Basic principles of Thermodynamics

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State functions

- **<u>Postulate:</u>** There is a function **U(V,…,S)**, called **internal energy**, which depends only on *extensive* parameters of the *states (at equilibrium)* of the *closed* system:
V (volume), N (number particles), etc…, and the **entropy S(V,…,U)**

- **U and S are exactly differentiable:**

$$dU = \frac{\partial U}{\partial V} dV + \cdots + \underbrace{\frac{\partial U}{\partial S}}_{=_{\text{def}} T} dS \qquad dS = \frac{\partial S}{\partial V} dV + \cdots + \underbrace{\frac{\partial S}{\partial U}}_{=1/T} dU$$

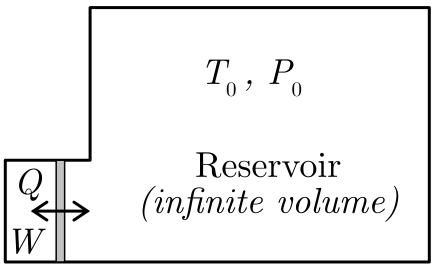
Laws of thermodynamics

- **1st Law,** when changing from one state to another:

$$\Delta U = \underbrace{\delta Q}_{\text{Heat}} + \underbrace{\delta W}_{\text{Work}}$$

- **2nd Law: for a closed system, ΔS ≥ 0**
  (work is converted into heat and never the converse)

Free enthalpy



- For a system evolving at T_0 and P_0 constant:

$$S \text{ is extensive, thus } \Delta S_{Tot} = \Delta S + \Delta S_{Res}$$

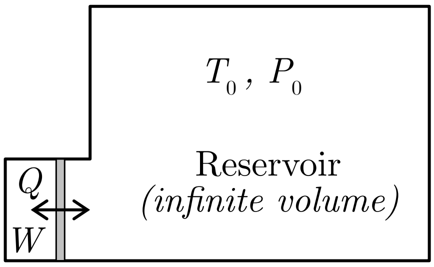
$$\text{1st Law: } \Delta U = Q + W = Q - P_0 \Delta V$$

$$\text{But } dU = -PdV + TdS$$

$$dV_{res} = 0 \text{ thus } \Delta S_{Res} = -\frac{Q}{T_0} = -\frac{\Delta U + P_0 \Delta V}{T_0}$$

$$\text{Finally, 2nd Law: } 0 \leq \Delta S_{Tot} = \Delta S - \frac{\Delta U + P_0 \Delta V}{T_0} = \frac{\Delta(T_0 S - U - P_0 V)}{T_0}$$

Free enthalpy



- For a system evolving at T_0 and P_0 constant:

$$\text{Let } G = U + P_0 V - T_0 S$$

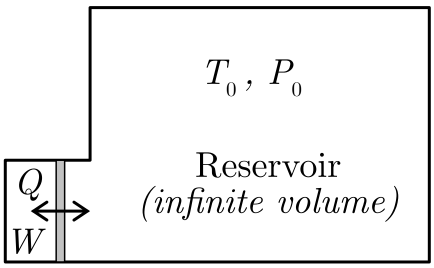
$$\text{Then, } \Delta G \leq 0$$

- G is the **free enthalpy**, it's a **state function**, **minimized at equilibrium => determine the parameters at equil. !**

$$\text{Indeed, at equil. } \frac{\partial G}{\partial S} = \frac{\partial U}{\partial S} - T_0 = T - T_0 = 0 \Rightarrow T = T_0$$

$$\text{and, } \frac{\partial G}{\partial V} = \frac{\partial U}{\partial V} + P_0 = -P + P_0 = 0 \Rightarrow P = P_0$$

Free enthalpy



$$G = \underbrace{U}_{\approx -\#\text{bonds}} + \underbrace{P_0 V}_{\text{Constant}} - T_0 \underbrace{S}_{\approx \#\text{molecules}}$$

- Typically: $U_{AT} = 1, \quad U_{CG} = 2, \text{ and } T_0 S_{/\text{molecule}} = 8$

- The state at equilibrium is the configuration which minimizes the tradeoff:

$$G(\#\text{bonds}, \#\text{molecules}) \approx \#\text{bonds} - 8\#\text{molecules}$$