Electrical example:

\[ V_L = \text{load voltage (pot. difference b/t x and y)} \]

net electrical power \[ W = V_S I_S + V_L I_L \]

\[ \text{Pin} - \text{Pout} \]

\[ \Rightarrow \text{if } V_L > 0 \text{ and } I_L > 0 \text{ then } P_{\text{out}} = -V_L I_L > 0 \text{ doing output work by moving charges against potential} \]

Assume circuit at temp. T:

\[ \dot{E} = \dot{Q} + \dot{W} \]

at steady state \[ \dot{E} = 0 \Rightarrow \dot{Q} = -\dot{W} \]

\[ 0 = \dot{S} = \frac{\dot{Q}}{T} + \dot{S}^i \Rightarrow \dot{S}^i = \frac{\dot{Q}}{T} = \frac{\dot{W}}{T} \]

\[ P_{\text{out}} = P_{\text{in}} \]

\[ \Rightarrow \dot{S}^i = I_S \frac{V_S}{T} + I_L \frac{V_L}{T} > 0 \]

\[ \equiv \varphi_g \equiv \varphi_L \]

Ohm's law:

\[ V_S = I_S R_A + (I_S + I_L) R_B \]

\[ V_L = (I_S + I_L) R_B \]

\[ \begin{pmatrix} V_S \\ V_L \end{pmatrix} = \begin{pmatrix} R_A + R_B & R_B \\ R_B & R_B \end{pmatrix} \begin{pmatrix} I_S \\ I_L \end{pmatrix} \]

\[ \equiv R \]
\[
\begin{align*}
\begin{pmatrix}
I_s \\
I_L
\end{pmatrix} &= L \begin{pmatrix}
\phi_s \\
\phi_L
\end{pmatrix} = \frac{L}{T} \begin{pmatrix}
V_s \\
V_L
\end{pmatrix} \\
\Rightarrow \quad L &= TR^{-1} = \begin{pmatrix}
\frac{1}{R_A} & -\frac{1}{R_A} \\
-\frac{1}{R_A} & \frac{1}{R_A} + \frac{1}{R_B}
\end{pmatrix} T
\end{align*}
\]

Fix \( \phi_s \):
\[V_{stall} = \text{max. load where } I_L = 0 \text{ and no } P_{out}\]
\[= -\frac{T L_{LL} s}{L_{LL}} \phi_s = \frac{R_B V_s}{R_A + R_B} \]

\[P_{out} = -V_L I_L \]

\[\max P_{out} \text{ occurs at: } V_L = V_{stall} \]

\[V_L = \frac{V_{stall}}{2} \]

At this point efficiency is:
\[\eta = \frac{P_{out}}{P_{in}} = \frac{-V_L I_L}{V_S I_S} \quad V_L = \frac{V_{stall}}{2} \]

\[= \frac{1}{2} \frac{q^2}{2-q^2} \leq \frac{1}{2} \]

Where \[q = \frac{L_{LL}}{\sqrt{L_{LL} L_{SS}}} = -\sqrt{\frac{R_B}{R_A + R_B}} \Rightarrow \max. \text{ efficiency at strong coupling } q = 1 \]

Only achievable when \( R_B \to \infty \).
Strong coupling \((R_B \to \infty)\) and max power means

\[
V_L = \frac{R_B V_s}{2(R_A + R_B)} = \frac{V_s}{2}
\]

\[
I_S = \frac{V_s}{2R_A}, \quad I_L = -\frac{V_s}{2R_A}
\]

Effective resistance of load:

\[
R_L = \frac{V_L}{I_L} = R_A
\]

Load "impedance" internal source "impedance" max power transfer

Equilibrium thermodynamics

Can one achieve equilibrium stationary state while coupled to a heat reservoir + external work?

