Heat, Energy and the Laws of Thermodynamics

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The Laws of Thermodynamics, I

0th A system is in thermal equilibrium when its temperature does not change over time. ($A \sim B$ and $B \sim C \Rightarrow A \sim C$.)

1st The total energy of a physical system is conserved. The increase in the internal energy of a system is equal to the amount of energy added by heating the system, minus the amount lost as a result of the work done by the system on its surroundings.

2nd The total entropy of a system will increase over time. Heat flow has a direction that tends to even-out heat distribution.

- In any physical system, any process that occurs will tend to increase the total entropy of the universe.
- Heat cannot flow spontaneously from a material at lower temperature to a material at higher temperature.
- It is impossible to convert heat completely into work in a cyclic process.

The Laws of Thermodynamics, II

3rd A statistical law relating entropy and the impossibility of reaching absolute zero temperature ($T \to 0 \Rightarrow S \to 0$).

- As a system approaches absolute zero, all processes cease and the entropy of the system *approaches* zero.

We imagine a game – pachinko, slots, poker – in which we try to win something for nothing:

The Laws Simplified

0st There's a game.

1st You can't win.

2nd You can't even break even.

3rd You can't quit the game.

From Forces to Energy

The study of heat in the 19th century took place in the social and economic context of the industrial use of heat to produce work (coal, steam, and so on) and in the intellectual contexts of German *Naturphilosophie* and, originally, the theory of caloric – a weightless, or imponderable, fluid.

Around 1850, physicists began to focus on *energy* as a fundamental quantity in physical processes. This came largely out of the realization that heat could be considered as a kind of energy. This lead to a metaphysical view that emphasized the existence of matter and energy.

The theory of heat changed three times in the 19th century: (1) fluid dynamics, (2) particle dynamics and (3) statistical dynamics.

The new reformulation of heat theory involved a *new worldview*, which placed *energy* in a central place.

Sadi Carnot (1793–1832)

Carnot was raised in turbulent times. His father was a member of the Revolutionary French government and then Minister of War for Napoleon I.

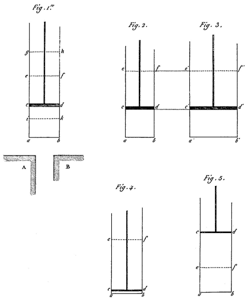
He was educated at the École Polytechnique, where his teachers were Gay-Lussac, Poisson, Ampère, and others.

He wrote a treatment of the heat engine, based on the choleric theory of heat, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* (1824), which was later developed analytically – that is, using the analytical equations of fluid mechanics – by Émile Clapeyron.

The Carnot Cycle

Carnot imagined an *ideal machine* that converts heat flow into mechanical motion. A piston moves in an sealed cylinder. The piston's rod is attached, at the other end, to a revolving wheel. A four-phase cycle is used to describe how heat transfer can produce motion.

- A cold body, *A*, touches the cylinder, drawing out heat and compressing the air. The piston is pulled in.
- *A* is removed, the wheel moves by inertia, the air compresses and warms.
- A hot body, *B*, touches the cylinder, adding heat and expanding the air.
- *B* is removed, the wheel moves by inertia, the air expands and cools.



