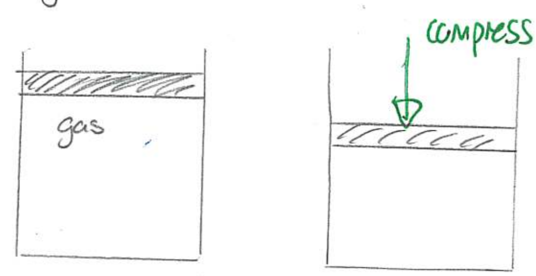
Lecture 4

Fri: HW 3 by 5pm

Tues: Read 2.8 – 2.10, 2.24.1

Thermodynamic Processes

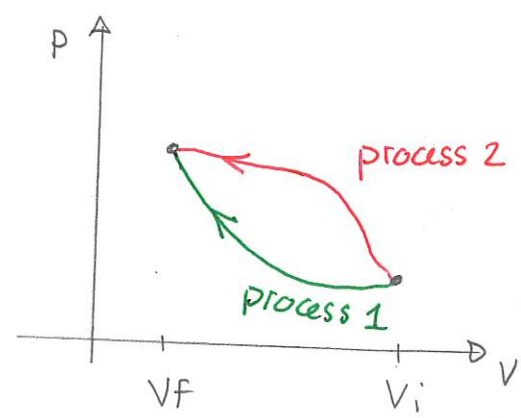
A thermodynamic process is one where the state of a thermodynamic system changes. For example we could compress a gas and this will change some or all of the bulk variables that describe the system. Thus the state of the system changes.



		changes	
volume	V_i	$\rightsquigarrow$	V_f
pressure	P_i	$\rightsquigarrow$	P_f
temperature	T_i	$\rightsquigarrow$	T_f

We will mostly consider quasistatic processes. These are processes where at all stages during the evolution, the system is in a thermal equilibrium state.

For a gas with a fixed number of particles, we can represent a quasistatic process as a curve on a PV-diagram. There are many possible processes between given initial and final states and these are represented by different PV curves. These will have the form

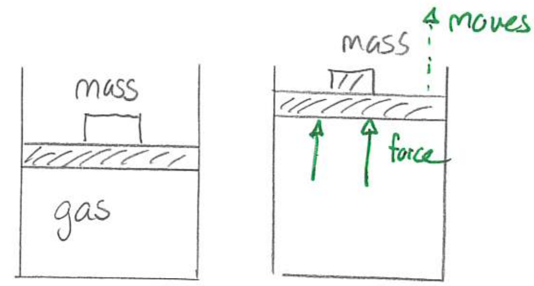


$$P = P(V)$$

for some function $P(V)$.

Work and energy in thermodynamic systems

Consider a gas that is initially compressed and subsequently expands. If we consider the motion of the supported mass then:



* in this process the mechanical energy

  $K + U_{grav}$

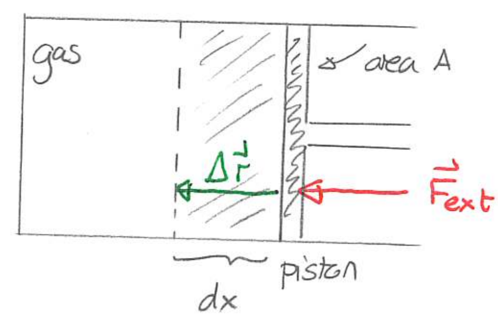
  of the mass increases

* the gas exerts a force on the "lid" and this force does work

How would this work and energy be related?
Once the gas stops expanding there is greater mechanical energy than before.
Where did this energy come from?

The work done by a gas can be analyzed mechanically. Consider:

* a gas in a cylinder, where one side is closed by a frictionless piston that can move horizontally



* let A be the area of the piston surface
* the piston is pushed so that it moves with constant speed. The external force that pushes is $\vec{F}_{ext}$.
* the piston moves an infinitesimally distance dx and the gas pressure while this happens is approximately constant at P.

