An Introduction to Thermodynamics

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Thermodynamics deals with quantities such as
work, heat and temperature.
It is concerned with **macroscopic**, not microscopic physics.

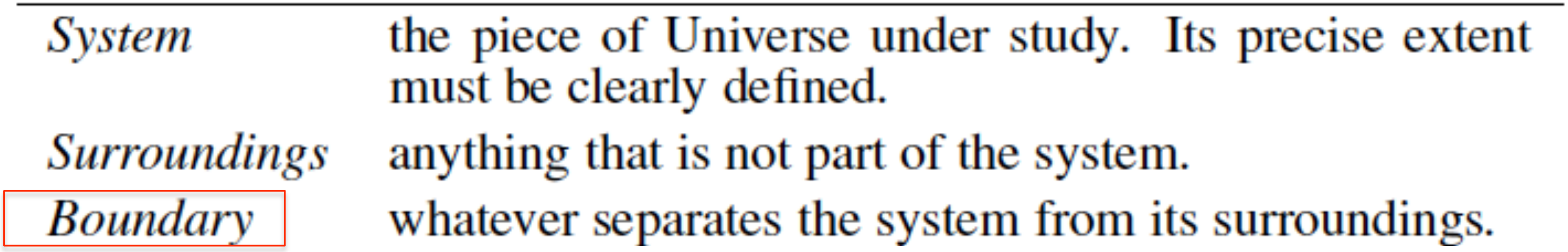
It is built from four fundamental laws deduced from experiments:

- Zeroth law: defines temperature.
- First law: defines internal energy and expresses the conservation of energy.
- Second Law: defines entropy and how efficiently one can convert heat to work.
- Third Law: establishes the unattainability of absolute zero.

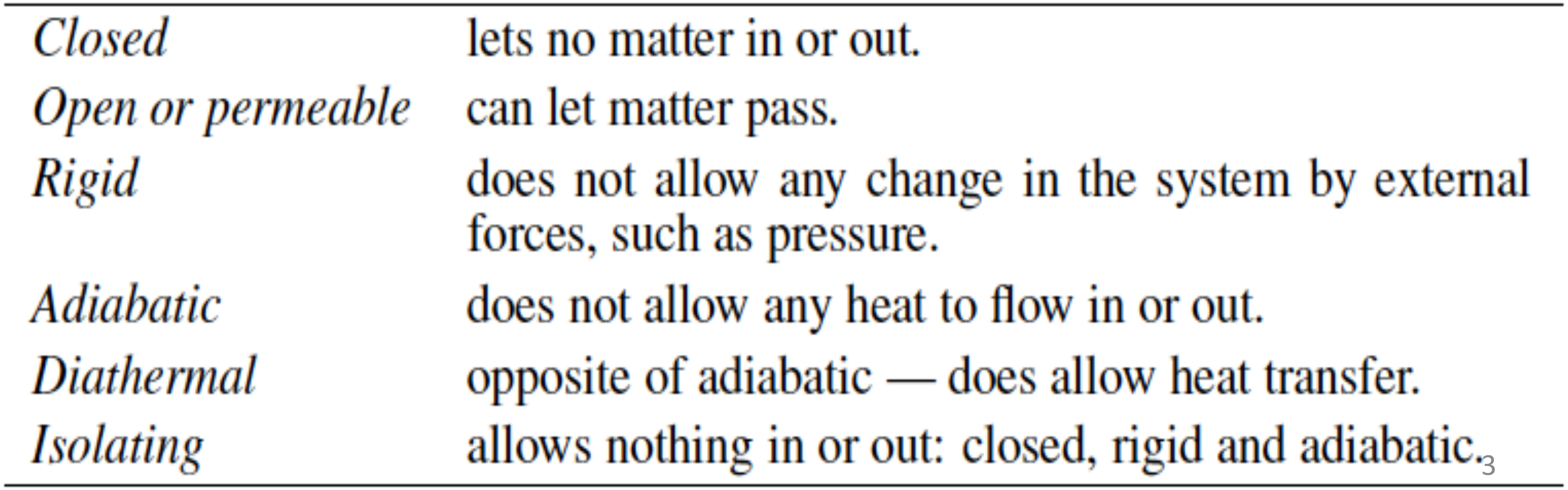
4.1 Thermodynamic Definitions

In thermodynamics, we are often concerned with changes of a system but very often these must be considered in conjunction with changes in the surroundings.