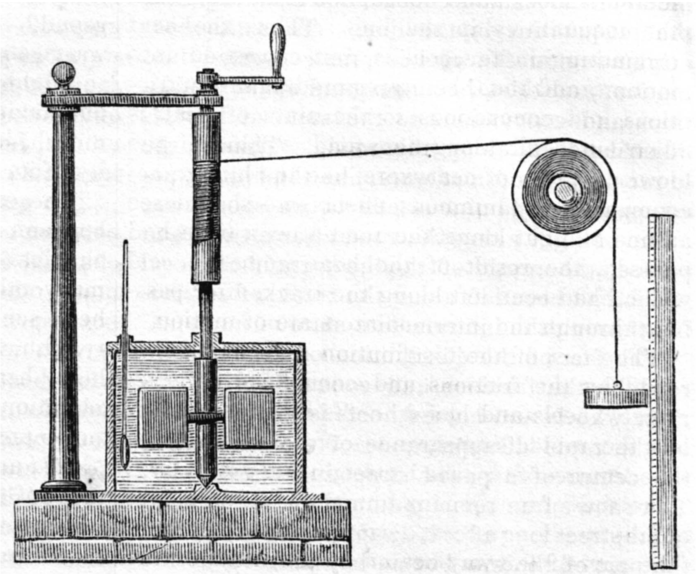
Carnot's ideal heat engine

Joule's Conversions

James Prescott Joule (1818-1889) – from a wealthy Manchester brewing family, educated by private tutors, including Dalton – was interested in producing *work* from a variety of sources.

In 1837, he made an engine from an electrical battery and investigated how much electricity it took to lift 15lb one foot in one minute. He went on to calculate the *work* produced by electromagnetic effects, falling bodies, chemical reactions, applying pressure to fluids, churning liquids, and so on, and began to focus on the fact that all these processes involve converting work into heat.

Joule abandoned the idea of *caloric* and instead imagined that heat was a *vibration* of fundamental particles. In Joule's view heat could be *generated* by moving bodies; likewise it could be *expended* in the creation of work. Since heat was not a substance but a state of motion, it was *not preserved through transformations*.



Joule’s apparatus for converting the force of a falling body into heat

Joule's "Living Force"

Joule, Lecture in St. Ann's Church, Manchester, 1847

"You see … that living force may be converted into heat, and that heat may be converted into living force, or its equivalent attraction through space. All three … – namely, heat, living force, and attraction through space… – are mutually convertible into one another. In these conversions nothing is lost… We can, therefore, express the equivalence in definite language applicable at all times and under all circumstances. Thus the attraction of 817lb through the space of one foot is equivalent, and convertible into, the living force possessed by a body of the same weight of 817lb when moving with the velocity of eight feet per second, and this living force is again convertible into the quantity of heat which can increase the temperature of one pound of water by one degree Fahrenheit."

Hermann von Helmholtz (1821–1894)

Helmholtz was the first son of a Prussian gymnasium teacher. He studied surgery at the Medical Institute in Berlin; worked as an army field MD for 9 years, researching and publishing on the side; and taught himself advanced mathematics.

He made important contributions to physiology, optics, color theory, acoustics, music theory, mathematics, electrodynamics, and thermodynamics, and became a professor at Königsberg, Heidelberg and Berlin. He was appointed first Director of the Physikalisch Technische Reichsanstalt, Berlin.

He worked to popularize science and to form international and cross-disciplinary ties.

The Conservation of Force, or Energy

In his technical paper "Über die Erhaltung der Kraft," 1847, Helmholtz drew from his wide ranging interests to argue that force (energy) was conserved in every natural process in the same way as matter. He differentiated between *innate* and *active* forces, which were defined in terms of potential and actual effects. He applied this principle to mechanical problems, heat effects, electromagnetism and biological organisms.

This can be taken as an early articulation of the first law of thermodynamics as a general principle underlying all physical processes, and unifying the conception of these processes through the framework of physics.

The 1st Law of Thermodynamics

Helmholtz, "On the Conservation of Force," 1862 (English)

"The force of falling water can only flow down from the hills when rain and snow bring it to them. To furnish these, we must have aqueous vapor in the atmosphere, which can only be effected by the aid of heat, and this heat comes from the sun. The steam engine needs the fuel which the vegetable life yields, whether it be the still active life of the surrounding vegetation, or the extinct life which has produced the immense coal deposits in the depths of the earth. The forces of man and animals must be restored by nourishment; all nourishment comes ultimately from the vegetable kingdom, and leads us back to the same source."