Then we calculate the work done by the external force on the piston. This is

$$dW = \vec{F}_{ext} \cdot \Delta\vec{r} = F_{ext}\, dx$$

If the piston moves with constant velocity then the net force on the piston is zero. Thus

$$F_{ext} = PA$$

So $\quad dW = PA\,dx.$

Now the change in volume of the gas is $\quad dV = -A\,dx$. Thus, in this infinitesimal step, the work done on this piston is

$$\boxed{dW = -P\,dV}$$

If the piston moves with constant velocity then the net work done on the piston is zero since the piston kinetic energy is constant. It follows that the gas does work $dW = PdV$ <u>on</u> the <u>piston.</u> We then say that the piston does work $dW = -PdV$ <u>on</u> the <u>gas.</u>

We extend this to a non-infinitesimal process by integration.

The work done <u>on</u> a gas in <u>any</u> <u>quasistatic</u> process is

$$W = -\int_{\text{initial state}}^{\text{final state}} P(V)\,dV$$

where $P(V)$ describes the process by expressing the pressure as a function of volume.

<u>Important points:</u>

1) the rule provided above applies for any <u>quasistatic</u> process on <u>any</u> gas
2) the work done <u>by</u> the gas in any process is the negative of the work done <u>on</u> the gas
3) work is negative of the area under P vs V curve.

1 Work done in various processes

Consider an ideal gas initially at pressure P_i and with volume V_i. The gas is compressed to half of its initial volume by one of the following two processes:

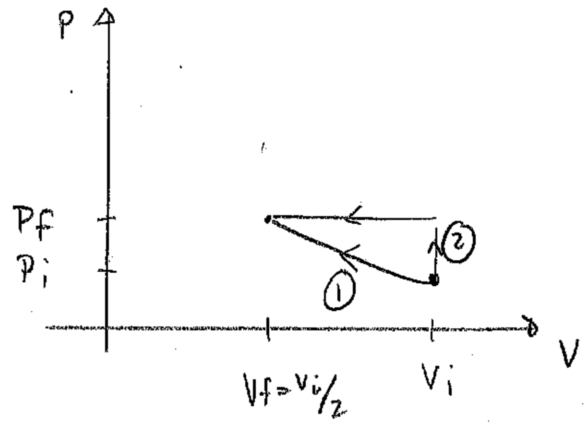
$\boxed{1}$ an isothermal process, where the temperature remains constant at all times,

$\boxed{2}$ a two-stage process in which the volume is held constant until the pressure doubles and then the pressure is held constant until the volume halves.

a) Sketch each of these on a PV diagram.

b) Determine the work done for each process, expressing the result in terms of N, k and the initial temperature T_i.

Answer: a)



isothermal $\Rightarrow T = \text{const}$

$\Rightarrow PV = NkT = \text{const}$

b) for process $\boxed{1}$ $\quad PV = NkT \Rightarrow P = NkT \frac{1}{V}$

The temperature is constant so $T = T_i$ is constant

$$W = -\int_{V_i}^{V_f} P(V)dV = -NkT_i \int_{V_i}^{V_f} \frac{1}{V} dV = -NkT_i \ln V \Big|_{V_i}^{V_f}$$

$$W = -NkT \ln\left(\frac{V_f}{V_i}\right) = NkT \ln\left(V_i / V_i/_2\right) \Rightarrow W_1 = NkT_i \ln 2$$

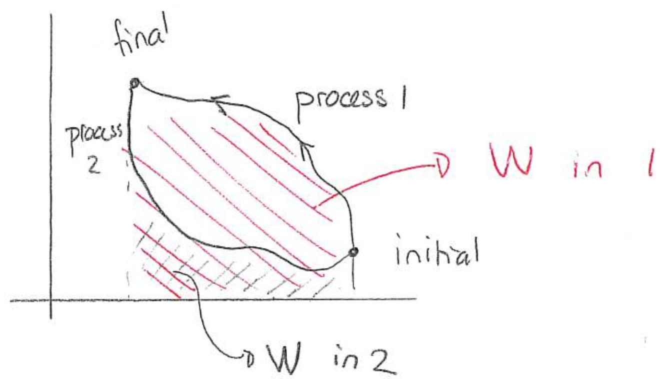
for process $\boxed{2}$

$$W = -\text{area under PV curve} = -\left[P_f(V_f - V_i)\right] = -P_f\left(\frac{V_i}{2} - V_i\right) = \frac{V_i P_f}{2}$$

Then $P_f = 2P_i \Rightarrow W = V_i P_i = NkT_i \qquad W_2 = NkT_i$

The example illustrates an important fact about work.