Look at:

\[
\frac{W_{nm}}{W_{mn}} = e^{-\beta(E_n - E_m + V_{nm})}
\]

Note this implies \(V_{nm} = -V_{mn}\) (true in general)

If equilibrium exists, then all currents = 0

\(\exists p^s_n\) such that:

\[
W_{nm} p^s_m - W_{mn} p^s_n = 0 \text{ for all } (n,m)
\]

\[
\Rightarrow p^s_n = \frac{W_{mn}}{W_{mn}} = e^{-\beta(E_n - E_m + V_{nm})}
\]
Consider any path in network that begins and ends at same point:

\[
1 = \frac{P_1^S}{P_2^S} \frac{P_2^S}{P_3^S} \frac{P_3^S}{P_4^S} \frac{P_4^S}{P_1^S} = e^{-\beta(V_{12} + V_{23} + V_{34} + V_{41})}
\]

\[
1 \rightarrow 2 \ 2 \rightarrow 3 \ 3 \rightarrow 4 \ 4 \rightarrow 1
\]

\[\Rightarrow V_{12} + V_{23} + V_{34} + V_{41} = 0\]

or \[V_{21} + V_{32} + V_{43} + V_{14} = 0\]

Same is true of any path that ends at starting point (may even overlap, doesn't have to be a cycle).

Hence there exists a "potential function":

choose arbitrary reference state, i.e. \( m = 1 \)

\[V_n \equiv \sum_{\text{some path from } 1 \rightarrow n} V_{m'm} \Rightarrow \text{definition indep. of path since:}
\]

\[\sum V_{m'm} \text{, path } 1 - \sum V_{m'm} \text{, path } 2 = 0\]

Hence \( V_{nm} = V_n - V_m \)

we call this external coupling "conservative"

total cycle sums to zero
note: our ratchet system w/ mass \( m > 0 \) has

\[
\begin{align*}
V_{21} &= -mg \Delta x = V_{32} = V_{13} \\
V_{21} + V_{32} + V_{13} &\neq 0
\end{align*}
\]

\[\Rightarrow\] nonconservative, hence not in equilibrium!

If \( V_{nm} \) is conservative, then:

\[
\frac{p_n^s}{p_m^s} = e^{-\beta (E_n - E_m + V_n - V_m)} \quad \text{for all } (n,m)
\]

implies:

\[
p_n^s = \frac{e^{-\beta (E_n + V_n)}}{Z} \quad \text{modified Boltzmann distrib.}
\]

\[\Rightarrow\] normaliz. constant

Typical form of conservative \( V_{nm} \):

\[
V_{nm} = f(x_n - x_m) = \frac{f x_n}{V_n} - \frac{f x_m}{V_m}
\]

"force" some internal property of state \( n \)

Example: \( x_n = V_n \) = volume of molecule in state \( n \)
\( f = P \) = outside fluid pressure

force \( P \mathrm{d}A \)

work done against pressure going from \( m \Rightarrow n \):

\[
\text{work} = -\int_{\text{surface in state } m} h P \mathrm{d}A = -P (V_n - V_m)
\]

potential change = - work = \( P (V_n - V_m) \)
Since \( p_n^s = \frac{e^{-\beta(E_n + f x_n)}}{Z} \equiv p_n^s(T, f) \),
depends on these parameters

All quantities that depend on \( p_n^s \) also depend on \( T, f \):

\[
E^s = \sum_n p_n^s E_n = E^s(T, f)
\]

\[
S^s = -k_B \sum_n p_n^s \ln p_n^s = S^s(T, f)
\]

**Detailed balance**

Now imagine parameters are changed with time: \( T(t), f(t) \)

\( \Rightarrow \) no longer in equilibrium (strictly speaking)

\[
\dot{S} = \dot{S}^i + \dot{S}^e = \dot{S}^i + \frac{Q}{T(t)}
\]

\[
\dot{E} = \dot{Q} + \dot{W}
\]

\[
= -\sum_{n,m} J_{nm}(t)[V_n - V_m] = -\frac{\dot{Q} \bar{x}}{T(t)}
\]

\[
= f_0(x_n - x_m) \text{ where } \bar{x} = \sum_n p_n x_n
\]

These are true b/c detailed balance holds instantaneously:

\[
W_{nm}(t) = e^{-\frac{1}{k_B T(t)}(E_n - E_m + f(t)(x_n - x_m))}
\]

and the definitions of

\[
\dot{S}^e = \frac{\dot{Q}}{T(t)} = k_B \sum_{n,m} J_{nm} \ln \frac{W_{mn}(t)}{W_{nm}(t)}
\]

and \( \dot{S}^i = -k_B \sum_{n,m} J_{nm} \ln \frac{W_{mn} p_n}{W_{nm} p_m} \)
Rewrite: \[ \dot{Q} = E + f(t) \cdot \dot{x} \]
\[ -T \dot{S}^i = \dot{Q} - T \dot{S} \]
\[ \Rightarrow -T(t) \dot{S}^i = \dot{E} - T(t) \dot{S} + f(t) \cdot \dot{x} \]