The Reception in Britain

In Great Britain, Helmholtz's work was well received by a number of colleagues who were also interested in these ideas – such as W. Thomson (1824–1907), P.G. Tait (1831–1901), and J.C. Maxwell (1831–1879).

Maxwell, 1862

"Helmholtz is not a philosopher in the exclusive sense, as Kant and Hegel … are philosophers, but one who prosecutes physics and physiology… He was one of the first, and is one of the most active, preachers of the doctrine that since all kinds of energy are convertible, the first aim of science at this time should be to ascertain in what way particular forms of energy can be converted into each other, and what are the equivalent quantities of the two forms of energy."

The British natural philosophers took it as *theological principle* that since God created energy, it could not be destroyed.

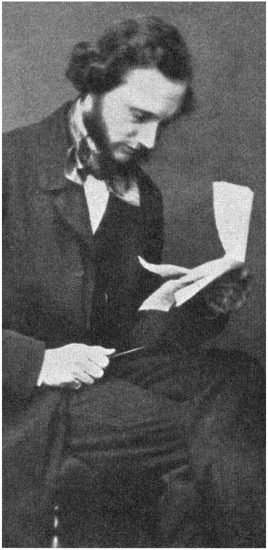
The 2nd Law of Thermodynamics

The 2th law of thermodynamics can be, and has been, expressed in a number of different ways. Hence, there has been considerable debate about who first formulated it.

It has to do with the directionality of heat flow, the dissipation of mechanical energy, the probability of thermal equilibrium, and the increase of a theoretical concept called *entropy*.

As the theory of heat changed, so too did the conceptual significance of the second law.

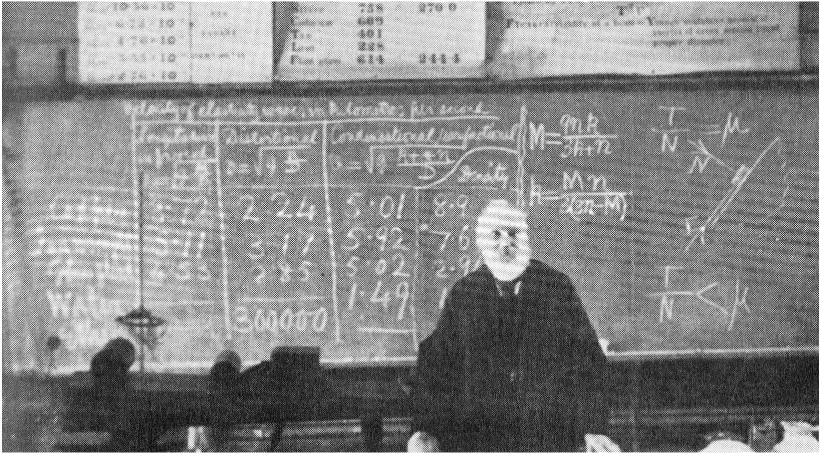
William Thomson, Lord Kelvin (1824–1907)



William was the son of a farm laborer who had become a professor of mathematics at University of Glasgow. The boy sat in on his father's university lectures from the age of 8, and published his first mathematics paper when he was 17. He was educated at Glasgow and Cambridge (2nd Wrangler, Smith Prize). Became professor of Natural Philosophy at the age of 23.

He became the most famous and wealthiest scientist in Britain in the 19th century. He was made a British Peer – Lord Kelvin, 1892. He worked widely and prolifically in the most important areas of classical physics. His international and industrial connections helped establish scientific standards and units.

William Thomson Lecturing



Lord Kelvin lecturing in 1899, at the age of 75

Thomson's Theory

Thomson first heard Joule's views on heat at a British Association for the Advancement of Science (BAAS) meeting in Oxford, 1847. At the time, he held Carnot's view of heat as a fluid, caloric, and had written a number of papers developing this theory. Being convinced that Joule was correct in some ways, they began to collaborate and correspond extensively. Thomson worked to formulate a theory of heat that reconciled the ideas of Carnot and Joule.

