

Tues: HW2 by 5pm

Thurs: Read 2.6, 2.7

Fri: HW 3

General HW solutions are on D2L

Determination of the equation of state.

Consider the example of a gas whose state is described by the variables:

$$P, V, N, T$$

These will be related by an equation of state:

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

For example, for an ideal gas

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

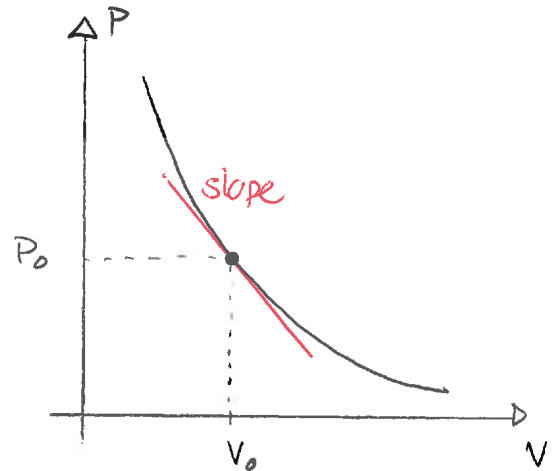
We now address the question of how to obtain the equation of state for any system which we might investigate. We need to consider:

- * possible experimental measurements and data
- * mathematics that manipulates the data to eventually produce an equation of state.

First consider the mathematical framework. Suppose that the temperature of the gas is kept constant. We then aim to determine how P fluctuates with V .

Demo Surface - show PV edge.

We want to determine the curve that is illustrated. One way to do this is:



Determine one location on the curve or equivalently P_0, V_0, T_0 for one equilibrium state

↳ Keeping the temperature fixed at T_0 determine how one variable (e.g. P) changes as the other variable (e.g. V) changes. This amounts to determining the slope of the curve.

↳ Use this slope information to determine (via integration) an expression for P versus V at this single temperature T_0 .

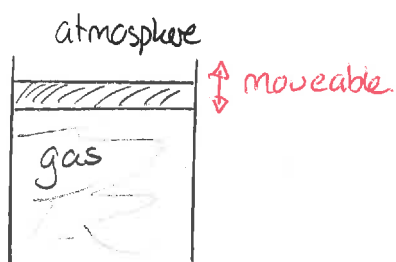
↳ Now repeat the procedure by keeping a different variable fixed (e.g. P) and observing how the other two (e.g. V, T) vary with respect to each other.

Demo Surface show V, T edge.

A cartoon of the associated experiment would be:

Step 1

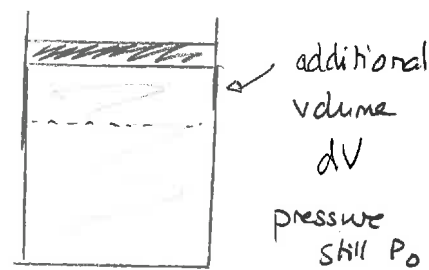
Ensure pressure
is fixed at P_0



Observe temperature: T_0
volume: V_0

Step 2

Vary temperature: $T_0 \rightarrow T_0 + dT$
observe volume change: $V_0 \rightarrow V_0 + dV$



heat

changes temp by dT

Step 3

Relate dV to dT . This gives

$$\frac{dV}{dT} = \dots \text{observed quantity.}$$

Step 4

Integrate to obtain V as a function of T
at this pressure.

In order to analyze this mathematically we note that we have obtained dV in terms of dT . This is conventionally described via:

$$dV = \alpha V dT$$

where α is a quantity called the isobaric expansion coefficient.

This has been well measured for very many materials.

How can this yield information about the equation of state?

Suppose that we rewrite this as $V = V(P, T)$. Then a standard rule of calculus gives:

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

In any experiment or situation where the pressure is fixed, $dP = 0$ and thus

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

$$\Rightarrow \alpha V = \frac{\partial V}{\partial T}$$

Thus we get

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T}$$

Then mathematically:

Knowing how α depends on V, T :

$$\alpha = \alpha(V, T)$$

which one can learn from measurements.

→ Integrate to get information about how V depends on T while P is constant

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) $PV = NkT$

$$\Rightarrow V = \frac{Nk}{P} T$$

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

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

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

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

c) Starting with

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

So $\ln V = \ln T + f(P)$ where $f(P)$ is a function of P .