Many consequences:

First, assume define \( G(t) = \bar{E}(t) - T(t) S(t) + f(t) \cdot \dot{x}(t) \)
\[ \equiv \text{Gibbs free energy} \]

**case 1:**
\[ T(t) = T, \ f(t) = f \] fixed parameters
\[ \dot{G} = \dot{E} - T\dot{S} + f \cdot \ddot{x} = -T \dot{S}^i \]

Hence out of equilibrium \( (\dot{S}^i > 0) \) we see \( \dot{G} < 0 \)
\[ \Rightarrow G(t) \text{ decreasing} \]
and in equilibrium \( (\dot{S}^i = 0) \) \( \dot{G} = 0 \)
\( G(t) \) reaches minimum
\[ G(t) \rightarrow G^* \text{ in equilibrium} \]

**case 2:** \( T(t), \ f(t) = f \) only vary temperature
\[ \dot{G} = \dot{E} - T\dot{S} - T\dot{S}^i + f \cdot \ddot{x} = -T \dot{S}^i - T \dot{S} \]

If we assume variation of \( T(t) \) is so slow that
\[ \dot{S}^i \approx 0 \] [Reversible thermodynamic change]
\[ \Rightarrow \dot{G} \approx -T \dot{S} \Rightarrow \frac{dG}{dt} \approx -S \]
\[ G(t) \approx G^*(T(t), f(t)) \]
\[ \frac{dG^*}{dT} \bigg|_f = -S^* \]

**case 3:** \( T(t) = T, \ f(t) \) only vary force
\[ \dot{G} = \dot{E} - T\dot{S} + f \cdot \ddot{x} + f \cdot \ddot{x} = f \ddot{x} - T \dot{S}^i \]

Note:
\[ G^*(T, f) \]
Since \( p_n^*(T, f) \) depends on \( T, f \)
If \( \dot{S}^i \approx 0 \Rightarrow G = \int f \, \dot{x} \Rightarrow \frac{dG}{df} \Bigg|_T = \dot{x} \Rightarrow \frac{dG^s}{df} \Bigg|_T = \bar{x}^s \)

By equality of 2nd derivatives:

\[ -\frac{\partial \tilde{S}^s}{\partial f} \bigg|_T = \frac{\partial \bar{x}^s}{\partial T} \bigg|_f = \frac{d^2 G^s}{df \, dT} \]

"Maxwell relation"

We can imagine more complicated simultaneous variation of \( T(t) \) and \( f(t) \).

**Case 5:** change \( T(t) + f(t) \) in such a way as to keep \( \dot{S} = 0 \) (entropy constant \( \Rightarrow \) isentropic process)

Our main equation reads:

\[ -T(t) \dot{S}^i = \dot{E} + f(t) \dot{x} = \dot{Q} \]

define \( H(t) = \bar{E}(t) + f(t) \bar{x}(t) \equiv \) enthalpy

- If \( f(t) = \bar{f} \) and \( S(t) = \bar{S} \) then
  \[ \dot{H}(t) = \dot{E} + f \dot{x} = -T(t) \dot{S}^i \leq 0 \text{ when } \dot{S}^i > 0 \]
  \[ = 0 \text{ in equilibrium} \]

\( H(t) \) in this case decreases until reaching \( H^s \), which must depend on \( f \) and \( S \)

\[ \Rightarrow H^s(f, S) \]

[since \( f \) is fixed, and fixing \( S \) must determine \( T \)]

- If \( f(t) \) varies and \( S(t) = \bar{S} \) then
  \[ \dot{H}(t) = \dot{E} + \dot{f} \dot{x} + f \ddot{x} = \dot{f} \dot{x} - T(t) \dot{S}^i \]
  when \( \dot{S}^i \approx 0 ; \dot{H} \approx \dot{f} \dot{x} \Rightarrow \frac{\dot{H}}{\dot{f}} \approx \frac{dH^s}{df} \bigg|_{\bar{x}^s} = \bar{x}^s \]
note when $\dot{S}^i \approx 0$ and $\dot{S} = 0$ we have $\dot{Q} = 0$

