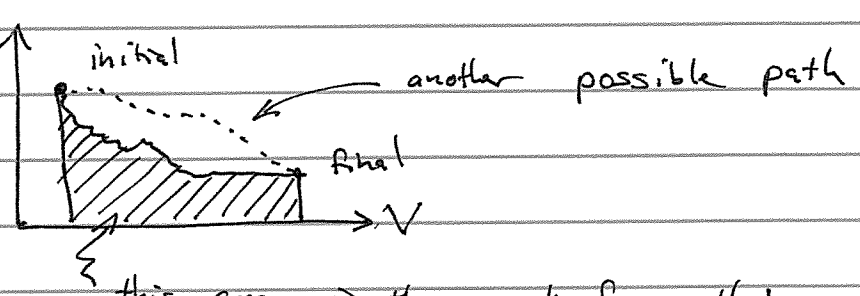
State variables

P_1, V_1, T_1 → add heat q under various conditions → calculate w P_2, V_2, T_2, ΔU and ΔS

If we change the state variables, we can do work:



Work depends on the path we take from initial to final states

$$\delta w = -\int_i^f P\,dV$$

1st law of thermodynamics:

$$dU = \delta w + \delta q$$

dU: state function; δw, δq: path dependent

A state function doesn't depend on the path we take, just on the initial & final states:

$$\int_i^f dU = U_f - U_i = \Delta U$$

$\delta q > 0$ when heat flows into a system

$\delta w > 0$ when work is performed on a system

Examples of State Functions

U = internal energy

S = entropy

H = enthalpy

G = gibbs free energy

A = Helmholtz free energy

Non-state functions

work (w)

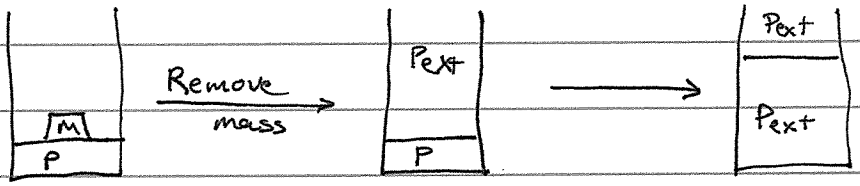
heat (q)

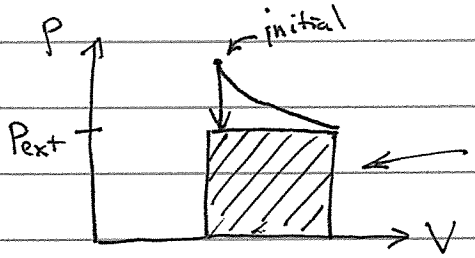
Pressure-Volume work : $\delta w = -P_{ext} dV$

valid only if the expansion or compression occurs very slowly in a quasistatic process

Note: $\delta w > 0$ if $dV < 0$ work done on system

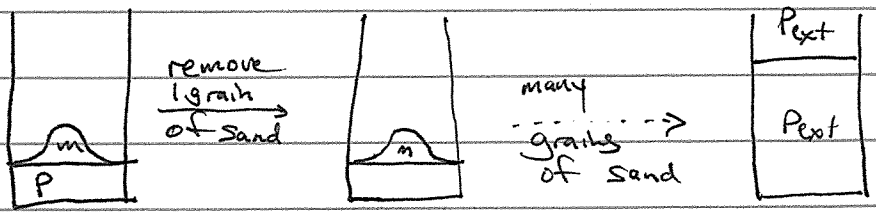
Consider this expansion:



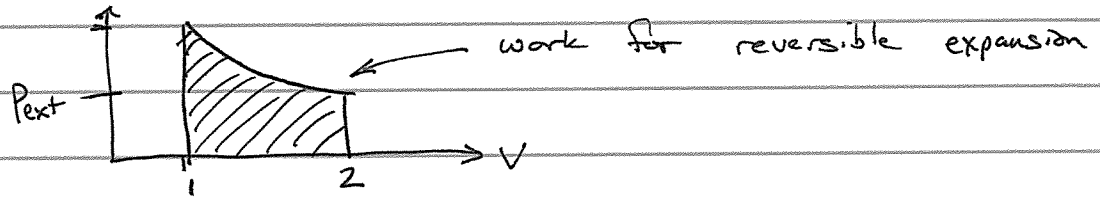


work done if m is removed suddenly is against P_{ext} only

Another way to do the same expansion



In this gradual expansion, the external pressure is kept just above P for the entire expansion



$$w_{rev} = -\int_1^2 P_{internal}\, dV$$

If the gas is an ideal gas, $P = \frac{nRT}{V}$

$$w_{rev} = -\int_1^2 \frac{nRT}{V}\, dV = -nRT \int_1^2 \frac{1}{V}\, dV$$

$$= -nRT\left[\ln V\right]_1^2 = -nRT \ln \frac{V_2}{V_1}$$

- If $V_2 > V_1$ $w_{rev} < 0$ so the system has done work (remember, $\oplus$ → surroundings do work)

- If $V_2 < V_1$ $w_{rev} > 0$, so the surroundings did work on the gas.

∴ Reversible (isothermal) expansions & compressions make w_{rev} as close as possible to zero!

Heat

- Heat describes energy transfer via thermal exchange
- Heat capacity is heat uptake per unit temperature change:

$$C_V = \left(\frac{\delta q}{\delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)$$

since V is fixed $\delta w = 0$

Energy is a state function:

$$\int_1^2 \delta w = w$$ ← inexact differential; ← path function

$$\int_1^2 \delta q = q$$ ← heat & work are generally path functions

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$ ← exact differential

If V is fixed:

$$\Delta U = \int_{T_1}^{T_2} C_V(T)\, dT = C_V (T_2 - T_1)$$

only if C_V is constant over temperature range $T_1 \to T_2$

In general, $C_V(T)$ must be measured experimentally or derived from statistical mechanics. Thermodynamics alone cannot deduce it.

Let's explore ideal gases for a bit:

$U = U(T, V)$ ← internal energy, $\langle E \rangle$ depends only on these because $Q(N, V, T)$

$$U = \frac{\langle E \rangle}{N}$$

So:

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

exact differential

all the stuff U can depend on.

We know:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$ for an ideal gas

(they don't interact so their energy can't depend on density changes.)

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

We've derived $C_V = \frac{3}{2}R$ for an ideal gas,

$$\Delta U = C_V (T_2 - T_1)$$

Reversible processes

Consider 3 possibilities

1) work → work
2) work → heat
3) heat → work

1) in principle, work → work can be done with 100% efficiency (if friction can be eliminated) typical electric motors convert electricity to mechanical work with 95% efficiency

2) work → heat can be done with 100% efficiency (sandpaper, stirring water)

3) Heat → work is only possible with efficiencies < 30% - 50%

Why?

- Interconverting work ↔ just requires slow conversion (quasistatic) with maximal efficiency
- Heat → Work with maximal efficiency requires reversible processes.

A reversible process is one in which returning the system to its initial state also returns the surroundings to their initial conditions

$$dS = \frac{\delta q_{rev}}{T} \quad \text{for a reversible process}$$

$$\delta q_{rev} = dU = C_V\, dT$$

$$\Delta S = \int_{T_A}^{T_B} \frac{C_V}{T}\, dT = C_V \ln\left(\frac{T_B}{T_A}\right)$$

↑ any reversible process

↑ only if C_V is constant like an ideal gas.

Next time we'll go into the 4 basic kinds of transformation we can do to an ideal gas.