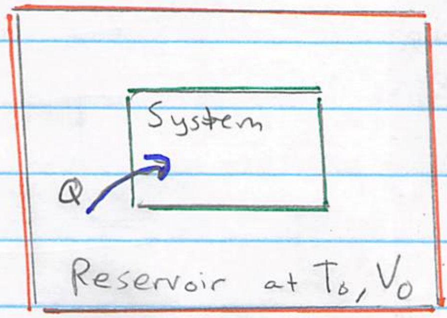
Reaching Equilibrium (Follows Blundell)



First consider volume of system fixed

- First consider the system to be at fixed volume but held at constant temperature T_0 with the surroundings.
- Now suppose we do some extra work W_{extra} (e.g. by breaking chemical bonds, doing photosynthesis) to change the state of the system.
- If heat Q enters the system, the reservoir changes its entropy by $dS_0 = -đQ/T_0$. Since $dS + dS_0 \geq 0$ and since $đQ = dE - đW_{extra}$ we have

$$T_0 dS - (dE - đW_{extra}) \geq 0$$

Or

$$dW_{extra} \geq dE - T_0 dS$$

i.e

$$\boxed{dW_{extra} \geq dF}$$

So the work required is greater than the change in Free energy ΔF. It equals ΔF in equilibrium at const temperature

- Now if useful work is to be extracted from the system ($dW_{extra} < 0$), then the output i.e $dW_{out} = -dW_{extra}$, is less than the drop in the free energy ($\Delta F < 0$ and $W_{need} < 0$)

$$dW_{get} \leq |\Delta F|$$

- If no extra work is done Entropy will increase $dS + dS_0 \geq 0$ when the free energy decreases

$$\underline{0 \geq dF}$$

and equilibrium is when F is minimized.!

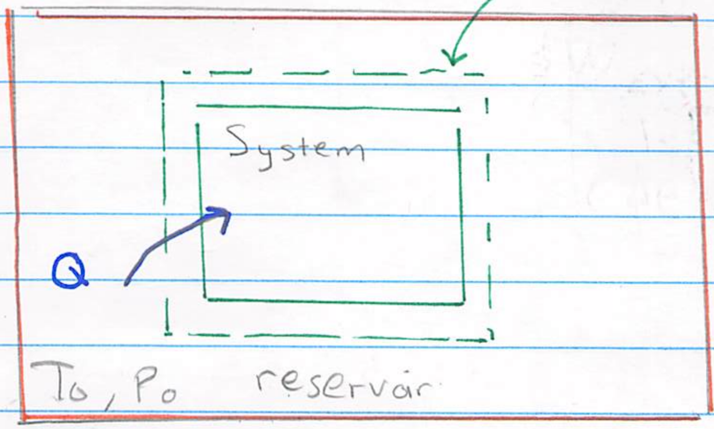
- In some ways, F is like a potential energy of the system when heat is involved, e.g. the work need to change the state in perfect equilibrium is $W_{need} = \Delta F$; the work we can get out is $W_{out} = |\Delta F|$

- The argument can be generalized to allow for ... volume changes. If heat Q enters the system

$$dQ = dU \underbrace{- dW_{extra}}_{\text{extra work}} \underbrace{- (-p_0\, dV)}_{\text{work by volume change}}$$

required to bring about the change in thermo state, (the change in state includes volume changes.)

Volume of system not fixed



- We are asking about the minimum amount of work W_{extra} required to change the state of system, accounting for heat inflows and outflows and that it might ~~change~~ do work by changing its volume

So

$$dS + dS_0 \geqslant 0$$

Or since $dS_0 = -dQ/T_0$ as before we get:

$$T_0\, dS - (dU - dW_{extra} + p_0\, dV) \geqslant 0$$

or

$$\boxed{dW_{extra} \geqslant \underbrace{dU + p_0\, dV - T_0\, dS}_{\text{the book calls this the ``availability''}}}$$

- So if pressure and temperature are held fixed then $dG = d(U + p_0 V - TS)$

$$\boxed{dW_{extra} \geqslant dG.}$$

So if dW_{extra} is zero the system (at constant temperature and pressure) will evolve to minimize its Gibbs free energy G.