

Thurs: Read 2.22

Fri: HW11

Helmholtz Free Energy

Much of the analysis of thermodynamic processes so far has considered quasistatic processes and has generally disregarded the thermodynamics of the environments that may absorb or provide heat. We now broaden this to

- 1) consider processes more generally including non-quasistatic processes
- 2) account for the environment.

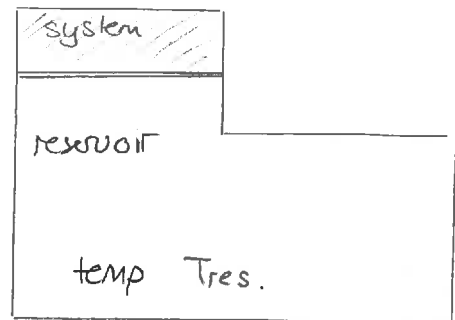
In all cases the two laws of thermodynamics still apply in their general form.

$$1^{\text{st}} \text{ Law} \quad \Delta E = Q + W$$

$$2^{\text{nd}} \text{ Law} \quad \Delta S \geq 0$$

We first consider a system interacting with a reservoir. The system and reservoir can exchange energy and do work on each other. They do so under the assumptions

- 1) the reservoir remains at a fixed temperature T_{res}



- 2) the system will be in thermal equilibrium with the reservoir at the beginning and end of the process but during the process the two will not necessarily be in equilibrium.

This implies that:

The temperature of the system at the initial and final states of the process is the same as that of the reservoir

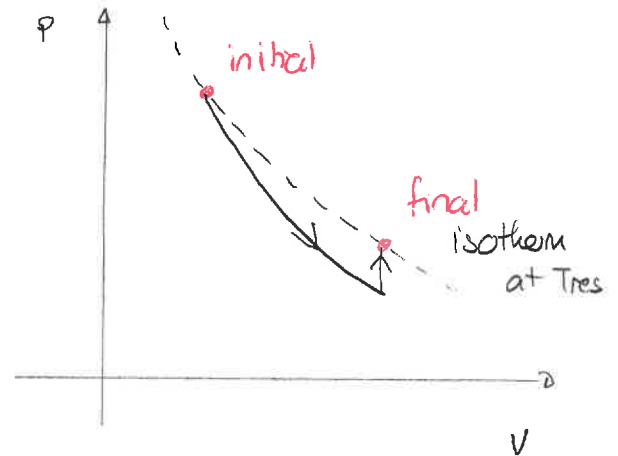
Examples could be

- 1) a free expansion of a gas
- 2) an adiabatic expansion followed by absorption of heat

Aside from the condition on the initial and final temperature there are no other assumptions about the process.

In general we will be concerned about the work done on or by the system in such processes. Let

$$W_{by} = \text{work done by system}$$



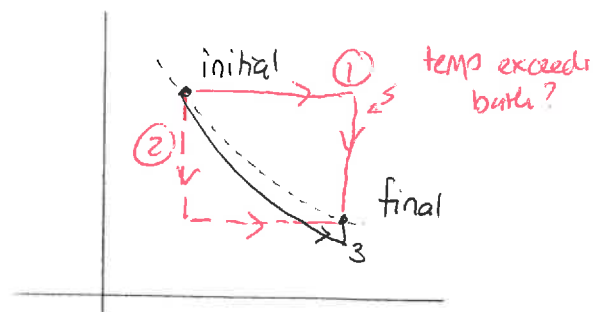
Possible questions are:

- 1) How much work can be extracted in such a process?

For a quasistatic process the work done by the system is the area under the PV curve.

Many such PV curves are possible in the illustration

$$W_{by 1} > W_{by 3} > W_{by 2}$$



It appears that any such work can be done. Are all these processes possible?

2) Is there a bound on the work for all such processes?

$$W_{by} \leq \Delta (\text{some quantity})$$

If so can one attain the upper limit of the bound. What process would do this?

The analysis uses the second law applied to both system and reservoir:

$$\Delta S_{tot} = \Delta S + \Delta S_{res} \geq 0$$

└──┬──┘
system reservoir

Clearly if the system absorbs heat the reservoir must lose heat. So then $\Delta S_{res} < 0$ which requires at least the commensurate positive change in ΔS for the system. This will restrict all possible processes. We use this to show:

If a system is in contact with a reservoir at temperature T and the system undergoes a process where its initial and final temperature equal that of the reservoir then the work done on the system satisfies:

$$W \geq \Delta F$$

and the work done by the system satisfies

$$W_{by} \leq -\Delta F$$

where the Helmholtz free energy is

$$F = E - TS \quad \text{units Joules}$$

where E, T, S are the energy, temperature and entropy of the system.