The two are linked by a boundary which can come in several different varieties.

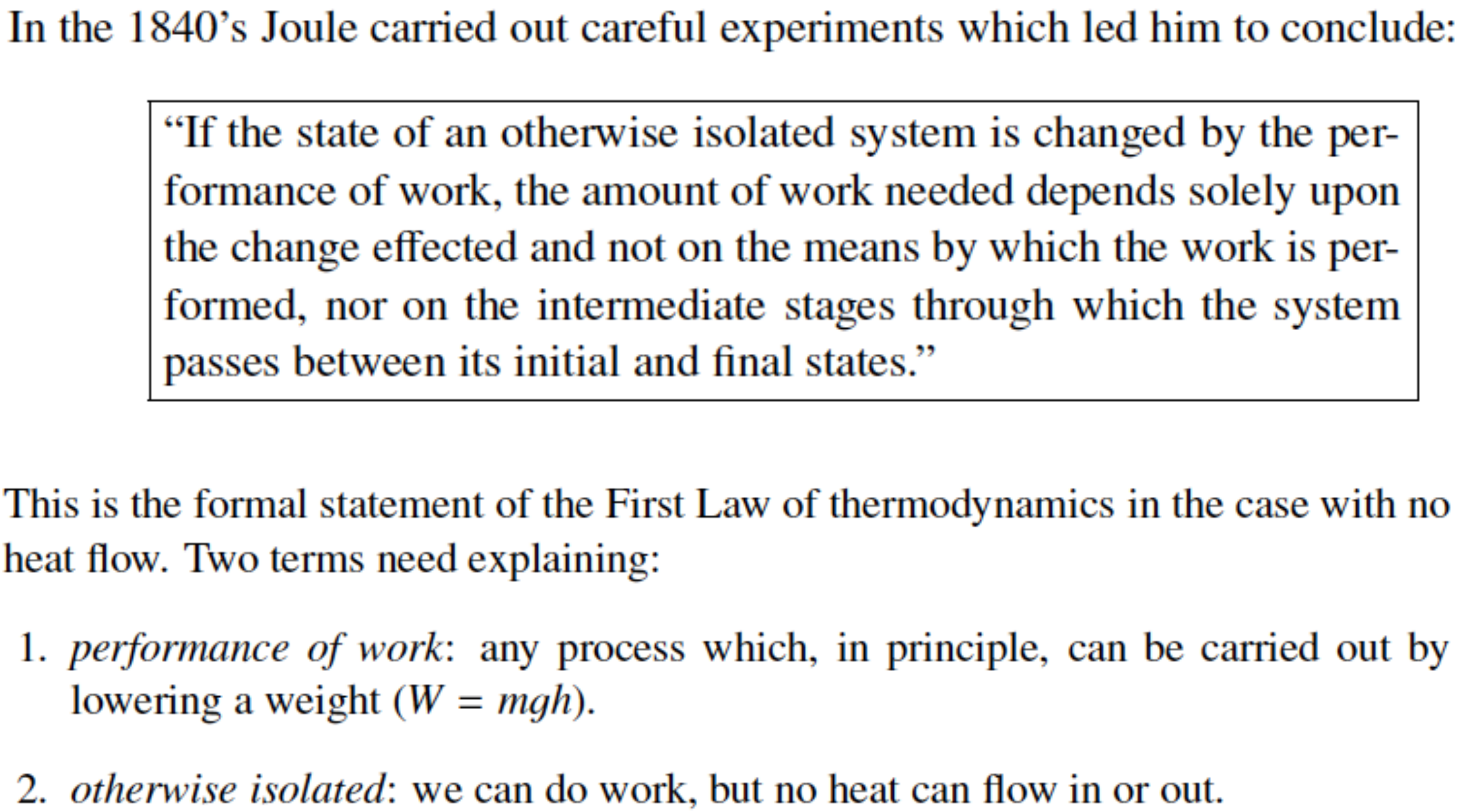


System	the piece of Universe under study. Its precise extent must be clearly defined.
Surroundings	anything that is not part of the system.
Boundary	whatever separates the system from its surroundings.



