Lecture 3

Tues: HW by 5pm

Thurs: Read

Seminar 12:30 Wubben 160

Fri: HW 3 by 5pm

Equation of State

Equilibrium states are described in terms of bulk variables and these are often not independent. For example a gas is described by the variables:

$$P, V, N, T$$

and they are related by an equation of state $P = P(V, N, T)$. As an example the (pressure) equation of state for an ideal gas is

$$P = P(V, N, T) = \frac{NkT}{V}$$

In many situations the equation of state is determined via observations. How would one do this?

Determining the equation of state.

There are two aspects to determining the equation of state:

* a system of experimental observations and measurements
* using the data and mathematics to eventually produce an equation of state.

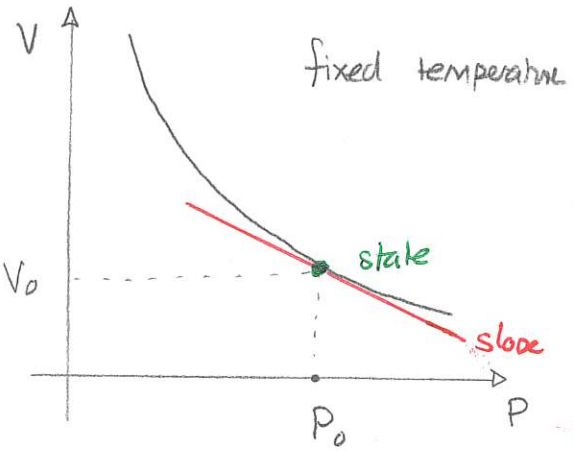
For gases there will be two parts:

* how volume changes with temperature
* how volume changes with pressure.

and we will assume a fixed number of particles

The basic mathematical idea can be illustrated by considering how to determine the relationship between volume and pressure

DEMO: Use yellow surface
show PV edge



We want to determine the expression for the curve. We can do this by

Determine how V varies as P varies at one temperature T_0

Determine one location on the curve i.e. P_0, V_0, T_0 for one state

Determine the slope of the curve experimentally. (mathematically this is $\frac{\partial V}{\partial P}$)

Integrate to determine an expression for V as a function of P at this single temperature T_0

Now repeat the process to determine how V varies with T at one pressure P_0

DEMO: Show VT edge.

Quite generally, if we regard pressure and temperature as the quantities we can vary, the change in volume is

$$dV = \left(\frac{\partial V}{\partial T}\right)dT + \left(\frac{\partial V}{\partial P}\right)dP$$

and we will effectively find $\frac{\partial V}{\partial T}$ and $\frac{\partial V}{\partial P}$.

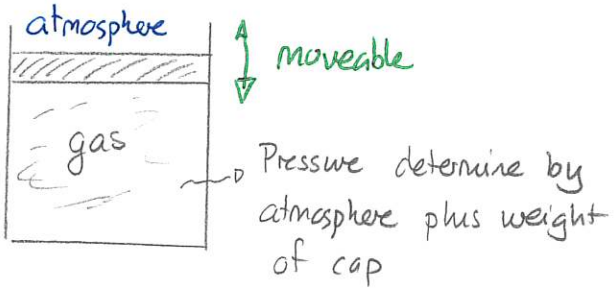
Volume versus temperature

A cartoon version of the process to determine how volume depends on temperature is

Step 1 Ensure pressure is constant at value P_0

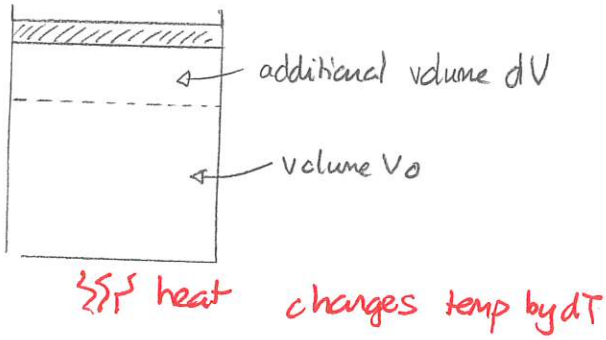
Observe volume V_0

Observe temperature T_0



Step 2 Vary temperature $T_0 \to T_0 + dT$

Observe volume $V_0 \to V_0 + dV$



Step 3 Relate dV to dT and we get

$$dV = (\ldots \text{observed quantity})\, dT$$

Step 4: Integrate to obtain V as a function of T at pressure P_0

It is conventional to express the relationship between volume change and temperature change as:

$$\boxed{dV = \alpha V dT}$$

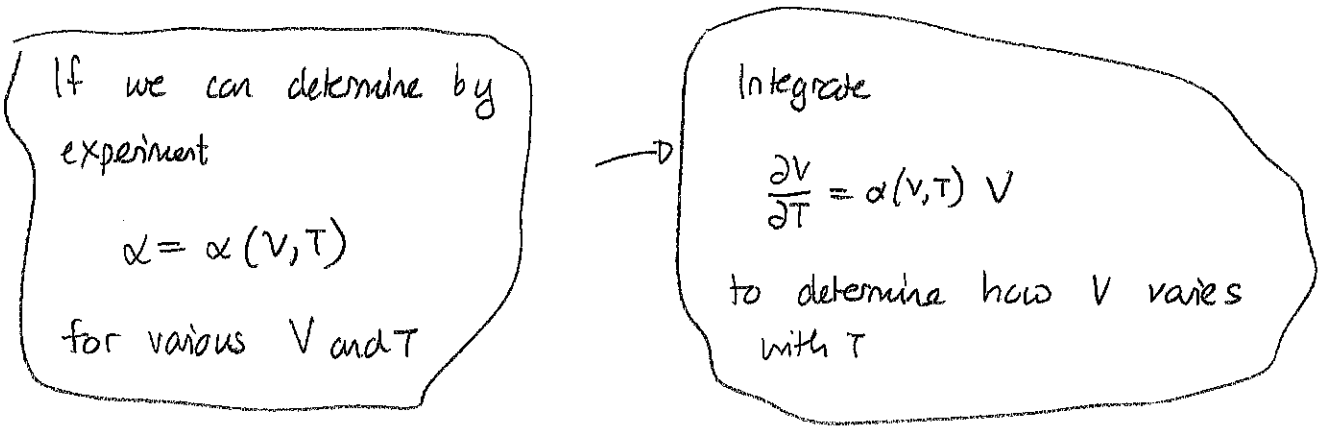
where α is called the isobaric expansion coefficient and has units K^{-1}. This has been measured very accurately for many materials. Now, at constant pressure

$$dV = \frac{\partial V}{\partial T} dT + \frac{\partial V}{\partial P} \cancel{dP}^{\,0} \Rightarrow dV = \frac{\partial V}{\partial T} dT$$

Thus $\partial V / \partial T = \alpha V$ and

$$\boxed{\alpha = \frac{1}{V} \frac{\partial V}{\partial T}} \quad \text{at constant pressure}$$

Schematically



1 Thermal expansion coefficient

a) Determine the thermal expansion coefficient for an ideal gas. Does this depend on temperature?

b) Show that the following general rule,

$$\frac{\partial V}{\partial T} = \frac{1}{\left(\frac{\partial T}{\partial V}\right)}$$

holds for an ideal gas.

c) Suppose that we did not know the equation of state for a system but we did know that the isobaric thermal expansion coefficient satisfies

$$\alpha = \frac{1}{T}.$$

Use this and integration to determine as much as possible about the equation of state for this system.

Answer: a) $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$ and $V = \frac{NkT}{P}$

Thus $\frac{\partial V}{\partial T} = \frac{Nk}{P} \Rightarrow \alpha = \frac{P}{NkT}\frac{Nk}{P} \Rightarrow \boxed{\alpha = \frac{1}{T}}$

b) We have $\frac{\partial V}{\partial T} = \frac{Nk}{P}$.

Then $T = \frac{PV}{Nk} \Rightarrow \frac{\partial T}{\partial V} = \frac{P}{Nk} \Rightarrow \frac{\partial V}{\partial T} = 1\Big/\left(\frac{\partial T}{\partial V}\right)$

c) $\alpha = \frac{1}{V}\frac{\partial V}{\partial T} \Rightarrow \frac{1}{V}\frac{\partial V}{\partial T} = \frac{1}{T} \Rightarrow \frac{\partial V}{V} = \frac{\partial T}{T} \Rightarrow \frac{dV}{V} = \frac{dT}{T}$

So integration gives

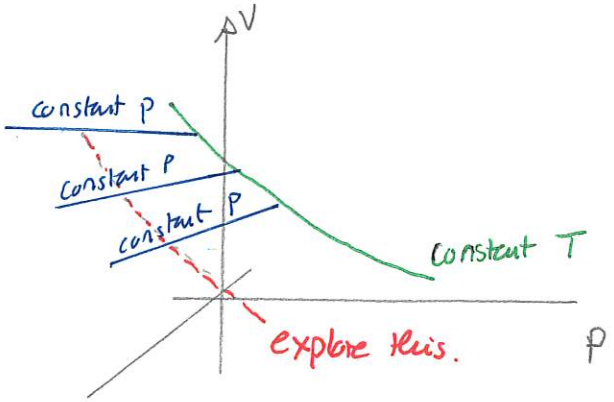
$\ln V = \ln T + f(P)$

where $f(P)$ is an arbitrary function of P. So

$e^{\ln V} = e^{\ln T + f(P)} \Rightarrow e^{\ln V} = e^{\ln T} e^{f(P)} \Rightarrow V = Te^{f(P)}$

This only partly determines the equation of state since there is still an unknown function $f(P)$. To determine this we would need to repeat the process by varying pressure and observing changes in pressure. We would ensure that the temperature is constant.