⇒ a reversible isentropic process is necessarily \underline{adiabatic} (no heat flow)

case 6: $f(t) = f$ and $S(t)$ varies

$\dot{H} = \dot{E} + f \dot{X}$

but now orig. equation applies:

$-T \dot{S}^i = \dot{E} - T \dot{S} + f \dot{X} = \dot{H} - T \dot{S}$

When $\dot{S}^i \approx 0 \Rightarrow \frac{\dot{H}}{\dot{S}} = T \Rightarrow \left. \frac{dH^s}{dS} \right|_f = T$

We get another Maxwell relation:

$$\left. \frac{dT}{df} \right|_S = \left. \frac{d\bar{x}^s}{dS} \right|_f = \left. \frac{d^2 H^s}{dS df} \right|_f$$

cases 7 → ad nauseam

fix $T$ and $\bar{x}$: $F(t) = \bar{E}(t) - T(t) S(t)$

= Helmholtz free energy

decreases until reaching $F^s(T, \bar{x})$

vary either $T$ or $\bar{x}$:

$$\left. \frac{dF^s}{dT} \right|_{\bar{x}} = -S^s, \quad \left. \frac{dF^s}{\partial \bar{x}} \right|_T = -f, \quad \left. \frac{dS^s}{dT} \right|_{\bar{x}} = \left. \frac{df}{dT} \right|_{\bar{x}}$$

fix $S$ and $\bar{x}$: $\bar{E}(t)$ decreases until reaching $E^s(S, \bar{x})$

vary either:

$$\left. \frac{\partial \bar{E}^s}{\partial S} \right|_{\bar{x}} = T, \quad \left. \frac{\partial \bar{E}^s}{\partial \bar{x}} \right|_S = -f, \quad \left. \frac{\partial T}{\partial \bar{x}} \right|_S = -\left. \frac{\partial f}{\partial S} \right|_{\bar{x}}$$
Generic derivation of any thermodynamic potential:

\[ \bar{W} = - \sum_{v=1}^{M} f_v(t) \dot{X}_v \quad \text{M work terms} \]

\[-T(t) \dot{S}^i = \dot{E} - T(t) \dot{S} + \sum_v f_v(t) \dot{X}_v \]

If you fix M+1 quantities in this equation that don't vary in time, then

\[-T \dot{S}^i \equiv \dot{\mathcal{W}} \text{ where } \mathcal{W} \text{ is the corresponding potential that gets minimized in equilibrium} \]

Allowing each of these M+1 quantities to individually vary (keeping others fixed) gives you derivatives of \( \mathcal{W} \), assuming \( \dot{S}^i \approx 0 \).

Generality of the \( V_{nm} \) term:

Conservative \( V_{nm} = V_n - V_m \) does not always obviously look like a "force" times a "distance".

Example: coarse-graining degenerate states

![Diagram showing coarse-graining process with energy levels and degeneracy](image)

In equilibrium (no work for simplicity):

\[ P_1^s = \sum_{n \text{ energy level } E_1} P_n^s = \frac{N_1 e^{-\beta E_1}}{Z}, \quad P_2^s = \frac{N_2 e^{-\beta E_2}}{Z} \]
For coarse-grained description to make sense,

$$\frac{W_{12}}{W_{21}} = e^{-\beta(E_1 - E_2)} \frac{N_1}{N_2} = e^{-\beta \left[ E_1 - E_2 - k_BT \ln \frac{N_1}{N_2} \right]}$$

Thus we have:

$$\frac{W_{nm}}{W_{mn}} = e^{-\beta \left[ (E_n - E_m) + V_n - V_m \right]}$$

where $V_n = -k_BT \ln N_n$ "degeneracy potential"
describing entropic cost of going
bit levels w/ different degeneracies

There is a penalty going from a state w/ $N_m$ degenerate levels to
one with $N_n < N_m$,

Another example of $V_{nm} = V_n - V_m$: chemical potential

Imagine a large volume $V$ filled with molecules
diffusing ($N_{mol}$ in total). There is a single enzyme
core molecule $E$ with a binding site, capable of forming
a bond w/ the molecules in solution. Focus on enzyme
as the system.