The Helmholtz free energy only depends on the state of the system.

Proof: Let Q be the heat gain/lost by the system. Then the heat gained or lost by the reservoir is $Q_{res} = -Q$. The second law applied to both states

$$\Delta S + \Delta S_{res} \geq 0$$

But the reservoir is constantly at temp T . Thus

$$\Delta S_{res} = \frac{Q_{res}}{T} = -\frac{Q}{T}$$

So

$$\Delta S - \frac{Q}{T} \geq 0$$

$$\Rightarrow T\Delta S - Q \geq 0$$

But for the system $\Delta E = Q + W \Rightarrow Q = \Delta E - W$, So

$$T\Delta S - \Delta E + W \geq 0$$

$$\Rightarrow W \geq \Delta E - T\Delta S$$

$$\begin{aligned} \text{For the system } T\Delta S &= T S_f - T S_i \\ &= T_f S_f - T_i S_i \quad \text{since } T_f = T_i = T \\ &= \Delta(TS) \end{aligned}$$

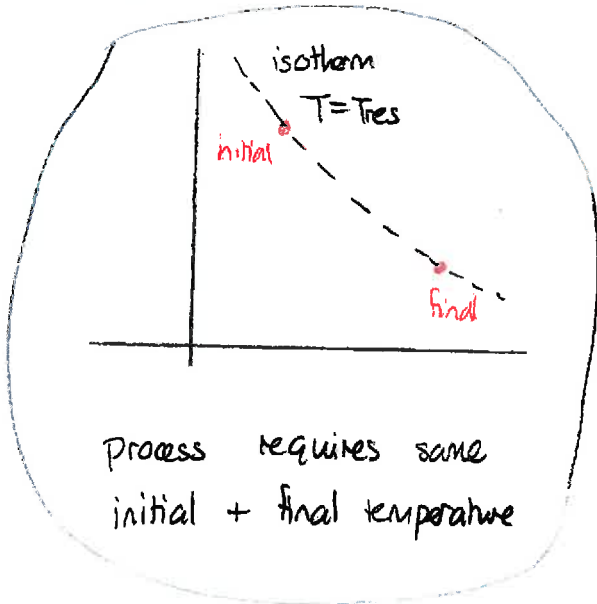
$$\text{Thus } W \geq \Delta E - \Delta(TS) = \Delta(E - TS) = \Delta F \quad \square$$

The Helmholtz free energy therefore bounds the work done by the system.

For a system in contact with a reservoir at fixed temperature, any process that begins and ends at the reservoir delivers work:

$$W_{by} \leq -\Delta F$$

We have:



Initial free energy

$$F_i = E_i - TS_i$$

Final free energy

$$F_f = E_f - TS_f$$

only depend on states

Determine change in free energy

$$\Delta F = F_f - F_i$$

Work done by system is bounded by drop in free energy (NOT energy)

$$W_{by} \leq -\Delta F$$

Thus changes in free energy cap the ability of the system to do work if the system is only interacting with a reservoir at fixed temperature. We can see that:

In order for the system to do work in the scenario above, its free energy must drop

1 Helmholtz free energy and an isothermal process

Consider a quasistatic isothermal process in any gas.

- Show that the work done on the gas satisfies $W = \Delta E - T\Delta S$.
- Show that the work done by the gas satisfies $W_{\text{by}} = -\Delta F$ where F is the Helmholtz free energy.

Answer:

$$a) \quad dE = TdS + \delta W$$

$$\int dE = \int TdS + W$$

$$\begin{aligned} \Rightarrow W &= \Delta E - \int TdS &= \Delta E - T \int dS \\ & &= \Delta E - T\Delta S \end{aligned}$$