Count Rumford shown that heat could be produced endlessly by boring cannons; H. Davy had rubbed blocks of ice together at constant temperature and they had melted. Now Joule could warm water with determinate quantities of *work*. Clearly motion could produce heat.

The converse claim that heat was lost in producing work, was not experimentally demonstrated at that time, so Thomson used various arguments to try to assert its validity.

Thomson's Papers

Thomson wrote a series of papers on what he called thermodynamics. Their were two fundamental principles:

Thomson, "On the Dynamic Theory of Heat," 1851–1855

"Prop. I (Joule). - When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.

Prop. 2 (Carnot and Clausius). - If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motion are all reversed, it produces as much mechanical effect as can be produced by any thermo-dynamic engine, with the same temperatures of source and refrigeration, from a given quantity of heat." [An ideal upper limit.]

But in any actual machine there was "an absolute loss of mechanical energy available to man."

Rudolf Clausius (1822–1888)

Rudolf's father was a pastor and a school principal. He was educated in mathematics and physics at Berlin and Halle, and taught in a number of Swiss and German universities. At the age of 50 he commanded an ambulance corps in the Franco-Prussian war.

He worked on the theory of heat for many years, writing "Über die bewegende Kraft der Wärme," 1850, "Über die Art der Bewegung, die wir Wärme nennen," 1857, and "On the Determination of the Energy and Entropy of a Body," 1866. Like Joule, he was committed to a kinetic theory of heat and he worked to reformulate Carnot's heat engine along these lines.

Clausius' Early Theory of Heat Flow

Clausius took the equivalence of heat and work as an *axiom*. However, heat could be lost in the process of converting between the two, and the total quantity of heat or work would decrease. Hence, the work produced from heat, had to be taken as a *limiting maximum*. There are many cases where there is heat transfer with no mechanical effect.

The general tendency of heat was to "annul differences of temperature, and therefore to pass from a warmer body to a colder one." He showed that any system that did not obey this principle could be made to produce work for nothing.

Like the northern British, he took as given the *economic principle* that you cannot get something for nothing. Hence, according to Clausius, Carnot was right to state the theoretical directionality of heat flow from hot to cold, but for the wrong reasons.

Clausius' Concept of Entropy

The directionality of heat flow became a fundamental principle: "Heat cannot pass from a colder body to a warmer body without some other change, connected therewith, occurring at the same time."

Changes in heat and temperature could be mathematically related to the change in an unknown quantity that always increases through the natural processes of heat flow. Clausius called this quantity *entropy*.

Clausius, "On the Determination…," 1866

"I call the magnitude S the *entropy* of the body, from the Greek word *trope*, transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied as to their physical meanings, that a certain similarity of designation appears desirable."

The Dissipation of Mechanical Energy, Heat

The authors of the new theory of heat pointed out that there were far reaching implications for cosmology.

Thomson, 1852

"There is at present in the material world a universal tendency toward the dissipation of mechanical energy."

That is, in any natural process, some energy is transformed in such a way that it is not possible to derive useful work out of it.

Thomson, 1852

"Any *restoration* of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life, or subjected to the will of an animated creature."

A Temporal Directionality of Processes

Due to this dissipating effect of radiant heat, all processes have a temporal directionality.

Thomson, 1853

"It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding bodies."

Hence, as the surrounding bodies are warmed by radiation, the amount of work the system can produce decreases. These effects always tend in one direction, toward a *dissipation* of the ability to produce work.

A Beginning

In a speech to the 1870 meeting of BAAS, J.C. Maxwell articulated the idea that this science pointed towards a new cosmology that predicted the existence of a certain beginning.

Maxwell, BAAS Meeting, 1870

"If we reverse the process of [diffusion], and inquire into the former state of things by causing the time symbol to diminish, we are led to a state of things which cannot be conceived as the result of any previous state of things, and we find that this critical condition actually existed at an epoch, not in the utmost depths of a past eternity, but separated from the present time by a finite interval. This idea of a beginning is one which the physical researches of recent times have brought home more than any observer of the course of scientific thought in past times would have had reason to suspect."