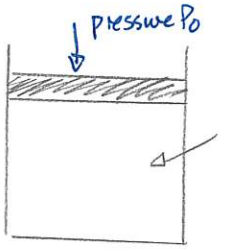
The cartoon version of the experiment is



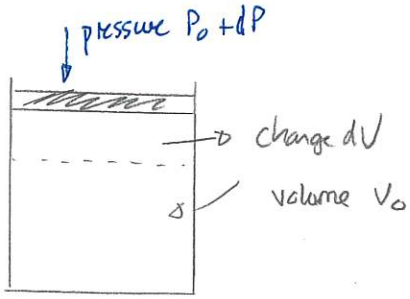
Step 1 Keep pressure fixed at P_0

Determine volume V_0

Determine temperature T_0



Step 2 Change pressure while temperature stays constant



Step 3 relate dV to dP

$$dV = (\ldots \text{observed quantity} \ldots)\, dP$$

Step 4 integrate to obtain V as a function of P.

It is common to describe the changes as:

$$\boxed{dV = -KV\,dP}$$

where K is the isothermal compressibility and has units of Pa^{-1}. Then

$$dV = \frac{\partial V}{\partial T}\cancel{dT}^{\,0} + \frac{\partial V}{\partial P}\,dP$$

gives

$$\boxed{K = -\frac{1}{V}\frac{\partial V}{\partial P} \quad \text{at constant temperature}}$$

2 Isothermal compressibility

Consider a system for which the isobaric thermal expansion coefficient satisfies

$$\alpha = \frac{1}{T}.$$

Then the equation of state has the form

$$V = Te^{f(P)}$$

where $f(P)$ is an arbitrary function of P.

a) Determine a differential equation for f in terms of the isothermal compressibility, κ.

b) Suppose (this is a hypothetical system) that κ is constant. Determine the equation of state for this system.

Answer: a) $\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{V} T e^{f(P)} \frac{df}{dP}$

$$= -\frac{Te^{f(P)}}{Te^{f(P)}} \frac{df}{dP}$$

$$\Rightarrow \quad \frac{df}{dP} = -\kappa$$

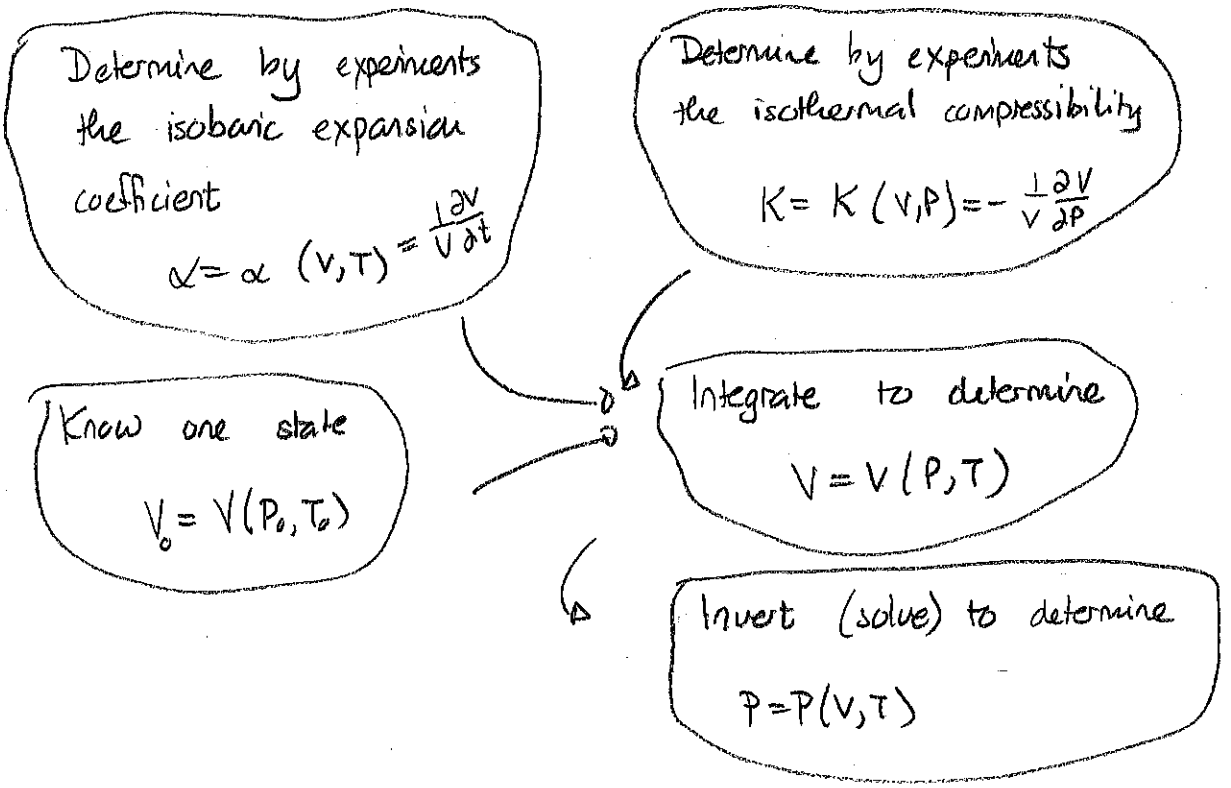
b) Integration gives $f = -\kappa P + \text{const}$. Thus

