Statistical Molecular Thermodynamics

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Video 5.1

First Law of Thermodynamics

Classical Thermodynamics

Thermodynamics has at its foundation three fundamental laws named, not very imaginatively: the First Law, the Second Law, and the Third Law. There are no known exceptions to these laws.

This week will be devoted to examination of *the First Law*. This law, remarkably powerful given its simplicity, allows us to address questions such as whether a gas will cool upon expansion, or to calculate the energy changes for chemical reactions.

A colloquial, but perfectly acceptable, statement of the First Law is: Energy can neither be created nor destroyed, but it may be distributed in different ways. Or, more succinctly: Energy is conserved.

First Law History

Considerable philosophical and scientific effort has gone into addressing the concept of “heat”

Heat is an invisible fluid, called “caloric”, which flows from warmer bodies to cooler ones. — Antoine Lavoisier

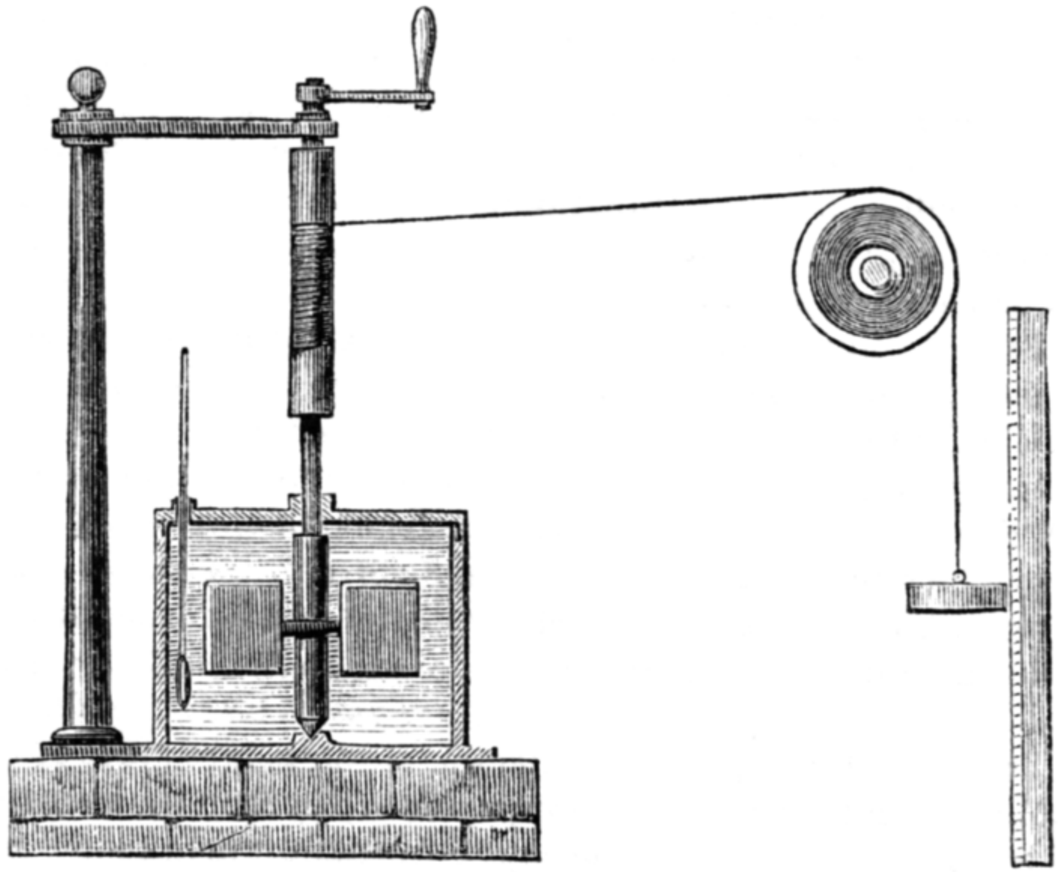
First Law History

Heat is a Form of Motion: An Experiment in Boring Cannon
Benjamin Thompson (Count Rumford), *Philosophical Transactions* (vol. 88), 1798

Careful analysis of weight and temperature changes for various processes led to suggestion of work/heat equivalence