> The work done on a thermodynamic system depends on:
>
> 1) the initial and final states of the process
>
> 2) the nature of the process.
>
> Two processes from the same initial to same final states can yield different works



Although we mostly consider work for gases similar rules apply for other thermodynamic systems. For example consider a collection of nuclear spins. Here the variables are:

$N \equiv$ number of spins

$\vec{M}$ = magnetization

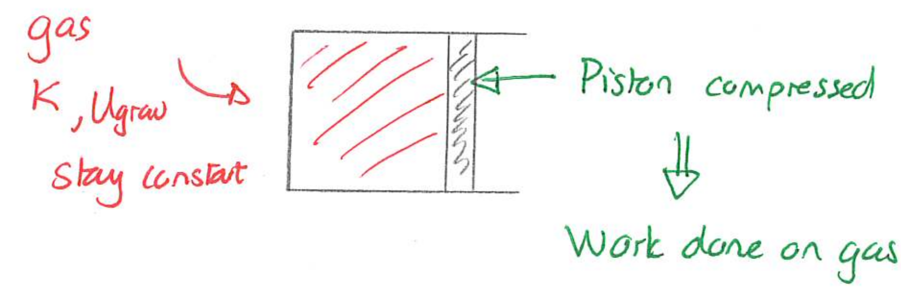
$\vec{B}$ = magnetic field.

Then work can be done by changing the magnetic field or other manipulations. Classical electrodynamics gives that the work done on the spins is

$$W = \mu_0 \int_{\text{initial}}^{\text{final}} \vec{B} \cdot d\vec{M}$$

Energy and thermodynamics

A thermodynamic system can have energy associated with its bulk motion. However, for the compression process described earlier, there was no change in the bulk kinetic or gravitational potential energy of the system. The work done by the piston must be reflected in some other type of energy.

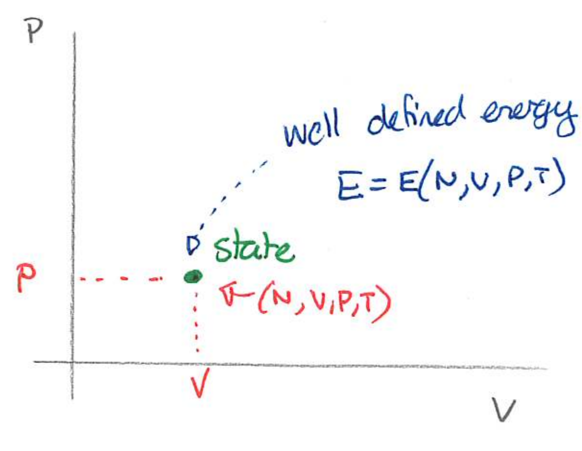


Without refering to the constituents of the system, a general postulate for thermodynamic systems is

> For any thermodynamic system, there exists an (internal/thermal) energy, E, that only depends on the state of the system.

Thus

> There exists a function
>
> $$E = E(N, V, P, T)$$
>
> that only depends on the state of the system



To proceed we will need

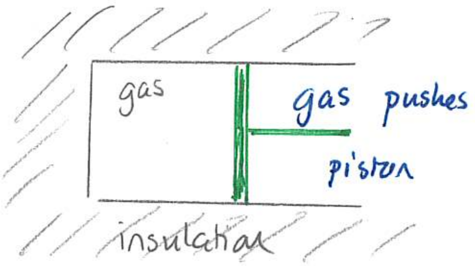
1) a method that accounts for changes in E when a system undergoes thermodynamic processes

2) a method for determining the function E for any thermodynamic system.

To deal with the first question, we classify two types of quasistatic process.

Thermally isolated process	Non-isolated process

Thermally isolated process



Except for the piston, the gas does not interact with its surroundings. The gas can only exchange mechanical energy with the piston.

