

Tues: Read: ~~2.9~~ 2.9, 2.10

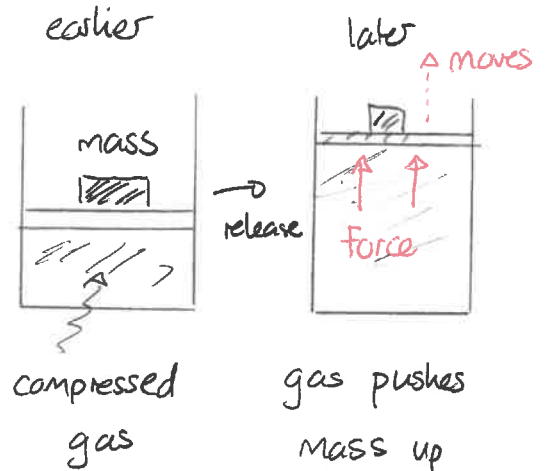
Fri: HW 3

Work and Thermodynamic Systems

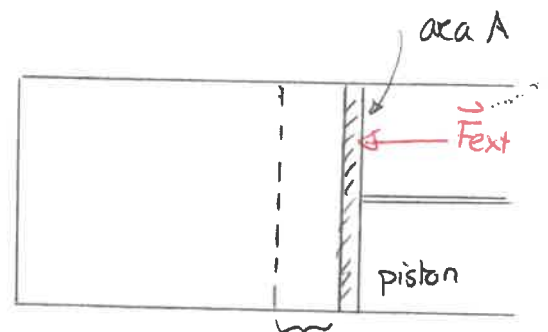
We have seen that a thermodynamic system can do work on its surroundings.

In the illustrated situation it can be made to lift a massive object. Clearly the gas can do work on its surroundings.

Conversely we could compress the gas via a heavier masspiece on the piston and the surroundings must then be doing work on the gas.



The situation can be analyzed by considering a gas in a cylinder which is compressed along the cylinder axis. Suppose that the piston is



compressed by distance  $dx$

- 1) pushed at constant velocity by a constant external force  $F_{ext}$
- 2) the piston moves an infinitesimal distance  $dx$
- 3) the displacement of the piston is so small that the pressure of the gas stays constant at  $P$ .

Then the work done on the gas is small and is denoted  $dW$ .

From  $W = \vec{F} \cdot \Delta \vec{r}$  we get

$$dW = F_{\text{ext}} dx$$

Since the piston moves with constant velocity the net force on it is zero.

Thus

$$F_{\text{ext}} = PA$$

So

$$dW = PA dx$$

Now  $A dx$  is related to the change in volume of the gas by

$$A dx = -dV$$

Thus

$$dW = -PdV$$

For a non-infinitesimal process:

The work done on a gas in any quasistatic process is:

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

where  $P(V)$  is the pressure expressed as a function of volume during the process

Note 1) this basic rule applies for any type of gas

2) work done by the gas in any process is the negative of the work done on the gas.

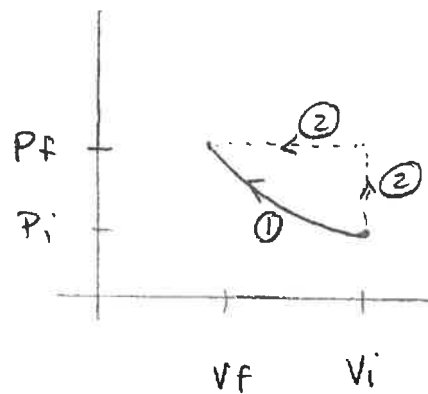
3) work is negative of area under  $P$  vs  $V$  curve.

## 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:

1. an isothermal process, where the temperature remains constant at all times,
  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)



b) For process (1)  $PV = NkT_i = \text{const}$

$$\Rightarrow P(V) = \frac{NkT_i}{V}$$

$$W = - \int_{V_i}^{V_f} \frac{NkT_i}{V} dV = - NkT_i \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Rightarrow W = - NkT_i \ln V \Big|_{V_i}^{V_f} = - NkT_i \ln \frac{V_f}{V_i} = - NkT_i \ln \frac{V_f/2}{V_f}$$

