

Sept. 13 2002: Lecture 5:

Thermodynamic Systems and Processes

Last Time

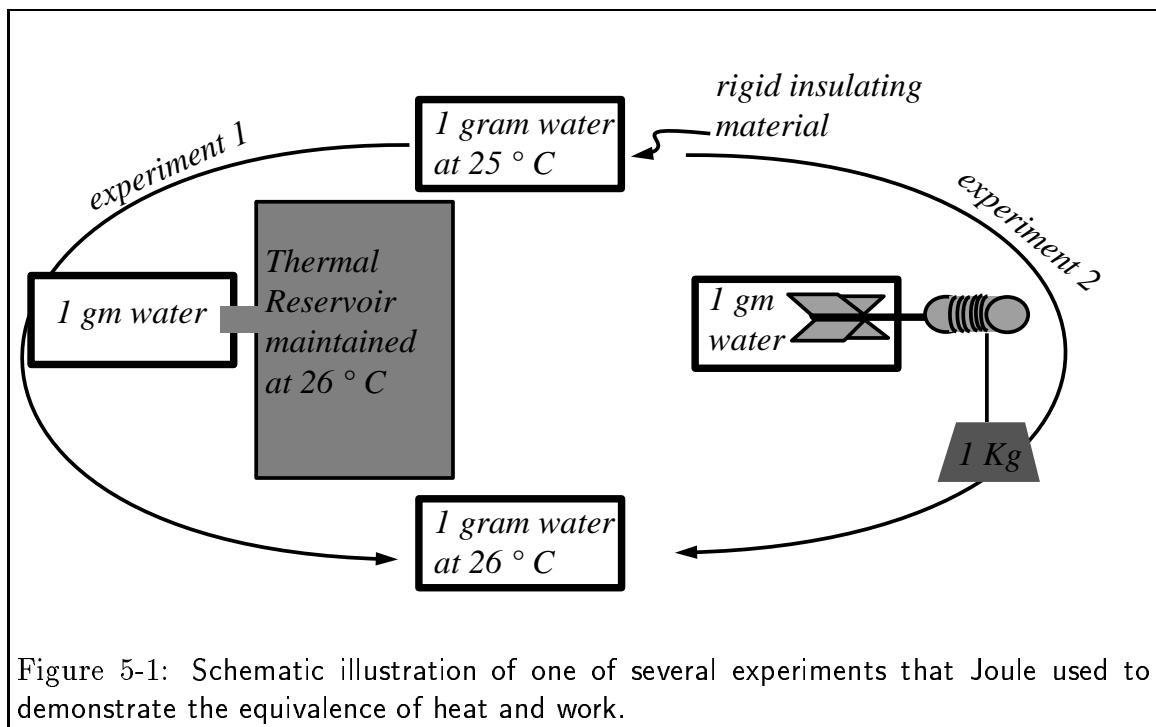
State Functions

Limiting Cases of Path Dependent Processes

James Joule, Hero of the First Law

First Law

Consider again the classical experiment that illustrates the equivalent effects of adding heat to a system and doing an equivalent amount of work on a system.



The final conclusions of Joule's paper were:

That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force extended.

That the quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken between 55° and 60°F) by 1°F requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lb. through a space of one foot.

This states that work, defined here as a mechanical force exerted over a displacement, can be converted into an equivalent amount of heat.

Question: How long would it take to heat water about 5 degrees F?

We can state the first law as follows:

First Law of Thermodynamics: Version 1
<i>A state function, called the internal energy, exists for any physical system—and the change in the internal energy during any process is the sum of the work done on the system and the heat transferred to the system.</i>

There are several interpretations of the first law:

1. A restriction on the processes that occur in any system.

2. A definition.

3. A bookkeeping device.

And, now for something completely different:

A Sonnet to the First Law

How could I have have doubted your constancy
your warmth and labors summed, signify
your ever unchanging incessancy.
Though some virtues wane, will others supply
perfect completeness in my universe.
Are we not a pair, born of heat and toil,
controvertable, not better nor worse.
Though shoulders may be cold or blood may boil,
you are balanced and never violated.
Timeless compass of perfect reckoning,
northern star of mislaid paths translated,
you, the first, though a second, beckoning
Nature, forever, through her laws eschew
 $dw + dq$ is dU

W. Craig Carter, 2002

To define work, we need to consider all of the possible ways that we can change the *extent* of a system. Let dx represent the change in some arbitrary extensive quantity (volume, charge,

number of atoms of a certain type, total magnetization, etc) of a system and suppose that we construct some mechanical device to produce that change—just like in Joule’s experiments. Let the force be exerted by the device—during the change dx —be F , then the rate at which work is done per change dx is $dw = Fdx$. If there are N different extensive quantities (dx_1, dx_2, \dots, dx_N) then the rate at which work is done is:

$$dw = F_1 dx_1 + F_2 dx_2 + \dots + F_N dx_N = \sum_{i=1}^N F_i dx_i \quad (5-1)$$

Important: the F_i refer to the device that is producing the extent dx , while the dx_i refer to the system’s extensive variables.