Closed	lets no matter in or out.
Open or permeable	can let matter pass.
Rigid	does not allow any change in the system by external forces, such as pressure.
Adiabatic	does not allow any heat to flow in or out.
Diathermal	opposite of adiabatic — does allow heat transfer.
Isolating	allows nothing in or out: closed, rigid and adiabatic.

4.2 The First Law of Thermodynamics



In the 1840's Joule carried out careful experiments which led him to conclude:

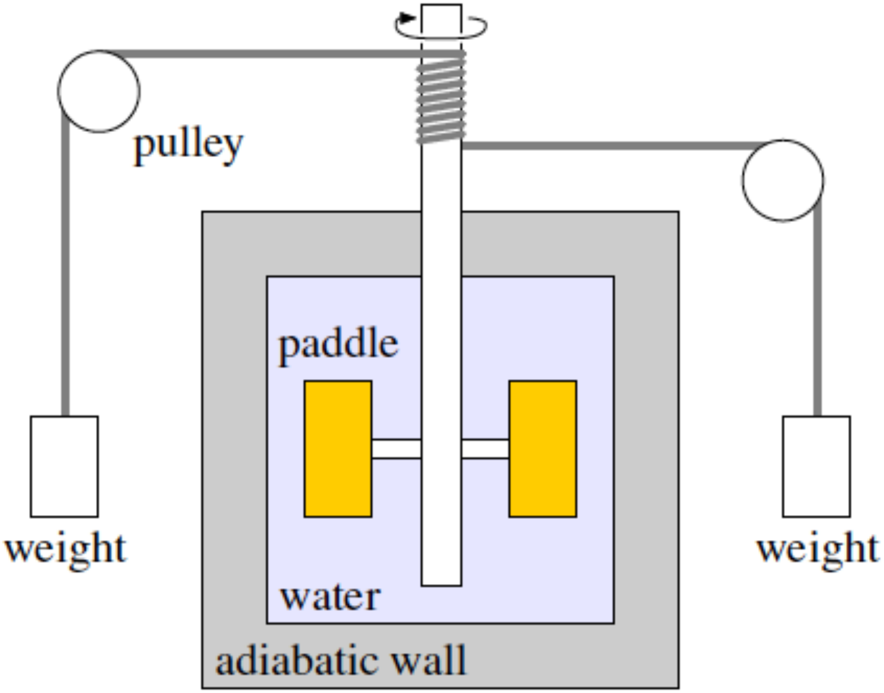
> "If the state of an otherwise isolated system is changed by the performance of work, the amount of work needed depends solely upon the change effected and not on the means by which the work is performed, nor on the intermediate stages through which the system passes between its initial and final states."

This is the formal statement of the First Law of thermodynamics in the case with no heat flow. Two terms need explaining:

1. *performance of work*: any process which, in principle, can be carried out by lowering a weight ($W = mgh$).
2. *otherwise isolated*: we can do work, but no heat can flow in or out.

4.2.1 What did Joule do?

Joule deduced the first law by trying different ways of carrying out work on a system, measuring the amount of work and determining the change in the system via its change in temperature.



Adiabatic wall does not allow any heat to flow in or out.

use of a paddle wheel driven by weights to stir water

What Joule found was that the amount of work required to change a system, when no heat is allowed to enter or escape, depends only upon the initial and final states of the system.

The First Law is nothing more than
the conservation of energy.

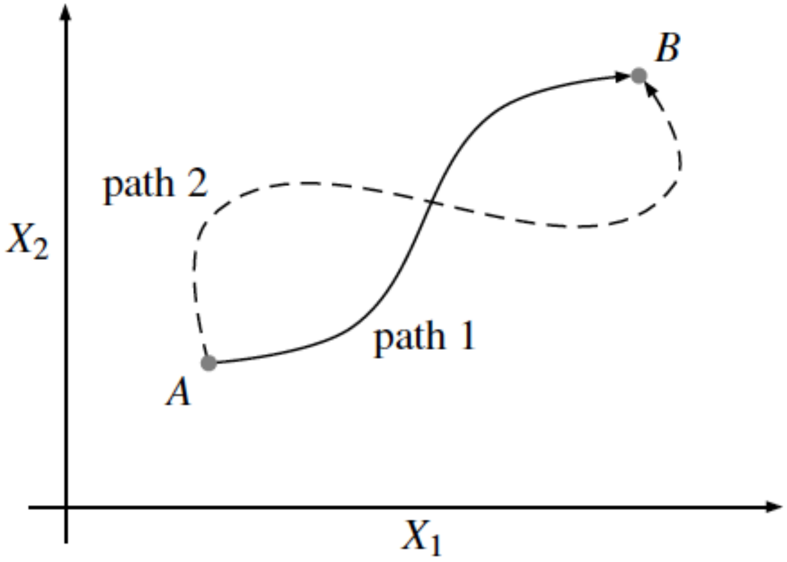
The energy represented by the performance of the same amount of work causes the same change in a system.

