Thermodynamics at the Macroscopic and Microscopic Levels

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The Macroscopic Approach
The Microscopic Approach
References

Internal Energy and Entropy
Enthalpy
Gibbs Free Energy

Fundamental Equations

Extensive Parameters

$$U = \overbrace{U(S, V, \vec{N})}$$

Requirements:

1. $U \in \mathcal{C}^1$, **convex**:

$$U(\lambda x + (1 - \lambda)y) \leq \lambda U(x) + (1 - \lambda)U(y)$$

2. U positively homogeneous of degree 1:

$$\forall \alpha > 0, \ U(\alpha x) = \alpha U(x)$$

3. $\frac{\partial U}{\partial S} \geq 0$, temperature is positive

$$\underbrace{T \equiv \frac{\partial U}{\partial S}, \ P \equiv -\frac{\partial U}{\partial V}, \ \mu_i \equiv -\frac{\partial U}{\partial N_i}}$$

Intensive Parameters

$$S = S(U, V, \vec{N})$$

1. $S \in \mathcal{C}^1$, **concave**

2. S positively homogeneous of degree 1

3. $\frac{\partial S}{\partial U} \geq 0$
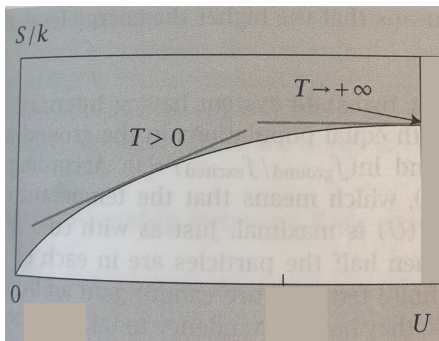
$$\frac{\partial S}{\partial U} = 1/T$$
$$\frac{\partial S}{\partial V} = -P/T$$
$$\frac{\partial S}{\partial N_i} = -\mu_i/T$$

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What is Temperature ?

$T(S, V, \vec{N}) = \frac{\partial U}{\partial S}(S, V, \vec{N})$, $1/T = \frac{\partial S}{\partial U}$

$T(\lambda x) = T(x)$, T is **intensive** (homogeneous of degree 0)

Source: Molecular Driving Forces, p.223

At small temperature, a gain in energy will result in a bigger gain in entropy than at high temperature.

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Principles of Thermodynamics

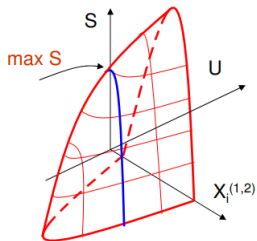1. Energy can vary for two reasons, heat or work:

$$dU = \delta q + \delta w$$

2. At fixed $U = U_0$, thermodynamic equilibrium is reached for the value of the extensive parameters which **maximize** entropy:

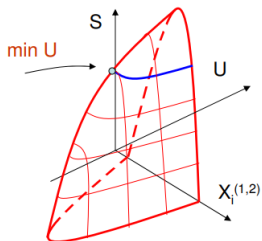$$S_{eq} = S(U_0, V_{eq}, \vec{N}_{eq}) \text{ is maximal}$$

Equivalently, at fixed $S = S_0$, thermodynamic equilibrium is reached for the value of the extensive parameters which **minimize** energy.

3. At $T = 0$ we have $S = 0$.

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Second Law Visualized

Maximizing S at fixed U

Minimizing U at fixed S

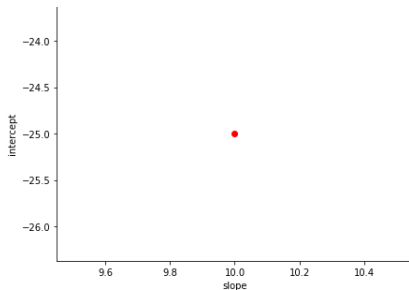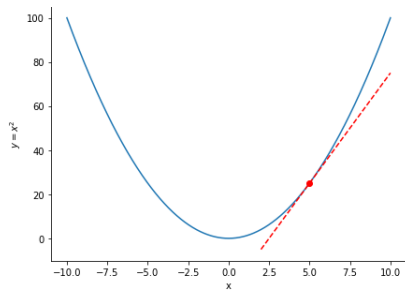Source: https://ps.uci.edu/~cyu/p115B/LectureNotes/Lecture13.pdf