Question: Suppose the system changes from some initial state $\mathcal{S}^{\text{init}} \equiv (x_1^{\text{init}}, x_2^{\text{init}}, \dots, x_N^{\text{init}})$ to some final state $\mathcal{S}^{\text{final}} \equiv (x_1^{\text{final}}, x_2^{\text{final}}, \dots, x_N^{\text{final}})$, could we just integrate to find:

$$\Delta w \equiv w(\mathcal{S}^{\text{final}}) - w(\mathcal{S}^{\text{init}}) \stackrel{?}{=} \int_{\mathcal{S}^{\text{final}}}^{\mathcal{S}^{\text{init}}} dw \stackrel{?}{=} \int_{\mathcal{S}^{\text{final}}}^{\mathcal{S}^{\text{init}}} \sum_{i=1}^N F_i dx_i \quad (5-2)$$

Because the forces refer their values during a change in a system, we can write the first law as a differential expression:

Differential Form of the First Law of Thermodynamics	
$dU = dw + dq$	

Those Pesky Minus Signs		
First Law Form	Work	Heat
$dU = dw + dq$		
$dU = dw - dq$		
$dU = -dw - dq$		
$dU = -dw + dq$		

Let’s work out a simple example for a capacitor:

Examples of different ways that work can be done will appear in later lectures.

For the definition of heat, let's use the definition of work and the first law and define *heat* is the *work-less transfer of internal energy from one system to another*. From our definition of the Zeroth law, it follows that heat flows from higher to lower temperature systems. To repeat, temperature refers a property of a system while heat refers to a process—the process of exchanging that part of internal energy that is not associated with work.

Types of systems

Question: What kinds of precautions did Joule have to make in his measurements such as those depicted in Figure 5-1

Notice that one must be very careful in defining what processes can and cannot happen and idealizations for the systems on which the experiments are being performed. For this reason, historically, a naming convention has arisen for certain types of systems, Definitions

Thermodynamic Systems		
TYPE	(Example)	
Isolated	(The Universe)	No energy and no matter may be passed through the boundaries
Closed	(A <i>free</i> Pinball Machine)	Energy can pass through the boundaries, but matter cannot pass through the boundaries. ^a
Adiabatic	(A <i>perfect</i> Thermos)	No heat (and therefore no matter) that can carry heat can pass through the boundaries.
Open	(An Aquarium)	Both energy and matter may be passed through the boundaries

^aThis does not exclude the possibility for a change in composition of the present phases or a change in the phase content.

Question: What kind of system is a refrigerator?

Question: What is the universe (i.e., all possible systems that must be considered to conserve energy) for a closed refrigerator plugged into an electrical socket

Types of Processes

Similarly, one needs a naming convention to describe types of processes.

Process Type	
Adiabatic	No heat passes through boundaries of the system
Isochoric	No work is transfer to the system from its surroundings
Isothermal	The temperature remains constant
Isobaric	The pressure remains constant
⋮	⋮
Isosomething	<i>Something</i> remains constant

Notice that *adiabatic* appears in both the definitions of systems and processes—it is used interchangeably. Adiabatic systems are those that have adiabatic boundaries which are defined by not being able to conduct heat. An adiabatic process is one that occurs without the transfer of heat.

Question: Considering a sheet of glass as a system, what kind of process is dropping and letting it crash onto the floor?

Question: Considering a bathroom scale, what kind of process is stepping onto it?

The definition of an adiabatic process allows an alternative definition of the first law:

First Law of Thermodynamics: Version 2
<i>The work done on a system during an adiabatic process is a state function and numerically equal to the change in internal energy of the system.</i>

Composition vs Concentration

It is useful to reiterate the definitions of concentration and composition.

Concentration is the number of something per unit volume:⁷

$$\text{Molar Concentration of Species } j = \frac{n_j}{V_{\text{total}}} \quad (5-3)$$

where n_j is the number of moles of j :

$$n_j \equiv \frac{N_j}{N_{\text{avag.}}} \quad (5-4)$$

where N_j is the number of j -type atoms or molecules.

⁷Or, alternatively, per unit mass. The conversion clearly involves the density. You can always tell which (mass or volume scaling) by looking at the units.

Mole fractions or number fractions are defined by:

$$\overline{N}_j = \frac{N_j}{N_{\text{total}}} \equiv X_j \quad (5-5)$$

Mole fractions are unit-less—they are just numbers and each must satisfy $0 \leq X_j \leq 1$ and their sum must satisfy:

$$1 = \sum_{j=1}^C X_j \quad (5-6)$$

Composition describes the molar chemical complexion of a system—it is the set of mole fractions: $(X_1, X_2, \dots, X_C) = \frac{1}{N_{\text{total}}}(N_1, N_2, \dots, N_C)$.

In the special case of the binary alloys (those that have only two possible components A and B), the composition can be identified with a single variable $X = X_B$ because X_A is fixed by the relation $X_A + X_B = 1$.