$$\Rightarrow W = NkT_i \ln 2$$

For process (2)  $W = - \text{area under } P(V) \text{ curve}$

$$= - P_f (V_f - V_i)$$

$$= - P_f \left( \frac{V_i}{2} - V_i \right) = \frac{V_i P_f}{2}$$

Now  $P_f = 2P_i \Rightarrow W = V_i P_i = NkT_i$

$$\Rightarrow W = NkT_i$$



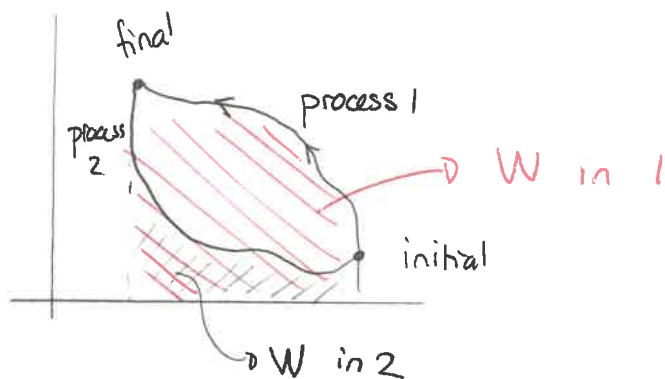
The example illustrates an important fact about work.

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

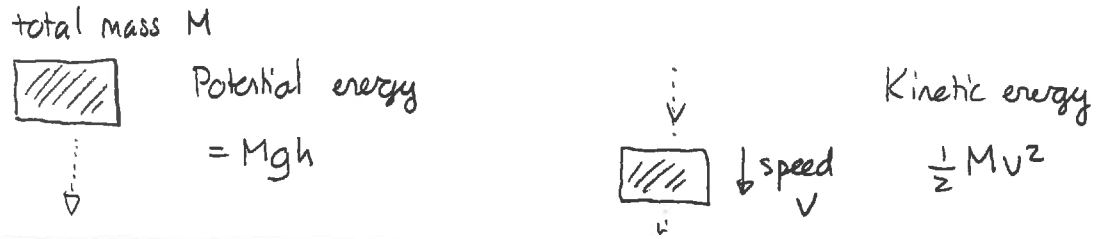
$\vec{B} =$  magnetic field.

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 + thermodynamics

The work done on a gas must surely be related to energy. There are certainly bulk energy properties for the entire gas:



We do not want to assess the bulk motion and the bulk energy of the gas. The processes that we have described could occur without any change in the center of mass and therefore these bulk energies.

Rather there must be an energy that is internal to the gas and perhaps associated with its constituents. Classical thermodynamics does not consider the constituents but just the entire bulk system.

A general postulate for such thermodynamic systems is

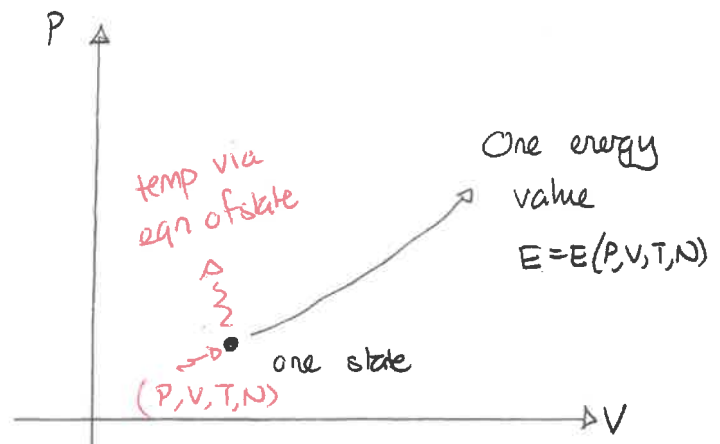
For any thermodynamic system, there exists an (internal/thermal) energy,  $E$ , which only depends on the state of the system

Conceptually:

There is a function

$$E = E(P, V, T, N)$$

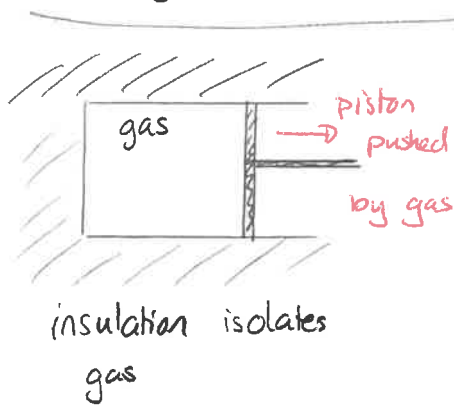
that only depends on the system state.