An End, a New Cosmology

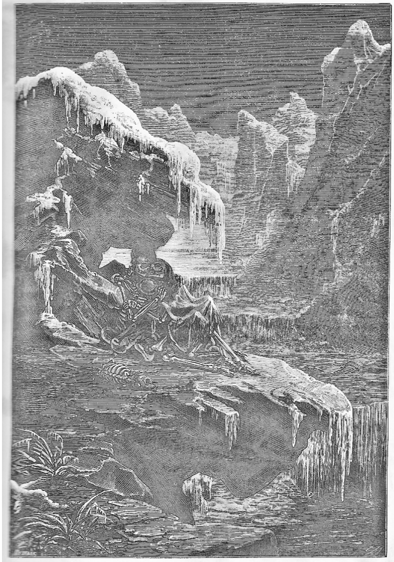
Thomson, 1862

"The result would be a state of universal rest and death, only if the universe were finite… But it is impossible to conceive a limit to the extent of matter in the universe; and therefore science points rather to an endless progress, through an endless space, of action involving the transformation of potential energy into palpable motion and thence into heat, than to a single finite mechanism, running down like a clock, and stopping forever."

Clausius summarized this at the end of his 1866 paper. Stating Thomson's priority, he pointed out that "the fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat" are

1. The energy of the universe is constant.
2. The entropy of the universe tends to a finite maximum.

In popular accounts and science fiction, it was imagined that the heat of the sun would eventually run out, and human beings would freeze to death.



Surprise par le froid, la dernière famille humaine a été touchée du doigt de la Mort, et bientôt ses ossements seront ensevelis sous le suaire des glaces éternelles ..

A Dynamic Theory of Heat

All of the early versions of the *kinetic* theory of heat assumed that heat was some kind of *motion*, but they were unclear on what kind: vibration, locomotion, rotation, and so on. In 1857, Clausius made explicit the idea that this motion was a molecular motion. On this basis, he developed a *dynamic* theory of gasses.

Clausius argued that gasses are made up of molecules that move in every direction and at varying speeds. He showed how known properties of the gas, like pressure, could be related to the *mean* motion of the assumed molecules. He made calculations about the average speeds at which molecules would move, and the average distances that molecules would travel before striking one another.

Maxwell's Statistical Theory

J.C. Maxwell read Clausius' papers and began to work with the model. At first, he did not believe in the actual truth of the model as a depiction of reality but he was exited by the mathematics involved. He worked out more detailed mathematical methods and some experimental techniques for determining some of the parameters. He realized the potential of applying statistical methods to physical problems.

Maxwell developed a fully statistical model of gasses, in which the velocities were "distributed according to the same formula as the errors are distributed" in observations – the normal distribution. He explicitly made this assumption on the basis of the ideas of Adolphe Quetelet (1796–1874) and Henry Buckle (1821–1862). On this foundation, he was able to produce a mathematical theory which explained the known properties of gasses and made new predictions which could be tested – viscosity, pressure friction, and so on.

A Distribution of Velocities

Maxwell, Lecture to the BAAS, 1873

"The modern atomists have adopted a method which is, I believe, new in the department of mathematical physics, though it has long been in use in the section of Statistics... The data of the statistical method as applied to molecular science are the sums of large numbers of molecular quantities. In studying the relation between quantities of this kind, we meet with a new kind of regularity, the regularity of averages…

If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision, so that after a certain time the *vis viva* [energy] will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable, though the velocity of each particle changes at every collision."

Statistical Derivation of the Gas Laws

Maxwell applied a statistical model to derive the known properties of gasses, and to predict some new phenomena that had not yet been observed.