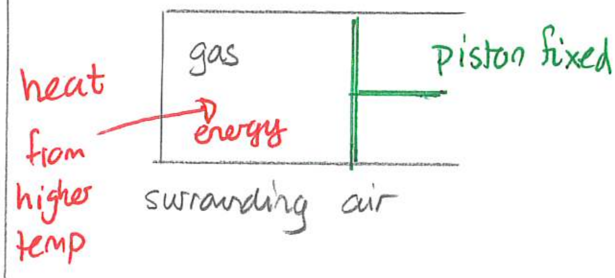
If the piston expands $dV > 0$ and

$$W < 0$$

The gas:

* loses energy to the piston

Non-isolated process



There is no work done since the volume is constant

$$W = 0$$

But if the piston were released the gas would expand and do work.

So energy must have been added to the gas. This energy

* came from the surroundings
* is not mechanical.

First Law of Thermodynamics

There are processes on thermodynamics where all modifications to the energy are done via work. These are called adiabatic

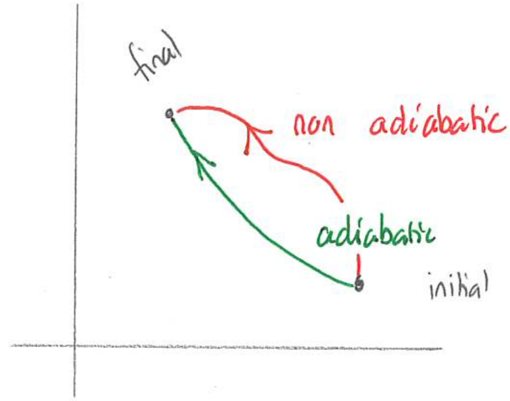
> For an adiabatic process the change in energy is
>
> $$\Delta E = W$$
>
> where W is the work done on the system

DEMO: U Iowa Fire Syringe.

We will eventually describe an adiabatic process for an ideal gas via an equation relating P and V.

Now consider other possible processes.

We can compare the changes in energy and work done for these.



2 Adiabatic versus non-adiabatic process

Two compression processes will be illustrated for an ideal gas. Both start at the same initial state and end at the same final state. One is adiabatic and the other is not.

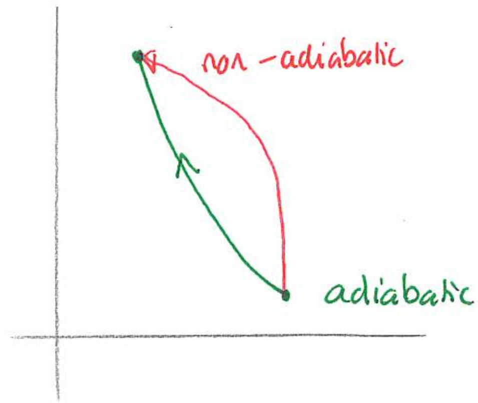
a) How does the change in energy, ΔE, compare for the processes?

b) How does the work done compare for the processes?

c) For the non-adiabatic process is $\Delta E = W$, $\Delta E > W$, $\Delta E < W$.

Answer: a) The energy only depends on the initial + final states. So

$$\Delta E = \text{same}$$



b) $W = -$area under P vs V

$$W_{non} > W_{adiabatic}.$$

c) for adiabatic $\quad \Delta E = W_{adiabatic}$

$$\Rightarrow \quad \Delta E < W_{non}.$$

If the process is non-adiabatic then there is clearly a form of energy that is not mechanical work that is involved. This is energy, called heat, is specifically not associated with changes in volume. So

Heat, Q, is energy that enters or leaves a thermodynamic system that
- is not a result of mechanical work on the system
- requires interaction with another thermodynamic system.

The First Law of Thermodynamics describes this precisely

Suppose that a system undergoes a process from an initial to a final state. Then

$$\Delta E = W + Q$$

where $\Delta E = E_f - E_i$ and E_f = energy final state

E_i = energy initial state

W = work done on the system

Q = heat entering the system

Notes about heat

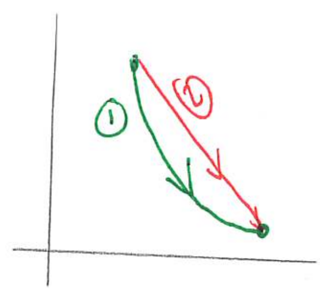
1) Heat is always associated with a change in state. It is not associated with a state.