First Law History

James Prescott Joule



First to quantitatively establish the equivalence of heat and work

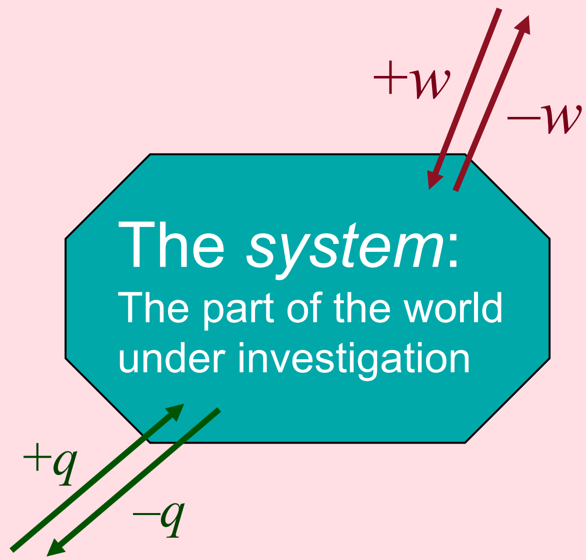
many other contributions, including pioneering refrigeration via gas expansion

Some Definitions

There are two ways that energy can be transferred between a *system* and its *surroundings*, *work* (w) and *heat* (q).

The *surroundings*: everything else

Work, w: transfer of energy as a result of unbalanced forces



Convention: positive, $+w$, energy of system increases, "work is done *on* the system" (opposite case, $-w$, "the system does work"*)*

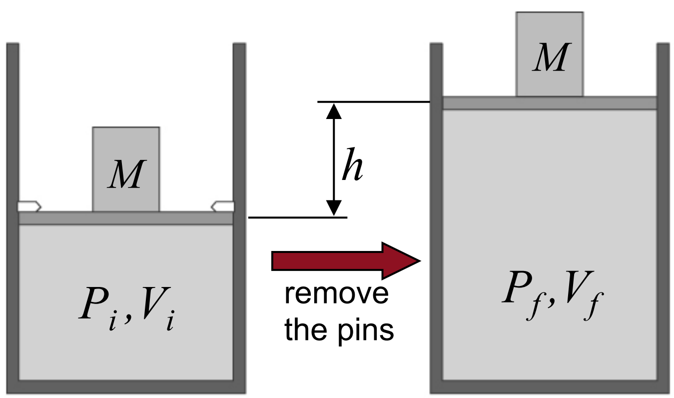
Convention: positive, $+q$, heat is *input* to the system

Heat, q: transfer of energy resulting from a temperature difference (cf. zeroth law of thermodynamics)

Gas Expansion and Work

Consider the work done *by the gas on the surroundings* in an *expansion* as a result of the difference in pressure exerted by and on the gas (unbalanced forces):

Work is required to raise a mass, M, a distance, h, against gravity, g



i = initial $\qquad$ f = final

$$P_i > P_{\text{ext}} = \frac{Mg}{A} \qquad P_f = P_{\text{ext}}$$

$$w = -Mgh$$

$$w = -\frac{Mg}{A}Ah$$

$$\frac{\text{force}}{\text{area}} = \text{pressure} \qquad \text{area} \cdot \text{height} = \text{volume}$$

$$w = -P_{\text{ext}}\Delta V$$

ΔV positive $\rightarrow$ w negative

Self assessment insert here

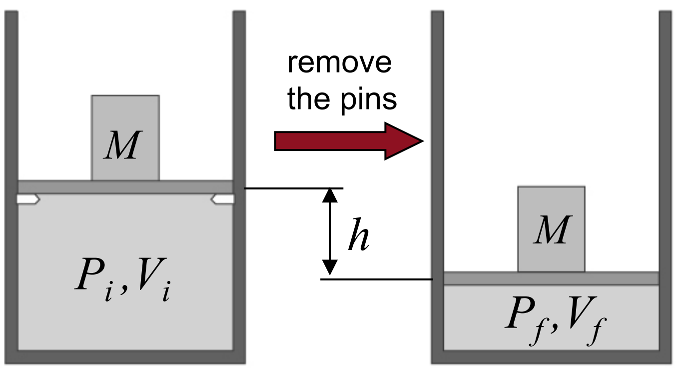
- If the internal pressure of 1 L of an ideal gas is twice the external pressure, by how much will the volume of the gas expand as it does work on the surroundings if the temperature is held constant?
- Answers a) the gas will not expand, b) 0.5 L, c) 1 L, d) 2 L
- correct answer is c

Gas Compression and Work

Consider the work done *on the gas by the surroundings* in a *compression* as a result of the difference in pressure exerted by and on the gas (unbalanced forces):

Work is done by a mass, M, falling a distance, h, against gravity, g

$$w = -Mgh = -\frac{Mg}{A}Ah$$



i = initial

f = final

$$P_i < P_{\text{ext}} = \frac{Mg}{A}$$

$$P_f = P_{\text{ext}}$$

$$w = -P_{\text{ext}}\Delta V$$

$$\Delta V \text{ negative} \rightarrow w \text{ positive}$$

Same result as for expansion, but $\Delta V < 0$ so w is positive