This brings up two considerations:

- 1) we need a method for determining the internal energy function for a gas
- 2) we need methods for accounting for changes in internal energy during processes.

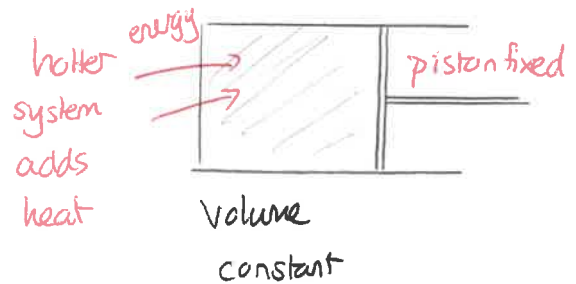
We consider the second issue first. Consider two processes for a gas:



The gas can push the piston and then the work done on the gas is negative

$$W < 0$$

Work describes bulk mechanical change in gas (i.e. change in  $V$ )



Volume is constant so  $W=0$

However energy is added to gas because it could subsequently push piston. This energy, not accounted for by work is called heat,  $Q$

Heat accounts for energy that can be supplied without bulk change

### First Law of Thermodynamics

If a system is isolated from its surroundings then the only way to modify the energy is by doing work. In this case the process is called adiabatic

Strictly:

For an adiabatic process the change in energy is

$$\Delta E = W$$

where  $W$  is the work done on the system.

We will eventually describe adiabatic processes for an ideal gas.

Consider other possible processes between the same initial + final states.

In these processes.

- 1)  $\Delta E$  is same for both
  - 2)  $W$  is different
- }  $\Rightarrow$  In general  $\Delta E \neq W$

The remaining energy that is supplied is called heat,  $Q$ , measured in Joules specifically

Heat,  $Q$ , is the energy that enters or leaves the system and which is not accounted for via the work done on the system.

This has a precise definition via the First Law of Thermodynamics

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

$$\Delta E = W + Q$$

where

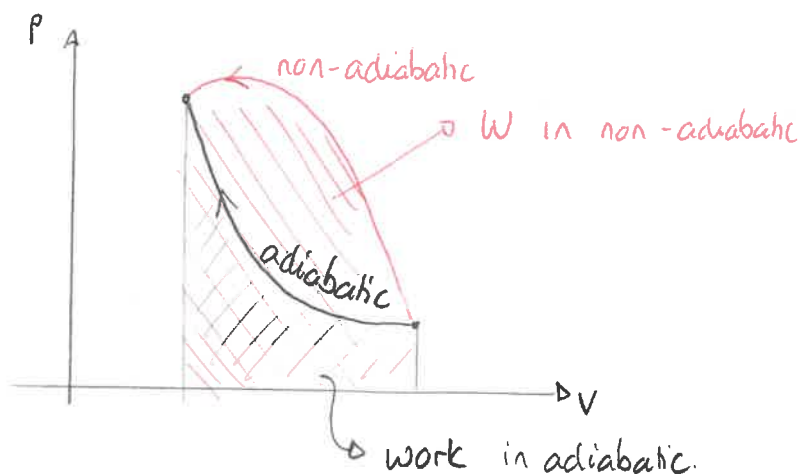
$$\Delta E = E_f - E_i$$

$E_i$  = energy initial state

$E_f$  = energy final state

$W$  = work done on the system

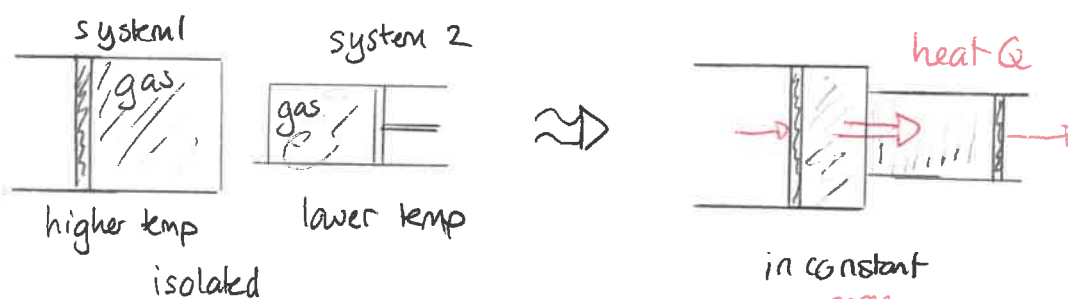
$Q$  = heat entering the system.