Enthalpy

$U = U(S, V, \vec{N})$
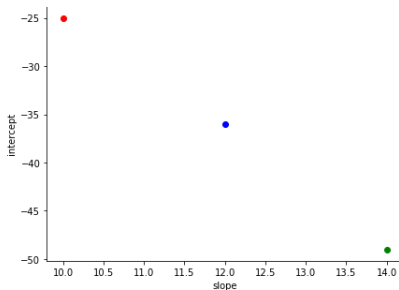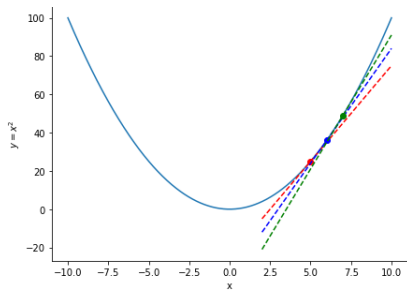$P \equiv -\frac{\partial U}{\partial V}$

Enthalpy is the **Legendre Transform** of U with respect to V:

$$H = H(S, P, \vec{N})$$

Legendre Transform

Legendre Transform

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Legendre Transform

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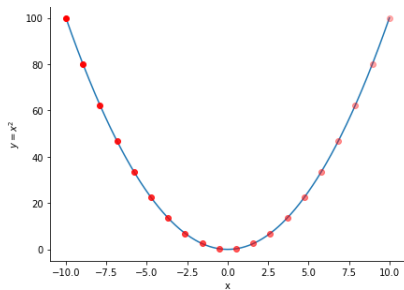
Legendre Transform
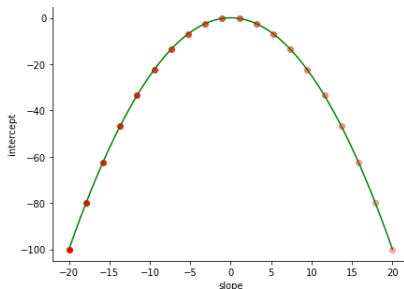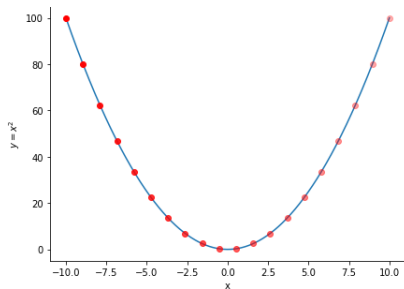
The **Legendre Transform** of a strictly convex function $f : \mathbb{R} \to \mathbb{R}$ is the representation of f in the slope/intercept plan. It is always a strictly concave function.

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Legendre Transform

Formally, the Legendre Transform of a strictly convex function $f : \mathbb{R} \to \mathbb{R}$ is the function g such that:

$$\begin{cases} g(s) = f(x) - s * x \\ f'(x) = s \end{cases} \Leftrightarrow g(s) = f(f'^{-1}(s)) - s * f'^{-1}(s)$$

Alternatively and more generally it can be defined as:

$$g(s) = \inf_x \left(f(x) - s * x \right)$$

The Legendre Transform of f expresses f in function of $\frac{df}{dx}$.

Example. The Legendre Transform of $x \mapsto x^2$ is $s \mapsto -s^2/4$

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Legendre Transform

The Legendre Transform is **involutive**.