This leads to the recognition of the concept of internal energy.

4.3 Internal Energy

Joule's experiments show that the work done depends only upon the initial and final states of a system.

In other words, when a system changes from state A to B, the work done can be written as W = f (B) - f (A), where f is a function of the state of the system and not the path taken.



X_1 and X_2 define the state of the system, and could be, for instance, pressure and volume.

Examples of functions of state:

- pressure and volume
  the same state of a system must have the same volume by definition
- internal energy

NOT a function of state:

- Distance travelled
- Work
- Heat

The internal energy, U, is defined as:

$$W = U_{\text{final}} - U_{\text{initial}} = \Delta U$$

The work done on the system W changes its internal energy by W.

Note the sign convention: work done on the system is positive
work done by the system is negative

4.4 Heat

> *Heat* is the transfer of energy between a system and its environment due to a temperature difference between them.

we can define the heat entering a system, Q, in the case of no work, as:

$$Q = \Delta U$$

Heat added to a system is positive.
Heat given up by a system is negative.

Joule showed that heat and work are two forms of the same thing, which we call energy.

$$1\ \text{calorie} = 4.2\ \text{J}$$

the amount of heat needed to raise the temperature of 1 g of water by 1C.

$$1\ \text{Calorie} = 4200\ \text{J}$$

the amount of heat needed to raise the temperature of 1 kg of water by 1C.

4.5 Mathematical expression of the First Law

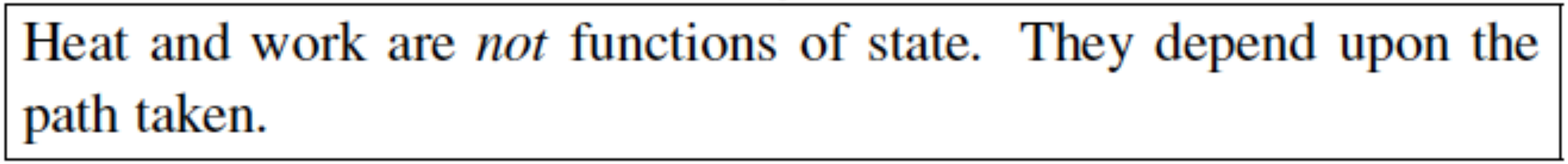
If heat is added and work is performed on a system,
then the first law becomes:

$$\boxed{\Delta U = Q + W}$$

$$\Downarrow$$

- energy is conserved,
- generalises conservation of kinetic + potential energy,
- defines heat as a form of energy.

Given a change in internal energy U it is impossible to say how much of it was work or how much was heat, without more information.
An infinity of different combinations of Q,W values can give the same U.



Heat and work are *not* functions of state. They depend upon the path taken.

For infinitesimal changes, we write the first law as:

$$\boxed{\mathrm{d}U = \text{đ}Q + \text{đ}W}$$

đ is used to remind that Q and W are not functions of state (unlike U)

4.6 Perpetual Motion Machines of the First Kind

The first law implies that you cannot create energy from nothing.

Devices that apparently run for ever without the need for fuel are known as perpetual motion machines of the first kind.

Imagine that the first law was not true.
Then moving from state A to B via path 1 could require us to put in work W_1, while we could extract work W_2 when moving back from B to A via path 2.
If $W_2 > W_1$, we could then extract a total amount of work
$W = W_2 – W_1$
if we went round the cycle in the right direction, we could ensure that $W > 0$.
This would be a perpetual motion machine.