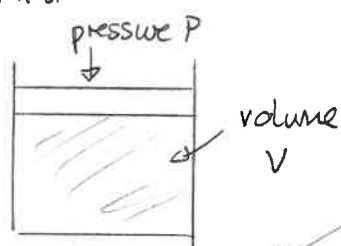
$$\Rightarrow e^{\ln V} = e^{\ln T} e^{f(P)}$$

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

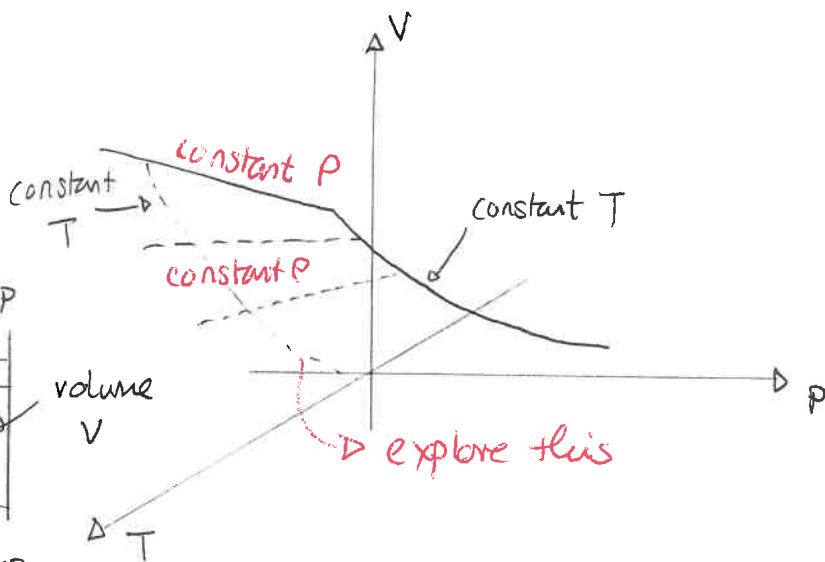
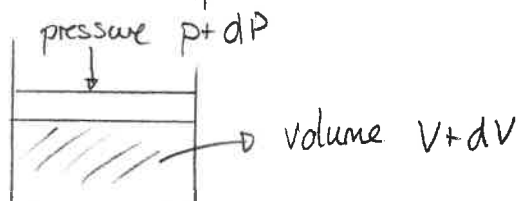
We cannot say anything more about V .

This procedure clearly does not completely determine the equation of state as there is still an unknown function of pressure present. It effectively only determines the PVT surface along one dimension (P constant). In order to determine the full expression we need to consider how the volume varies as a function of pressure while the temperature stays constant. We can therefore imagine an experiment/process:

- ① Keep temperature fixed at T_0



- ② Increase pressure is fixed. Observe change in volume.



- ③ Relate dV to dP . \leadsto gives $\frac{dV}{dP} =$ observed quantity.

- ④ Integrate $\frac{dV}{dP}$ to relate V to P at constant T .

This is done via

$$dV = -KV dP$$

where K is the isothermal compressibility. Using the same mathematics as before:

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

In general

$$\frac{\partial V}{\partial P} < 0 \Rightarrow K > 0$$

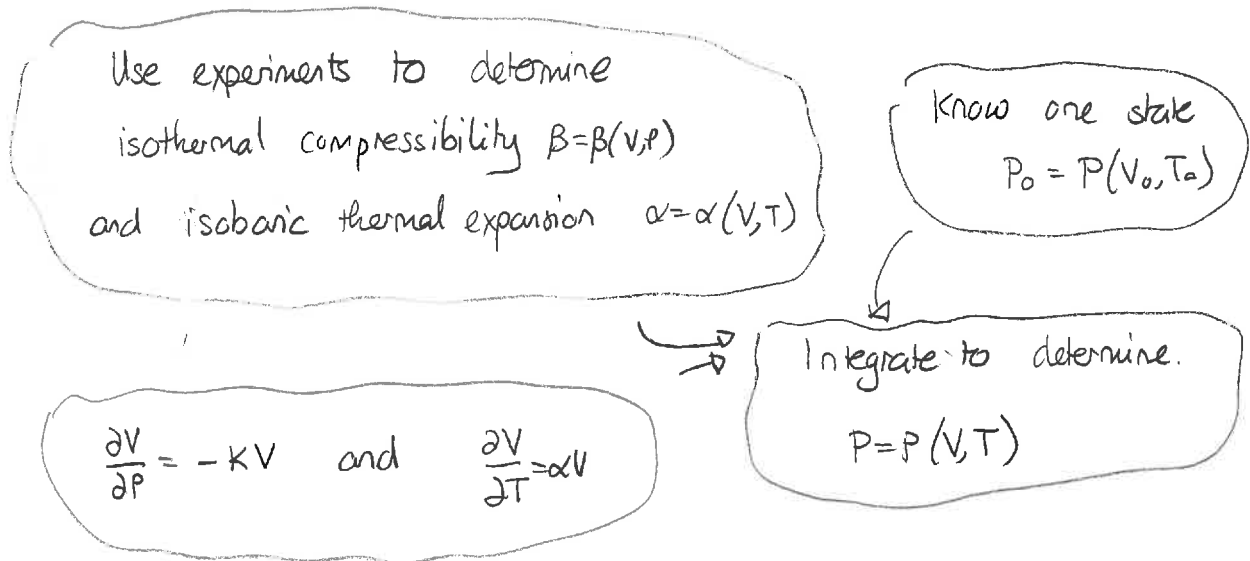
In the previous example:

$$V = T e^{f(P)}$$

$$\Rightarrow \frac{\partial V}{\partial P} = T e^{f(P)} \frac{df}{dP} = -K V$$

$$\Rightarrow \cancel{T e^{f(P)}} \frac{df}{dP} = -K \cancel{T e^{f(P)}} \Rightarrow \frac{df}{dP} = -K(P, V)$$

and integration would eventually give an expression for $f(P)$. This would complete the equation of state. The scheme is therefore:



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:

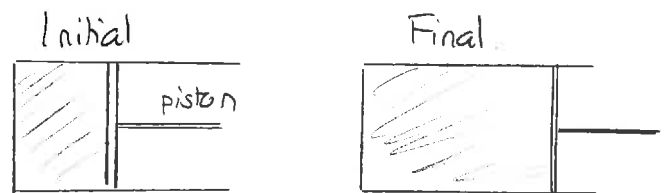
Example: Slow expansion

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

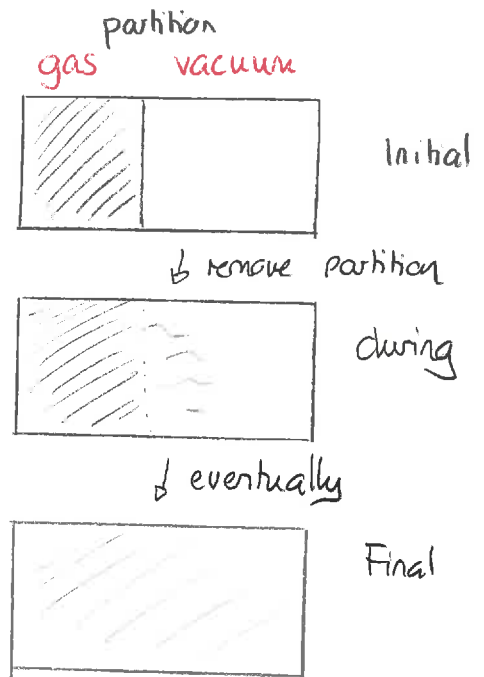
Consider a gas inside a container with a partition. The gas is contained to one side of the partition. The partition is then removed and the gas expands to fill the container.

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.

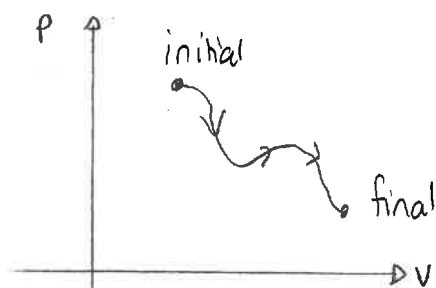
Eventually the gas settles into an equilibrium state but during the process the states are non-equilibrium states. This is a non-quasistatic process.



Quasistatic process

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

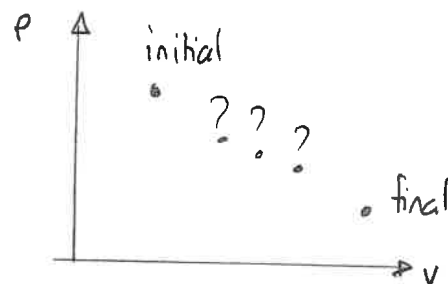
- can be described by a trajectory on the P, V, T surface
- can be described by a curve of P vs V "PV diagram"



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



Quasistatic processes are idealizations but they allow for mathematical description of the process and evaluation of associated quantities. This is impossible for non-quasistatic processes.

In all cases however we can assess overall changes between initial/final states, such as ΔV , ΔP , ΔT , ...

Thermodynamic processes and energy

We aim to consider energy flows in processes. Consider two examples.

1) Gas expansion

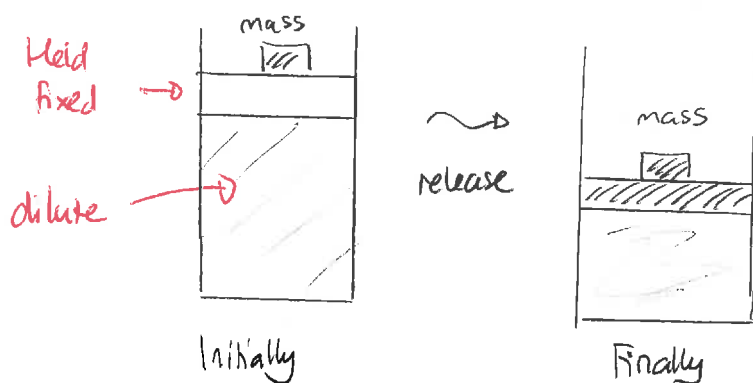


Here the gas expands and

- * adds energy to the mass
- * suffers a temperature drop.

Where did the energy come from?

2) Gas compression



Here the gas compresses:

- * mass loses energy
- * gas temperature increases.

Where did energy go?