Why is the inclusion of heat not simply bookkeeping for the purpose of preserving energy conservation? There are at least two reasons:

- 1) one can eventually calculate heat flow in ways other than  $Q = \Delta E - W$
- 2) if systems interact and exchange heat then this form of energy is conserved in the transfer



Then

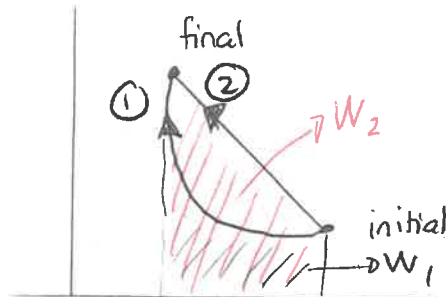
for system 1	$\Delta E_1 = W_1 -  Q $	}	$\Rightarrow \Delta E_1 + \Delta E_2 = W_1 + W_2$
for system 2	$\Delta E_2 = W_2 +  Q $		

$\swarrow$  same  $\nwarrow$  same

The following facts about heat are important:

- 1) Heat is associated with a process from state to another. It is not associated with a state.
- 2) Heat depends on the process and not just the initial / final states

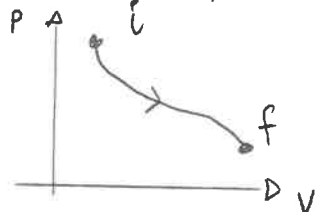
Consider the illustrated processes. Since the initial / final states are the same  $\Delta E$  is the same. Thus



For process 1 : $\Delta E = W_1 + Q_1$	}	$\Rightarrow$	$W_1 + Q_1 = W_2 + Q_2$
For process 2 : $\Delta E = W_2 + Q_2$			$\Downarrow$ If $W_2 > W_1$ , then $Q_2 < Q_1$

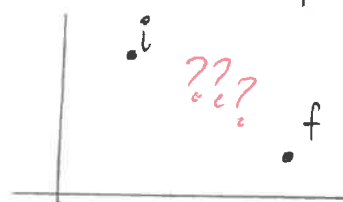
The first law applies to all processes. There will be differences in computing heat in different processes:

Quasistatic process



- \* Find curve  $P=P(V)$
- \* Compute work
 
$$W = - \int P(V) dV$$
- \* Compute change in energy  $\Delta E$
- \* Compute heat
 
$$Q = \Delta E - W$$

Non-quasistatic process



- no curve
- cannot integrate to get  $W$
- can compute  $\Delta E$
- 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  $E = E(N, T) = \frac{3}{2} NkT$

For a monoatomic v. d. Waals gas

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

## 2 Energy for an ideal gas process

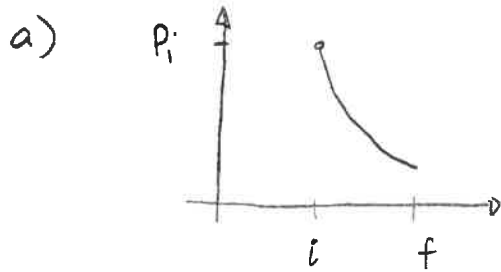
A monatomic ideal gas with  $N$  particles, initially at volume  $V_i$ , undergoes an expansion that doubles its volume. During this process,

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

where  $a > 0$  is a constant with units of Pa m<sup>6</sup>.

- 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



$$V_f = 2V_i$$

$$W = - \int_i^f P dV = - \int_{V_i}^{V_f} \frac{a}{V^2} dV = - a \int_{V_f}^{2V_i} \frac{1}{V^2} dV$$

$$\Rightarrow W = \left. \frac{a}{V} \right|_{V_i}^{2V_i} = \frac{a}{2V_i} - \frac{a}{V_i} \Rightarrow \boxed{W = -\frac{a}{2V_i}}$$

b)  $E = \frac{3}{2} NkT = \frac{3}{2} PV$  since  $NkT = PV$

$$\Delta E = E_f - E_i$$

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

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

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

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

c)  $\Delta E = W + Q$

$$\Rightarrow Q = \Delta E - W = -\frac{3a}{4V_i} - \left( -\frac{a}{2V_i} \right) \Rightarrow \boxed{Q = -\frac{a}{4V_i}}$$