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Back to Enthalpy

$U = U(S, V, \vec{N})$
$P \equiv -\frac{\partial U}{\partial V}$

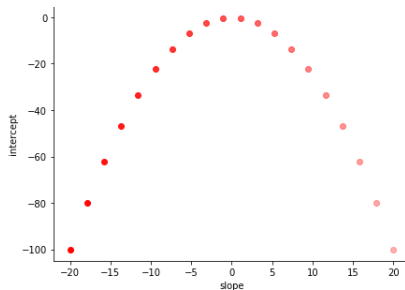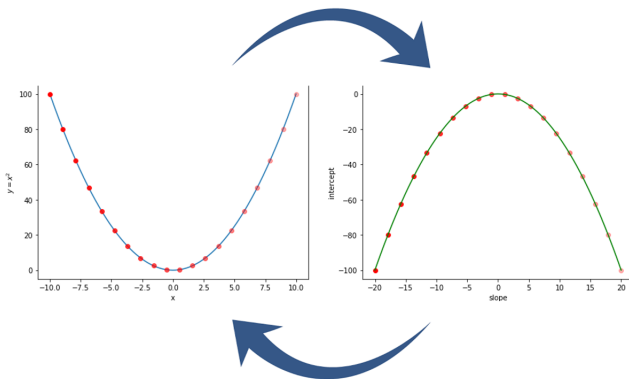Enthalpy is the **Legendre Transform** of U with respect to V:

$$g(s) = \inf_x \left(f(x) - s * x \right) \text{ with } s = \frac{\partial f}{\partial x}$$

Becomes:

$$H(S, P, \vec{N}) = \inf_V \left(U(S, V, \vec{N}) + PV \right)$$

$$H(S, P, \vec{N}) = U(S, V, \vec{N}) + PV \text{ with } V \text{ s.t } \frac{\partial U}{\partial V}(S, V, \vec{N}) = -P$$

Which, in physics, becomes:

$$H = U + PV \qquad dH = dU + VdP + PdV$$

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Why Enthalpy?

At constant pressure we have:

$$dH = dU + VdP + PdV$$
$$dH = dU + PdV \qquad \text{(Constant Pressure)}$$
$$dH = \delta q + \delta w + PdV \qquad \text{(First Principle)}$$
$$dH = \delta q - PdV + PdV \qquad \text{(Quasi-static Process)}$$
$$dH = \delta q$$

At constant pressure, enthalpy changes reflect exactly the gain/loss in heat of the system.

$$dH = \delta q$$

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Why Enthalpy? Because Heat

At constant pressure, enthalpy changes reflect exactly the gain/loss in heat of the system.

$$dH = \delta q$$

Since the quantity $\frac{\delta q}{\partial T}$ is **physically measurable**, we have access to $\frac{\partial H}{\partial T} = C_P$, the **isobaric heat capacity**.
Hence we can measure enthalpic and entropic changes since:

$$\Delta H = \int_{T_A}^{T_B} C_P(T)dT \text{ and } \Delta S = \int_{T_A}^{T_B} \frac{C_P(T)}{T}dT$$

For the second point, notice: $\frac{\partial H}{\partial T} = \frac{\partial H}{\partial S}\frac{\partial S}{\partial T} = T\frac{\partial S}{\partial T}$.

Isobaric Heat Capacity of Water

Water Specific Heat Capacity vs Temperature (p = 1 bar)
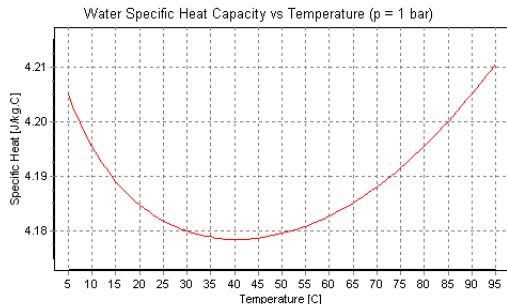
Source:
https://www.engineersedge.com/physics/properties_of_water_14467.htm

$P = RI^2$ $Q = P\Delta t$
Δt time required to elevate water temperature by $1°$

Knowing the isobaric heat capacity of water allows to do **Coffee Cup Calorimetry**.

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From Theory to Experiment and Vice Versa

For a *simple monoatomic ideal gas*, $C_P = \frac{5}{2}R$ is constant:
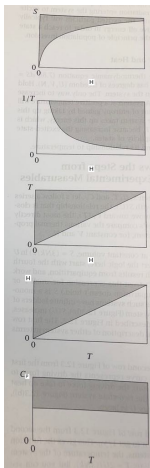
$$1/T = \frac{\partial S}{\partial U}$$

$$H = \int_T C_P dT$$

Source: Molecular Driving Forces, p.226

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Gibbs Free Energy

Gibbs Free Energy is $G = G(T, p, \vec{N})$ is the Legendre Transform of $H(S, p, \vec{N})$ with respect to S.