Maxwell, "On the Dynamic Theory of Gases," 1866

"I propose in this paper to apply this theory to the explanation of various properties of gases, and to show that, besides accounting for the relations of pressure, density, and temperature in a single gas, it affords a mechanical explanation of the known chemical relation between the density of a gas and its equivalent weight, commonly known as the Law of Equivalent Volumes. It also explains the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases."

* The Law of Equivalent Volumes, is Avogadro's hypothesis that equal volumes of gases, at the same temperature and pressure, have the same number of molecules.

On Stochastic Laws

Maxwell argued that physicists have to use probability theory because of a lack of complete knowledge.

Maxwell, Lecture to the BAAS, 1873

"The equations of dynamics completely express the laws of the historical method as applied to matter, but the application of these equations implies a perfect knowledge of all data. But the smallest portion of matter which we can subject to experiment consists of millions of molecules; so that we are obliged to abandon the strict historical method, and to adopt the statistical method of dealing with large groups of molecules… In studying relations of this kind, we meet with a new kind of regularity, the regularity of averages, which we can depend upon quite sufficiently for all practical purposes, but which can make no claim to that character of *absolute precision* which belongs to the *laws of abstract dynamics*."

Maxwell's Demon

Maxwell's work on the statistics of gases lead him to the realization that the second law could be no more than a statistical regularity. It does not have the same force as the laws of dynamics. In private communication with Thomson and Tait, he introduced a purely theoretical counterexample to the 2nd law. He imagined two gases of different temperatures in containers attached by a small diaphragm or gate.

Maxwell, Letter

"Conceive a finite being who knows the paths and velocities of all the molecules by simple inspection but who can do no work except to open and close a hole in the diaphragm by means of a slide without mass."

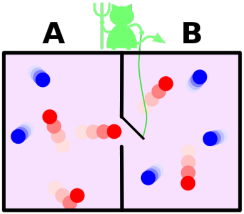
It allows the fastest molecules to pass from the cold to the hot and the slowest to move in the other way. This being, which Thomson called *Maxwell's Demon*, can cause heat to flow backwards or pressures to change without doing any work.

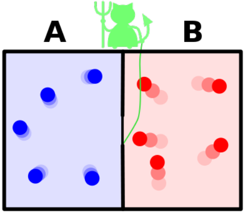
A Thought Experiment

The demon is a *thought experiment*, which is meant to reveal the statistical nature of the 2nd law. (It was later argued that it takes work to figure out the paths of the molecules and to open the gate, and so on.)

Maxwell, A postcard

"Concerning Demons.
1. Who Gave them this name? Thomson.
2. What were they by nature? Very small BUT lively beings incapable of work but able to open or shut valves which move without friction or inertia.
3. What was their chief end? To show that the 2nd Law of Thermodynamics has only statistical certainty."





Ludwig Boltzmann (1844–1906)

A drawing by Przibram

Boltzmann was from a middle class Austrian family, educated at University of Vienna, and worked in a number of Austrian and Prussian universities, eventually returning to Vienna. He was manic-depressive and committed suicide.

He worked on the dynamic theory of gases, developed the field of *statistical mechanics*, and argued for the existence of *real atoms*.

Boltzmann studied the statistical properties of the Maxwell-Boltzmann distribution and showed that this is the most *probable* distribution. Moreover, he showed that *entropy* is maximized in the M-B distribution. In other words, *entropy* can be taken as a measure of the probability of the energy state.

Loschmidt's Objection

One of Boltzmann's older colleagues at the University of Venna, J.J. Loschmidt (1821–1895), introduced an objection to Boltzmann's work that is functionally equivalent to Maxwell's demon.

Loschmidt was concerned with the idea of "heat death," which the laws of thermodynamics predicted would occur when all heat was equally distributed. He pointed out that the second law was *irreversible*, while the fundamental mechanics on which it was supposedly founded were fully reversible.

That is, if all the molecules of a system moved in exactly the opposite direction, as is allowed in classical mechanics, one would get entropy decreasing; heat flow in the opposite direction, spontaneous production of order, and so on. But since this never happens, he did not see how the 2nd law could be fully stochastic in character.

