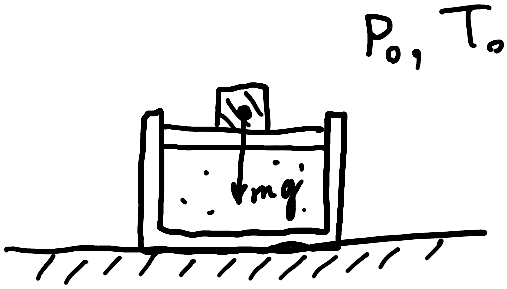
Irreversible processes. Thermodynamic potential. Free energy

Assume that a system is placed in an environment with temperature T_0 and pressure P_0

Energy conservation for the entire system: Isobaric process

$$\delta E + \delta E_{env} + \delta W = 0$$

δW – work done by the entire thing



The system may do some work on an external body

$$\delta V = -\delta V_{env}$$

$$\delta E_{env} = \underbrace{T_0 \delta S_{env} - P_0 \delta V_{env}}_{= T_0 \delta S_{env} + P_0 \delta V}$$

This is true because the system is very big and all processes happening with it are quasistatic

Thus, $\delta W = -\delta E - T_0 \delta S_{env} - P_0 \delta V$

2nd law: $\delta S + \delta S_{env} \geq 0$

Then $\delta W \leq -\delta E + T_0 \delta S + P_0 \delta V = -\delta \varphi$

Here $\boxed{\varphi = E - TS + PV}$

Indeed, $d\varphi = dE - TdS - \cancel{SdT} + PdV + \cancel{VdP}$

in the process under consideration

$$\delta W_{max} = -\delta \Phi$$

Φ – "thermodynamic potential" aka "Gibbs free energy"

Assume now that the system is being kept at a constant temperature $T = T_0$ and the volume is constant, $V = V_0$. Isochoric process

Although the system is being kept at a constant volume, it may still do some work. For instance, it may be in an external field, leading to inhomogeneity, or be a mixture of reacting chemicals.

$$\delta E + \delta E_{env} + \delta W = 0$$

$$\left.\begin{aligned} \delta E_{env} &= T \delta S_{env} \\ \delta S_{env} + \delta S &\geq 0 \end{aligned}\right\} \rightarrow \delta E_{env} \geq -\delta S\, T_0$$

$$\delta W = -\delta E - \delta E_{env} \leq -(\delta E - T_0 \delta S) = -\delta F$$

where $\boxed{F = E - TS}$ (Is it extensive or intensive?)

– free energy

Important thermodynamic functions:

$$\Phi = E - TS + PV$$

$$\varphi = E - TS + PV$$

$$F = E - TS$$

$$I = E + PV$$

(Other notations: H, W)

- enthalpy