The first law implies instead that $W = 0$ --> we can only break even.

4.7 Heat capacities

Let us consider the differential form of the first law:

$$đQ = \mathrm{d}U - đW.$$

And let us consider a change in temperature dT

We can define a heat capacity as
the heat input divided by the change in temperature:

$$C = \frac{đQ}{\mathrm{d}T} = \frac{\mathrm{d}U}{\mathrm{d}T} - \frac{đW}{\mathrm{d}T}$$

Note that the term heat capacity is inaccurate:
once heat enters a system, it loses its identity and should be thought of as energy.

If we don't allow a system to change its volume (rigid boundary) then it performs no work against external pressure.
The specific heat capacity at constant volume is usually denoted by C_V:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (W=0)$$

It is usually easier to measure the specific heat capacity at constant pressure, C_P.
In this case the system expands and does work on the surroundings, so the work done on the system, $W < 0$.

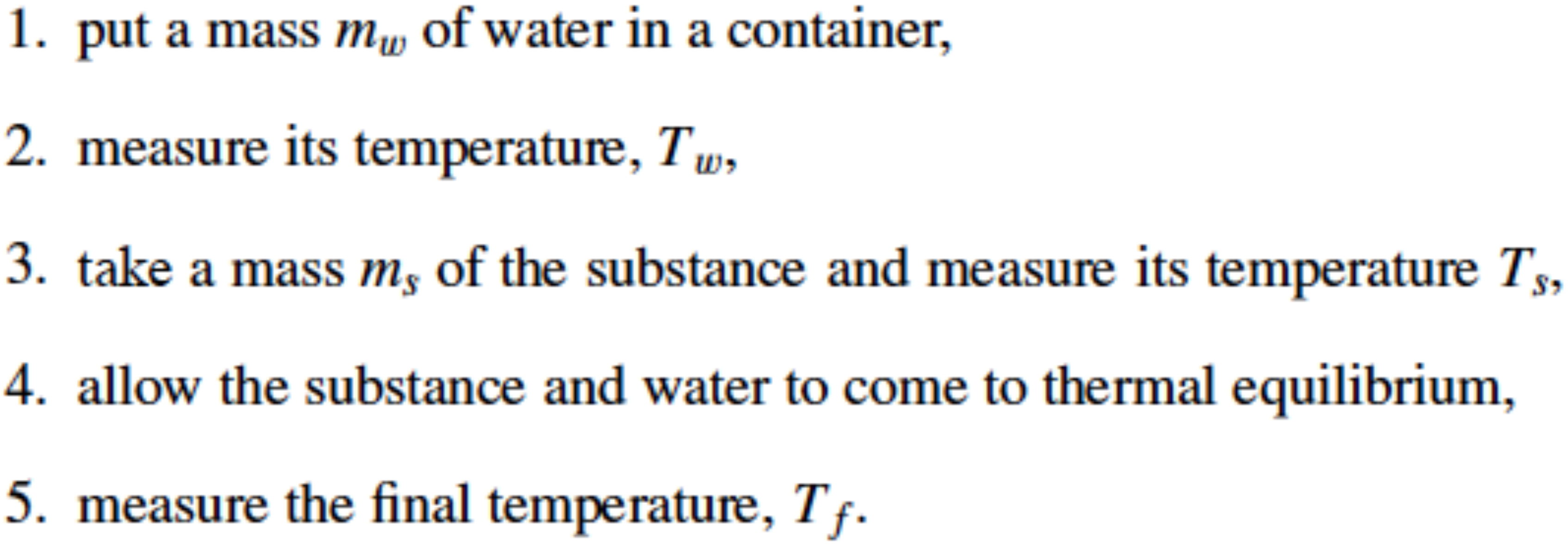
$$\Downarrow$$

$$C_P > C_V$$

4.8 Calorimetry

Calorimetry is the measurement of the heat of chemical reactions

We consider an isolating container, i.e. Q = W = 0 (not so easy to do), the specific heat capacity is then measured in the following way:



1. put a mass m_w of water in a container,
2. measure its temperature, T_w,
3. take a mass m_s of the substance and measure its temperature T_s,
4. allow the substance and water to come to thermal equilibrium,
5. measure the final temperature, T_f.