2) Heat depends on the process and not only the initial/final states.

In the illustrated processes ΔE is the same $\Rightarrow$ $W + Q$ = same

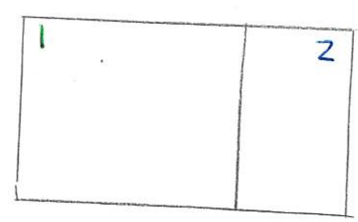
But $W < 0$ for both and thus

$W_1 > W_2 \Rightarrow Q_2 > Q_1$



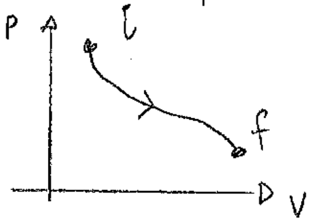
3) If two systems interact and do not do work on each other then they So if Q_1 leaves 1 and Q_2 enters 2 and no work is done, then

$$Q_1 + Q_2 = 0$$



The first law applies to all processes. There will be differences in computing heat in different processes:

Quasistatic process



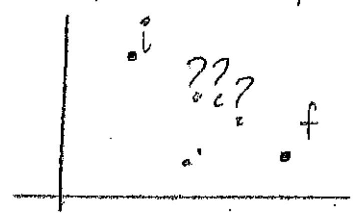
* Find curve $P = P(V)$
* Compute work

$$W = -\int P(V)\,dV$$

* Compute change in energy ΔE
* Compute heat

$$Q = \Delta E - W$$

Non-quasistatic process



- no curve
- cannot integrate to get W
- can compute ΔE
- first law still true

$$\Delta E = Q + W \Rightarrow Q = \Delta E - W$$

In order to do this we need the equation for energy.

Energy equation of state

The energy equation of state depends on the system in consideration. We will eventually find:

For a monoatomic ideal gas $\quad E = E(N,T) = \frac{3}{2} NkT$

For a monoatomic v. d. Waals gas

$$E = E(N,T,V) = \frac{3}{2} NkT - \frac{N^2}{V} a$$

3 Energy for an ideal gas process

A monoatomic ideal gas with N particles, initially at volume V_i, undergoes an expansion that doubles its volume. During this process,

$$P = \frac{a}{V^2}$$

where $a > 0$ is a constant with units of Pa m^6.

a) Determine the work done on the gas.

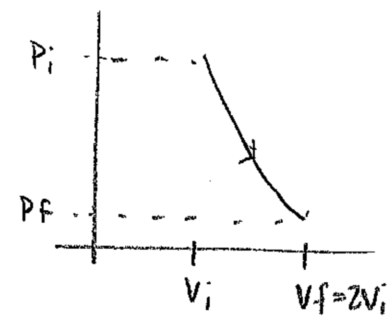
b) Determine the change in internal energy of the gas.

c) Determine the heat that enters or leaves the gas.

Answer: a) $W = -\int P\,dV$

$$= -\int_{V_i}^{V_f} \frac{a}{V^2}\,dV = \frac{a}{V}\Big|_{V_i}^{V_f}$$

$$= \frac{a}{V_f} - \frac{a}{V_i} = \frac{a}{2V_i} - \frac{a}{V_i} = -\frac{a}{2V_i}$$



$$W = -\frac{a}{2V_i}$$

b) $\Delta E = E_f - E_i = \frac{3}{2}NkT_f - \frac{3}{2}NkT_i$ Note $NkT = PV$

$$= \frac{3}{2}(P_f V_f - P_i V_i)$$

$$= \frac{3}{2}\left(\frac{a}{V_f^2}V_f - \frac{a}{V_i^2}V_i\right) = \frac{3}{2}a\left(\frac{1}{2V_i} - \frac{1}{V_i}\right) = -\frac{3a}{4V_i}$$

$$\Delta E = -\frac{3a}{4V_i}$$

c) $\Delta E = W + Q \Rightarrow -\frac{3a}{4V_i} = -\frac{a}{2V_i} + Q$

$$\Rightarrow Q = \frac{2}{4}\frac{a}{V_i} - \frac{3a}{4V_i} = -\frac{a}{4V_i} \Rightarrow Q = -\frac{a}{4V_i}$$