Caloric Theory

- The theory stated that heat (caloric) is a material substance, an elastic fluid whose particles strongly repel one another.

- The heat can be squeezed out by friction or flows out of a body when fire is applied.

- Note the similarities with the “eter theories” for electricity, magnetism etc.

Carnot

- Sadi Carnot (1796-1832) published “Réflexions” 1824.
- Considered heat engines and the question “Under what conditions could maximum mechanical work be achieved in a steam engine with a given temperature difference?”
- Studied the flow of heat from high to low temperature. In accordance with caloric theory assumed that heat could not be destroyed.
- For practical engineering Carnots “closed loop analysis” was of utmost importance.

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- Found that thermal efficiency $\eta = (t_{max} - t_{min})/(t_{max} + 267)$. Carnot draw two fundamental conclusions from this:

  1. Efficiency is not dependent on the substance involved in the process.

  2. The maximum temperature must be as high as possible since the practical minimum temperature cannot be lower than ambient.

- He used the efficiency result to refute the possibility of perpetual motion of heat engines.

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- Carnot stated the relationship of work known as the “first law of thermodynamics”

> Heat is simply motive power, or rather motion which has changed form. It is a movement among particles of bodies. Wherever there is destruction of motive power there is at the same time production of heat in quantity exactly proportional to the quantity of motive power destroyed. Reciprocally, whenever there is destruction of heat, there is production of motive power.
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> We can establish the general proposition that motive power is, in quantity, invariable in nature; that is, correctly speaking, never either produced or destroyed. It is true that it changes its form – that is, it produces sometimes one sort of motion, sometimes another – but it is never annihilated.

- Carnot here abandons the caloric theory.

Second law of thermodynamics

- In 1833 Clapeyron (1799-1864) noticed Carnots “Réflexions”. He considered the article and represented its essentials in analytic form.

- William Thomson (1824-1907, Lord Kelvin) and Rudolf Clausius (1822-1888) used this article to develop the “first” and “second law of thermodynamics”. Clausius stated (1850) “Heat cannot of itself pass from a colder to a hotter body.”

Kinetic-molecular theory

- Clausius made major contributions to span the gap between the atomic and thermodynamic theories.

- Ludwig Boltzmann (1831-1879) “bridged” the classical thermodynamics an molecular statistics. $S = k \ln \Omega$.