Said equivalently G is the Legendre Transform of $U(S, V, \vec{N})$ with respect to the pair (S, V).

$$G(T, p, \vec{N}) = \inf_S \left(H(S, p, \vec{N}) - TS \right)$$
$$= \inf_{(S,V)} \left(U(S, V, \vec{N}) - TS + PV \right)$$

Which, in physics, becomes:

$$G = H - TS \qquad dG = -SdT + Vdp + \sum_i \mu_i dN_i$$

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Why Gibbs Free Energy? Because Chemistry

From the Second Law we can deduce that at **constant T and P** equilibrium corresponds to the minimization of G.

Cool for chemistry! At equilibrium, $dG = 0 = \sum_i \mu_i dN_i$

More generally, we can revisit the second law of thermodynamics for all potentials:

Name	Variables	Reservoir	"Expression"	At Equilibrium
Entropy	$U, V, \vec{N}$	Constant U	S	Maximal
Energy	$S, V, \vec{N}$	Constant S	U	Minimal
Helmotz Free Energy	$T, V, \vec{N}$	Constant T	F = U - TS	Minimal
Enthalpy	$U, p, \vec{N}$	Constant P	H = U + pV	Minimal
Gibbs Free Energy	$T, p, \vec{N}$	Constant T, P	G = H - TS	Minimal

Thermodynamics potentials are **convex** in their extensive variables and **concave** in their intensive ones.

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Interpreting ΔG

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

For a chemical reaction $A \rightarrow B$ three possible cases:

1. $\Delta G > 0$: the reaction $A \rightarrow B$ cannot happen, $B \rightarrow A$ is favored

2. $\Delta G = 0$: equilibrium

3. $\Delta G < 0$: the reaction can happen (maybe not kinetically favored)

- $\Delta H < 0$: exothermic reaction, releasing heat
- $\Delta H > 0$: endothermic reaction, consuming heat

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Interpreting ΔG

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

In terms of ΔH and ΔS:

1. $\Delta H > 0$ and $\Delta S < 0$: thermodynamically impossible reaction. An increase in enthalpy must result in an increase in entropy. You can't turn graphite into diamond.

2. $\Delta H > 0$ and $\Delta S > 0$: entropy driven reaction. Depends on T. Example: $NaNO_{3(s)} \rightarrow Na+_{(aq)} + NO3-_{(aq)}$

3. $\Delta H < 0$ and $\Delta S > 0$: does not depend on T. Can be entropy or enthalpy driven. Diamond degrades into graphite (but it's slow).

4. $\Delta H < 0$ and $\Delta S < 0$: enthalpy driven reaction. Example: $Na_{(s)} + Cl2_{(g)} \rightarrow 2NaCl_{(s)}$.

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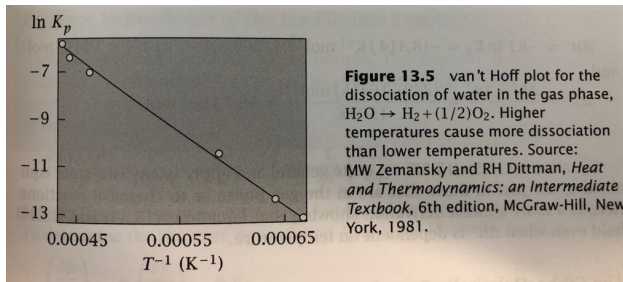Internal Energy and Entropy
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Measuring ΔG: Van't Hoff Plot

Dissociation Reaction: $AB \rightarrow A + B$
Isobaric Reaction Constant: $K_p = \frac{[A][B]}{[AB]}$

Van't Hoff Relations:

- $\Delta G = RT\ln(K_p)$
- $\frac{\partial \ln K_p}{\partial(1/T)} = -\frac{\Delta H}{R}$

Figure 13.5 van't Hoff plot for the dissociation of water in the gas phase, $H_2O \rightarrow H_2 + (1/2)O_2$. Higher temperatures cause more dissociation than lower temperatures. Source: MW Zemansky and RH Dittman, *Heat and Thermodynamics: an Intermediate Textbook*, 6th edition, McGraw-Hill, New York, 1981.