since Q = W = 0,
we have ΔU = Q + W = 0, and so U(initial) = U(final)

Since the internal energy of mass m of specific heat capacity C at temperature T is given by U = mCT (if C does not vary with temperature), we can write:

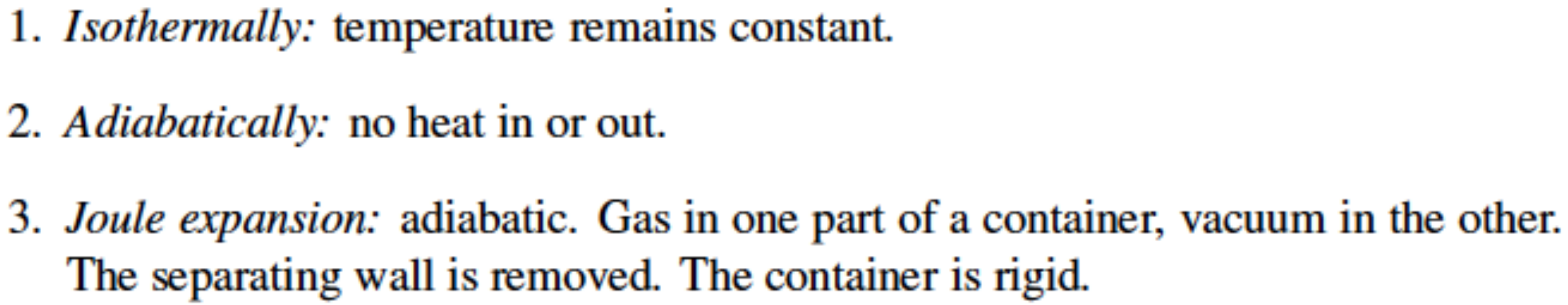
$$m_w C_w T_w + m_s C_s T_s = m_w C_w T_f + m_s C_s T_f$$

We can therefore write: $C_s = \frac{m_w C_w (T_f - T_w)}{m_s (T_s - T_f)}$

the heat lost by the substance equals the heat gained by the water.

4.9 Expansion & Compression of Gases

There are three distinctly different ways to expand or compress a gas:



1. *Isothermally:* temperature remains constant.
2. *Adiabatically:* no heat in or out.
3. *Joule expansion:* adiabatic. Gas in one part of a container, vacuum in the other. The separating wall is removed. The container is rigid.

4.9.1 Isothermal compression & expansion

If the gas is ideal, then U is a function of T_I only, i.e. $U(T_I)$. Therefore since T_I is constant, $\Delta U = 0$. Hence:

$$Q + W = 0$$

As the gas expands it does work, so $W < 0$, therefore $Q > 0$

During an isothermal expansion, the gas absorbs heat but does an exactly equivalent amount of work

⇓

its internal energy is unchanged (ideal gases only)

During compression,
you do work $W > 0$, which is given out as heat $Q < 0$.

4.9.2 Adiabatic compression & expansion

In the adiabatic case, $Q = 0$, so $\Delta U = W$.

All work done during compression
is stored
as internal energy in the gas.

4.9.3 Joule expansion

A Joule expansion is adiabatic and the container is rigid, so no work is done.

Therefore, $Q = W = 0$, and so $\Delta U = 0$
(valid also for non-ideal gases)

If U is a function of T and V:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Since the internal energy is zero, $dU = 0$ ➡

$$dT = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} dV.$$

Joule measured $dT = 0$ for gases and so deduced that:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0.$$

Joule measured dT = 0 for gases: if this is the case, then U is indeed a function of T only, U = U(T).

In this case, we no longer need to qualify the derivative as being at constant volume, and we can write:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT}.$$

This means that

$dU = C_V\, dT$

but this only applies when U = U(T).

4.10 Summary

The First Law is nothing more than the conservation of energy.

$$\boxed{\Delta U = Q + W}$$

Heat and work are *not* functions of state. They depend upon the path taken.

$$\boxed{\mathrm{d}U = \text{đ}Q + \text{đ}W}$$

Heat capacity: $$C = \frac{\text{đ}Q}{\mathrm{d}T} = \frac{\mathrm{d}U}{\mathrm{d}T} - \frac{\text{đ}W}{\mathrm{d}T}$$