Boltzmann's Theory of Entropy

Boltzmann responded to this objection by modeling entropy as a problem in *classical probability theory*. He used the idea of an urn filled with balls to model the energy states of the molecules of a gas. He assumed that the energy would come in whole-number intervals – which assumption and model would later form the basis of the first quantum theories. In this way, entropy became a purely *statistical attribute*, or measure, of the overall system. As the entropy increased, the configuration of the system became more *likely*, and the contrary

Boltzmann was able to calculate just how unlikely it was that the 2nd law would be violated for any length of time. He made analogies between this and other unlikely phenomena. He calculated how often oxygen and nitrogen would spontaneously separate. He pointed out that the frequency of these sorts of phenomena is mathematically the same as *never*.

Boltzmann's Stochastic Views

Boltzmann

"One may recognize this as equivalent to never, if one recalls that in this length of time, according to the laws of probability, there will have been many years when every inhabitant of a large country committed suicide, purely by accident, on the same day."

He framed his overall views as follows:

Boltzmann, 1886

"As is well-known, [Henry] Buckle demonstrated statistically that if only a sufficient number of people is taken into account, then not only is the number of natural events like death, illness, etc., perfectly consistent, but also the number of so-called voluntary actions – marriages at a given age, crimes, and suicides. It occurs no differently among molecules."

The Possibility of Life

In the 1890s, Boltzmann, influenced by the new evolutionary thinking in biology, began to suspect that the most *unlikely* thermodynamic states were necessary for the production of life.

The laws of thermodynamics alone should tend towards total thermal equilibrium and "heat death" – or rather cold death. That is, they tend toward homogenous, unstructured matter, with evenly distributed energy states and maximum entropy. The growth of living beings was thus seen as contrary to the 2nd law. It represents a *highly unlikely state*.

Boltzmann, 1895

"We assume that the whole universe is … in thermal equilibrium. The probability that one part of it is in a certain state is the smaller the further this state is from thermal equilibrium, but this probability is greater, the greater the universe itself is."

The Age of the Earth, Disciplinary Disputes

Going back to the middle of the 19th century, the northern British – Thomson, Tait, Maxwell – being opposed to the new evolutionary views, used the new theory of thermodynamics to argue against geologists and biologists about the possible age of the earth. They argued that the earth had definite age and, by making some arbitrary assumptions, set out to calculate it. Over the years they made a number of calculations getting results varying from 100 to 20 million years – Tait calculated 10 million.

Thomson, 1952

"Within a finite period of time past the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted."

Essentially this was a disciplinary dispute, with the physicists claiming that only they were in a position to make sound arguments about the age of the earth.

Controversy and Resolution

The dispute became especially heated because of the time required by Charles Darwin in his *Origin of Species*, 1859. Increasingly, the biologists and geologists realized they must be right that the earth was very old but they could not prove their position with physical arguments.

Eventually, physicists themselves began to see problems with Thomson's arguments. In the 1890s, George Darwin, Charles' son, among others, showed that Thomson's claim was based on a number of arbitrary assumptions and that by varying these the calculation of the earth's age would change considerably.

With the discovery of radioactive materials, in 1903, George Darwin, among others, realized that the age of the both the sun and the earth would be greatly extended.

Overview

- The theory of heat changed from that of an inponderable fluid, to a kinetic theory and dynamic theory, and finally to a statistical theory.
- The second law was reinterpreted as a statistical law, which was fundamentally related to singularities and irreversible processes.
- The ground was laid for dispensing with ontological *reductionism* and *hard determinism*.
- We see the possibility that the laws of one layer of phenomena (statistical) may not be reducible to those of its substrate (classical dynamics).
- We see a clear case of the *historicist* approach in 19th-century thought.
- We see the difficulty of the historical notion of closed determinism in dealing with the laws of thermodynamics.