$$b) \quad W_{\text{by}} = -W \quad \text{and}$$

$$W = \Delta E - T\Delta S$$

$$\Rightarrow W_{\text{by}} = -\Delta E + T\Delta S$$

$$\text{But } T \text{ is constant so } W_{\text{by}} = -\Delta E + \Delta(TS)$$

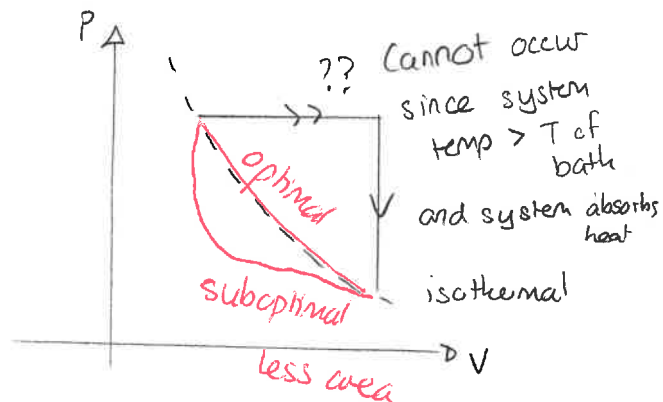
$$= -\Delta(E - TS)$$

$$= -\Delta F$$

This gives us the limiting case:

The optimal work that can be done by a system in contact with a reservoir at a fixed temperature and in a process which begins and ends with the system in equilibrium with the reservoir is a quasistatic isothermal process and here $W_{by} = -\Delta F$

This is illustrated for an ideal gas. Note that this accounts for all processes including non-quasistatic processes that cannot be illustrated on the graph



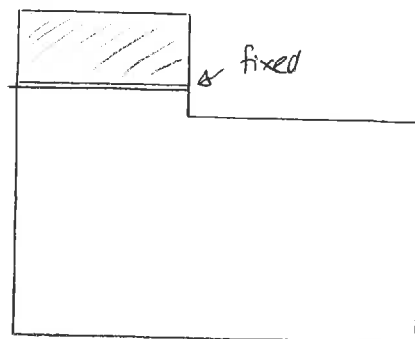
For a suboptimal process

$$\begin{aligned} \Delta E = Q + W &\Rightarrow 0 = Q + W \\ &\Rightarrow 0 = Q - W_{by} \Rightarrow W_{by} = Q \end{aligned}$$

Here heat must be absorbed from the reservoir and the reservoir is, in effect taxed for running the suboptimal process.

The Helmholtz free energy also describes equilibrium for a system in contact with a reservoir. Suppose that the system cannot do work or cannot have work done on it. Then

$$\begin{aligned} \Delta S_{tot} &= \Delta S + \Delta S_{res} \\ &= \Delta S - \frac{Q}{T} \\ &= \frac{1}{T} (T\Delta S - Q) \\ &= \frac{1}{T} (T\Delta S - \Delta E + W) = \frac{1}{T} (\Delta(TS - E)) \\ &= -\frac{1}{T} \Delta F. \quad \Rightarrow \quad T\Delta S_{tot} = -\Delta F \end{aligned}$$



So the system and environment attain equilibrium when S_{tot} is a maximum.
This means the F must be a minimum.

Thus a system in contact with a reservoir at fixed temperature will attain equilibrium when the Helmholtz free energy is a minimum at that temperature.

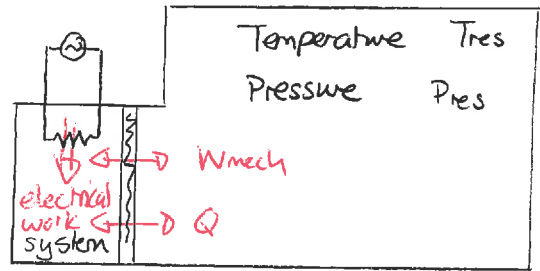
Gibbs Free Energy

We can generalize the notion of a reservoir at a fixed temperature to a reservoir whose temperature and pressure is fixed. In such a situation the system can do work on the environment via an expansion.

The system could also do non-mechanical work, say generating an electrical current.

The converse can also apply.

One can do non-mechanical



work on a system. This can increase the internal energy of the system but some of that may be lost to mechanical work done on the surroundings. We would like to relate this non-mechanical work to an energy change in any process constrained in this way. First we clarify that the mechanical work done on the system is

$$W_{\text{mech}} = - \int P dV$$

Then in general the work done on the system is

$$W = W_{\text{mech}} + W_{\text{non-mech}}$$

where $W_{\text{non-mech}}$ represents any other type of work done on the system (e.g. electrical, chemical, ...). Then we can show:

If a system is in contact with a reservoir whose temperature and pressure are fixed and the system undergoes any process in which its initial + final states are in equilibrium with the reservoir then:

$$\Delta G \leq W_{\text{non-mech}}$$

where the Gibbs free energy is $G = E - TS + PV$

Proof. In any process:

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{res}} \geq 0$$

$\underbrace{\hspace{1.5cm}}_{\text{system}}$

Then let Q be the heat absorbed by the system. This is the heat lost from the reservoir. So

$$\Delta S_{\text{res}} = -Q/T_{\text{res}}$$

$$\Rightarrow \Delta S - Q/T_{\text{res}} \geq 0$$

$$\Rightarrow T_{\text{res}} \Delta S - Q \geq 0$$

Now for the system $\Delta E = Q + W = Q + W_{\text{non-mech}} + W_{\text{mech}}$

$$\Rightarrow T_{\text{res}} \Delta S - \Delta E + W_{\text{non-mech}} + W_{\text{mech}} \geq 0$$

The mechanical work is done by the reservoir and

$$W_{\text{mech}} = P_{\text{res}} \Delta V$$

$$\Rightarrow W_{\text{non-mech}} \geq \Delta E - T_{\text{res}} \Delta S + P_{\text{res}} \Delta V$$

$$\begin{aligned} \text{Now for the system } T_f = T_i = T_{\text{res}} &\Rightarrow T_{\text{res}} \Delta S \\ &= T_f S_f - T_i S_i = \Delta TS \end{aligned}$$

$$\text{Similarly } P_{\text{res}} \Delta V = \Delta PV.$$

Thus

$$W_{\text{non-mech}} \geq \Delta (E - TS + PV) = \Delta G \quad \square$$

Now with the non-mechanical work done by the system satisfying

$$W_{\text{non-mech by}} = -W_{\text{non-mech}}$$

We get:

The non-mechanical work done by a system in equilibrium with a reservoir in its initial + final states satisfies

$$W_{\text{non-mech by}} \leq -\Delta G$$

This bounds the possible non-mechanical work done by the system in such processes. The Gibbs free energy describes the energy available for non-mechanical work in such processes. (P, T must be same at beginning + end)

Separately it shows the quantity of non-mechanical work required for any such process. It must be at least equal to ΔG .

In situations where the non-mechanical work is zero:

$$\Delta S_{\text{tot}} = -\frac{\Delta G}{T}$$

and this states that a system with these constraints reaches equilibrium when G is a minimum. So

A system in contact with a reservoir at a fixed pressure and temperature reaches equilibrium when the Gibbs free energy takes a minimum value (at the reservoir pressure + temp)

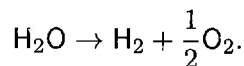
2 Energy required for electrolysis

a) Show that

$$\Delta G = \Delta H - T\Delta S$$

for a process that begins and ends at the same temperature.

b) In electrolysis of water, an electric current is passed through water and produces



Suppose that this reaction occurs while the water is in contact with the atmosphere at a temperature of 298 K and a pressure of 1.00 atm. The entropies of the constituents are

$$S(\text{H}_2\text{O}) = 70 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S(\text{H}_2) = 131 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S(\text{O}_2) = 205 \text{ JK}^{-1}\text{mol}^{-1}$$

and the enthalpy of formation of water from hydrogen and oxygen is $-285.83 \text{ kJ mol}^{-1}$. Determine the change in Gibbs free energy per mole for this reaction.

c) Determine the minimum non-mechanical energy required to produce 10.0 mol of hydrogen gas using this process.

Answer a) $G = E - TS + PV$

$$\equiv H - TS$$

$$\Rightarrow \Delta G = \Delta H - \Delta(TS)$$

$$= \Delta H - (T_f S_f - T_i S_i) \quad \text{But } T_f = T_i = T$$

$$= \Delta H - T\Delta S$$

b) $\Delta H = 285.83 \text{ kJ/mol}$

$$\Delta S = 131 \text{ J/K.mol} + \frac{1}{2} 205 \text{ J/K.mol} - 70 \text{ J/K.mol}$$

$$= 163.5 \text{ J/K.mol}$$

$$T\Delta S = 298 \text{ K} \times 163.5 \text{ J/K.mol} = 48.7 \text{ kJ/mol}$$

$$\Delta G = 285.83 \text{ kJ/mol} - 48.7 \text{ kJ/mol} = 237 \text{ kJ/mol}$$

c) $\Delta G = 10 \text{ mol} \times 237 \text{ kJ/mol} = 2370 \text{ kJ}$ $W_{\text{non-mech}} \geq \Delta G \Rightarrow W_{\text{non-mech}} \geq 2370 \text{ kJ}$