Energies $E_o = E^+$
and $E_1 < E_o$
bond energy $E_o - E_1 = \epsilon > 0$
\[ \frac{k_b}{k_{-b}} = e^{-\beta(E_t - E^\ddagger)} = e^{\beta e} \quad \text{(energy difference)} \]

But what about \( \frac{k_d}{k_{-d}} \)?

Even though \( E_0 = E^\ddagger \), the ratio is not 1, b/c our description of the enzyme is really a "coarse-grained" picture, ignoring the many possible configurations of the molecules in solution.

Divide \( V \) into \( N_{\text{pos}} = \frac{V}{V_{\text{mol}}} \) microscopic volumes of size \( V_{\text{mol}} = \text{volume of one molecule} \).

\[ N_0 = \text{# of ways of positioning } N_{\text{mol}} \text{ molecules among } N_{\text{pos}} \text{ positions} \]

\[ = \frac{N_{\text{pos}}!}{N_{\text{mol}}! \left(N_{\text{pos}} - N_{\text{mol}}\right)!} \]

\[ N^\ddagger = \text{# of ways of positioning } N_{\text{mol}} - 1 \text{ molecules among } N_{\text{pos}} \text{ positions} \]

\[ = \frac{N_{\text{pos}}!}{(N_{\text{mol}} - 1)! \left(N_{\text{pos}} - N_{\text{mol}} + 1\right)!} \]

\[ \frac{k_d}{k_{-d}} = e^{-\beta \left[-k_B T \left(\ln N^\ddagger - \ln N_0\right)\right]} \]

\[ = e^{-\beta \left[-k_B T \ln \left(\frac{N_{\text{mol}}}{N_{\text{pos}} - N_{\text{mol}} + 1}\right)\right]} \]

\[ \approx \frac{N_{\text{mol}}} {N_{\text{pos}}} \quad \text{since typically } N_{\text{pos}} \gg N_{\text{mol}} \]

\[ = \frac{N_{\text{mol}}}{V} V_{\text{mol}} \]
Define \( \frac{K_d}{K_{-d}} = e^{-\beta [-\mu]} \)

where \( \mu = K_B T \ln \frac{N_{\text{mol}}}{V} \)

\( \mu = \mu_0 + K_B T \ln C \)

\( k_B T \ln V_{\text{mol}} \) = reference value

= chemical potential of taking one molecule out of \( V \) and into pocket

Since \( N_{\text{pos}} \gg N_{\text{mol}} \), \( \mu \approx 0 \) so taking a molecule much less likely than releasing one, but as \( C \) increases, \( \frac{K_d}{K_{-d}} \) also increases.

For our full system, typically \( k_d, k_b \gg k_d, k_b \)

so time spent in \( \neq \) state is very short. Often we approximate such a system by considering only \( E_0 \) and \( E_1 \) states:

\[ k_r = \text{effective reaction rate} \]

\[ k_r \approx \frac{1}{\text{mean first passage time from 0 to 1}} \]

\[ k_p = \frac{K_d K_b}{k_d + k_b + k_{-d}} \]

Similarly: \( k_{-r} = \frac{k_{-b} k_d}{k_{-b} + k_d + k_b} \approx \frac{k_{-d} k_{-b}}{k_{-b} + k_{-d}} \)
\[ \frac{k_r}{k_{-r}} = e^{-\beta[(E_i-E_0) - \mu]} = \frac{k_d k_{atb}}{k_{d} k_{t-b}} \]

Most generally, if there are \( M \) types of molecules, with chemical potentials \( \mu_j \), \( j=1, \ldots, M \), then:

\[ \frac{k_r}{k_{-r}} = e^{-\beta} \]

\[ W_{nm} = e^{-\beta[(E_n-E_m) - \sum_{j=1}^{M} \mu_j (N_n^{(j)} - N_m^{(j)})]} \]

where

\[ N_n^{(j)} = \text{# of type } j \text{ molecules bound in state } n \]

Note: If chemical reactions occur, going around a cycle in network may not individually conserve each \( N_n^{(j)} \) leading to current generation [see homework].

\[ \dot{W} = \sum_{(n,m)} J_{n,m} \sum_{j=1}^{M} \mu_j (N_n^{(j)} - N_m^{(j)}) = -\sum_{(n,m)} J_{nm} V_{nm} \]

= "chemical power" from the "chemical potential reservoirs"

To maintain constant \( \mu_j \), need to keep \( N_m^{(j)} \) constant (replenish molecules in solution).