$$V = T e^{-\kappa P} \times \text{const}$$

Note that as P increases V decreases. This is typical and we will generally find

$$\frac{\partial V}{\partial P} < 0 \quad \Rightarrow \quad \kappa > 0.$$

This illustrates the complete scheme for determining the equation of state



Thermodynamic Processes

A thermodynamic process is one in which a thermodynamic system evolves (with time) from one equilibrium state to another equilibrium state. Classical equilibrium thermodynamics considers such processes and

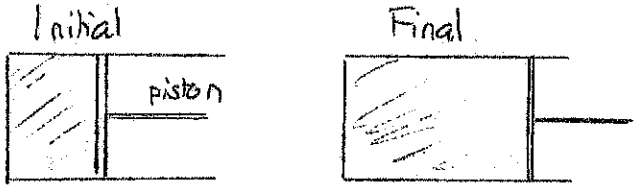
1) describes energy changes and flows in such processes
2) describes which processes are possible.

It will not describe the rate at which such processes occur or any other features of these processes as a function of time. We will classify processes broadly into the following categories:

quasistatic processes OR non-quasistatic processes.

These will now be illustrated:

Example: Slow expansion



Consider a gas in a cylinder. The volume of the cylinder can be manipulated via a controllable frictionless piston. Suppose that the gas is allowed to expand so slowly that at any stage during the expansion there is an (approximately) well-defined value of P,V,T,N for the gas. This means that:

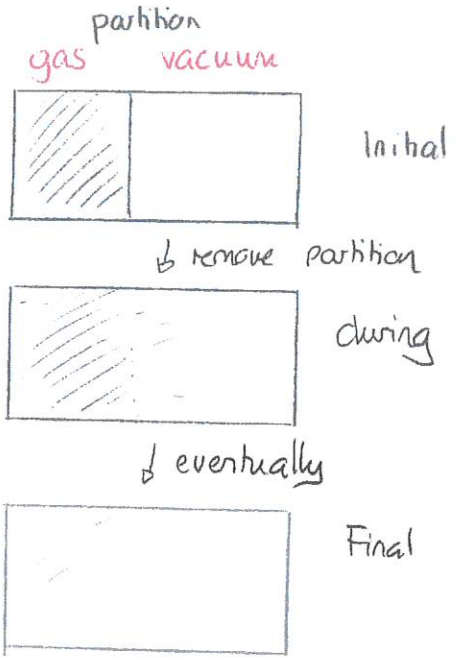
a) at each stage the gas is in a well defined thermal equilibrium state

b) the gas passes through a succession of thermal equilibrium states.

These last two conditions are the requirements for a quasistatic process.

Example: Free expansion

Consider a gas inside a container with a partition. The gas is contained to one side of the partition. The partition is then removed and the gas expands to fill the container.



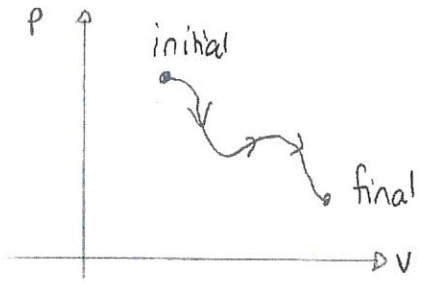
Demo: PSU Free expansion

During the expansion the pressure and volume of the gas are ill-defined and one cannot describe its state in terms of P, V, T, N variables. These are non-equilibrium states. Eventually the gas settles into an equilibrium state but during the process the states are non-equilibrium states. This is a non-quasistatic process.

Quasistatic process

A quasistatic process is such that at every instant the system is in an equilibrium state.

- can be described by a trajectory on the P, V, T surface
- can be described by a curve of P vs V "PV diagram"



Non-quasistatic process

A non-quasistatic process is one where at one or more instants the system is not in an equilibrium state.

- cannot be described by a trajectory on the P, V, T surface
- cannot be described by a curve of P vs V