video played in forward time and reverse time, then it's an irreversible process: for example, when milk is poured into a glass, it goes only in one way. You don't see milk spontaneously going out of a glass into the original container. [Here's a great video](#) that makes clear this notion of reversibility and its connection to the Second Law.

To summarize, entropy (S) increase with increasing disorder. In a closed system—no matter or energy can cross the boundaries of the system—entropy will never decrease. If the closed system is at equilibrium (only reversible processes can occur) entropy will be constant. If the closed system is not at equilibrium (irreversible processes occur), entropy will always increase.

Here's a quotation by Clausius that sums up the First and Second Laws:

“Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.”

(The energy of the World (Universe) is constant. The entropy of the World wants to be at a maximum (increases)).

There'll be more about the connection between entropy, order/disorder, probability and

information in Section 3

2.5. FREE ENERGY: THE BATTLE BETWEEN ENERGY AND ENTROPY

We've seen in the discussion above that the First and Second Laws of Thermodynamics give a natural direction for processes to go: to lower energy or to more disorder. Now which of these is most effective? If liquid water freezes to ice, energy decreases, but so does entropy. If a coiled protein unfolds, energy increases but so does entropy. How do we incorporate both energy and entropy changes into thermodynamics. Here's one clue; we know that as temperature increases, entropy becomes more important than energy. As you heat ice, it becomes liquid. As you heat liquid water, it becomes steam (water gas). The energy of the water is increasing, but so is its disorder, its entropy.

Josiah Willard Gibbs, "The Greatest Mind in American History," gave the answer in 1874, just a few years after the introduction of the First and Second Laws by Clausius. He introduced a thermodynamic function, the Free Energy, available to do non-mechanical work. This Free Energy combines energy temperature and entropy. Since it is a function only of state variables (like energy and entropy) the changes depend only on initial and final states, not the kind of process.^{3'} The Free Energy can be written in many forms, depending on variables are used to describe the system. The most common is that for G, "Gibbs Free Energy," used when temperature T and pressure are held constant:

$$G = \text{Energy}' - T \times \text{Entropy} \quad (5)$$

(Note; Energy' is a thermodynamic energy, "Enthalpy, H" used for constant pressure conditions; it includes mechanical work (pressure/volume expansion.) For constant temperature changes, this gives

$$\Delta G = \Delta \text{Energy}' - T \Delta S \quad (6)$$

For changes at equilibrium (constant pressure, temperature, no non-mechanical work), $\Delta G=0$. Note that for such equilibrium the energy and entropy terms balance out. For spontaneous (irreversible) changes, $\Delta G < 0$ (change is negative); in this case the temperature and entropy change overwhelms a positive energy change.. Also the maximum reversible work (non pressure-volume expansion) that can be done is given by the Gibbs Free Energy Change.

NOTES

¹Here's how the amount of heat transferred to the water, Q , is determined. Q is related to the temperature rise, ΔT , as follows: $Q = C \Delta T$. C is the "heat capacity," which is proportional to the amount of water in the apparatus and a constant, specific heat capacity, c , that depends on the substance. For liquid water at ordinary temperatures, $c = 1$ calorie/ (gram x degree Centigrade). or 4181 Joules/(kilogram x degree Centigrade).

²If we were to conform strictly to current usage we would use ΔU rather than ΔE , where U is the "internal energy" of the system (as distinct from kinetic energy of the system, for example). This "Internal Energy" is defined by the First Law: the Change in U is given by $Q+W$, but the "zero" of U is arbitrary. For example, if you're concerned with chemical reactions you can define a zero of U for elements in their most stable state under standard conditions (e.g. oxygen as O_2 , diatomic molecules, at 25 degrees Centigrade and 1 atm pressure—if oxygen were behaving as an ideal gas). But why make things more complicated than necessary? The goal of this discussion is to achieve an intuitive understanding of what thermodynamics is about, not to pass a final exam.

³Here's how the ideal efficiency of a heat engine is derived. First, the entropy change when the liquid is heated is Q_H/T_H ; when the liquid is cooled the entropy change is $-Q_L/T_L$; So we get for the total cycle

$$\Delta S = 0 = Q_H/T_H - Q_L/T_L$$

From which a relation between the Q's and T's follows:

$$Q_L = Q_H \times (T_L/T_H)$$

Using this last relation and the First Law requirement that $\Delta E = 0 = Q_H - Q_L - W$, one gets for the ratio of net work done in the cycle, W , to the heat input at the high temperature reservoir,

$$\text{thermodynamic efficiency} = W/Q_H = 1 - (T_L/T_H) = \Delta T / T_H$$

^{3'} Here's an example. Suppose you have supercooled water (say -2°C) in a thermos, effectively an isolated system. A dust particle settles into the water and it freezes. Aha, you say. Here's an isolated system that goes from relative disorder (liquid water) to order (ice). So entropy decreases! But that isn't so. If we construct a virtual process and calculate the entropy change for that it turns out to be positive: heat the liquid water reversibly from -2° to 0°C (the equilibrium freezing point for water), let the water freeze at 0°C , cool the ice down to -2°C . The total entropy change will be positive.

SECTION 3: Thermodynamics, a Molecular View (and Information as Entropy)

Let's try to get an intuitive idea of what entropy is and what the Second law of Thermodynamics has to say about it. Entropy measures order, and what is that? We can think of order as knowing about arrangements, putting things where we know where they are, so that if we turn our attention away from something (or a collection of somethings) we'll know what they will look like and where they'll be when we turn our attention back. For example, if we look at a marching band, we'll see a row of horns, then saxophones, then flutes, then drums and this'll be the same if we turn away and then look back. Or if we take

an electron microscope and look at an ice crystal, we'll see water molecules in regular positions, and these will stay the same (if the ice doesn't melt) if we look at that ice crystal next month.

What is disorder? The opposite of order,. For example, if we look at a large crowd rushing to catch a subway, we don't know what that crowd will look in another 10 minutes. If we look at water molecules in steam (water as a gas) they won't be at regular positions but moving around like a bunch of agitated flies.

So, Entropy measures disorder, the greater the disorder of a system, the greater its entropy.

There's a connection here with probability and information, as Shannon realized in assigning an entropy formula for the amount of information in a message. When we know more about something, the probability of its having certain properties is greater; when we have a wider range of possibilities for those properties (greater disorder), the probability for specific values is less. When you pop a balloon with a pin and the air escapes into the room, the probability of an air molecule being at a specific spot changes. Before the balloon is popped, we know the air molecules are inside the balloon and not outside; after it is popped a given air molecule can be anywhere in the room, so its probability characteristics have changed.

Here are some more examples. You drop an ice cube into a thermos of warm lemonade. The ice cube melts, the resulting liquid gets colder. The entropy of this system (ice cube + warm lemonade) increases: the entropy of the warm lemonade decrease a little as it cools, but the entropy of the ice cube increases by much more, because it becomes much more disordered as a liquid. No work is done on the system (the stuff inside the thermos) and no energy is transferred to it. Here's another example. You drop a sugar cube into a cup of hot tea. The sugar cube dissolves. The entropy of the whole system, sugar cube + tea, increases.

A common feature of these two examples is that they are “irreversible processes.” If you ran a video backwards of either of them, showing the ice cube forming from a solution of lemonade, or the sugar cube forming from a cup of hot tea, you’d know that the video was going backwards. Increase in entropy generally happens as time goes forward. That’s why entropy is often called “The Arrow of Time.”