Source: Molecular Driving Forces, p.245

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Measuring ΔG: Melting Temperature

The melting temperature is the temperature where half the double-stranded are dissociated.

$$T_m = -\frac{\Delta G}{R\ln\frac{[AB]_{\text{initial}}}{2}}$$

Easier way to get to ΔG!

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ΔG for DNA

Table 1. Nearest-neighbor parameters for DNA/DNA duplexes in 1 M NaCl.[13]

Nearest-neighbor sequence (5'-3'/3'-5')	$\Delta H°$ kJ/mol	$\Delta S°$ J/(mol·K)	$\Delta G°_{37}$ kJ/mol
AA/TT	−33.1	−92.9	−4.26
AT/TA	−30.1	−85.4	−3.67
TA/AT	−30.1	−89.1	−2.50
CA/GT	−35.6	−95.0	−6.12
GT/CA	−35.1	−93.7	−6.09
CT/GA	−32.6	−87.9	−5.40
GA/CT	−34.3	−92.9	−5.51
CG/GC	−44.4	−113.8	−9.07
GC/CG	−41.0	−102.1	−9.36
GG/CC	−33.5	−83.3	−7.66
Terminal A/T base pair	9.6	17.2	4.31
Terminal G/C base pair	0.4	−11.7	4.05

Simple secondary structure:

```
  ↓ ↓ ↓ ↓ ↓
5' C-G-T-T-G-A 3'
3' G-C-A-A-C-T 5'
```
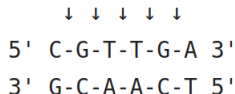
$\Delta G°_{37}$(predicted) = $\Delta G°_{37}$(C/G initiation) + $\Delta G°_{37}$(CG/GC) + $\Delta G°_{37}$(G
$\Delta G°_{37}$(GA/CT) + $\Delta G°_{37}$(A/T initiation)

Source: https://en.wikipedia.org/wiki/Nucleic_acid_thermodynamics

The Microscopic Setup

We have N possible states, with known energies E_i ($1 \leq i \leq N$).
In the case of DNA secondary structures, we have $E_i = \Delta G(s_i)$.
We wish to find $(p_1, \ldots, p_N)$ the probability distribution of
appearance of these states.

At a fixed temperature T, we choose this distribution to be the
solution of the following free energy minimization problem:

$$\min_{(p_1, \ldots, p_N)} G = \min_{(p_1, \ldots, p_N)} <E> - kTS$$

With:

- $<E> = \sum E_i p_i$ the average energy of the system
- $S = -\sum p_i \ln(p_i)$ which is the Shannon entropy of the
  distribution

Notice the implicit constraint: $\sum p_i = 1$.

The Boltzmann Distribution

The free energy minimization problem:

$$\min_{(p_1,\ldots,p_N)} G = \min_{(p_1,\ldots,p_N)} <E> - kTS$$

Admits one unique solution which is **Boltzmann Distribution**:

$$p_i = \frac{1}{Q} e^{-\beta E_i}$$

With $\beta = 1/kT$ and $Q = \sum_i e^{-\beta E_i}$ the normalization constant.

The Partition Function

The normalization constant $Q(\beta) = \sum_i e^{-\beta E_i}$ is also called the **partition function**. It is seen as a function of β.

We can deduce all equilibrium quantities from $Q(\beta)$ at temperature T:

- $<E>_{\text{opt}} = \frac{dQ}{d\beta}(\beta(T))$
- $S_{\text{opt}} = k \ln Q(\beta(T)) + <E>_{\text{opt}} / T$
- $G_{\text{opt}} = -kT \ln Q$

Nupack Example

$$Q = \sum_i e^{-\beta E_i} \qquad p_i = \frac{1}{Q} e^{-\beta E_i} \qquad G_{\text{opt}} = -kT \ln Q$$

Nupack Example

$$Q = \sum_i e^{-\beta E_i} \qquad p_i = \frac{1}{Q} e^{-\beta E_i} \qquad G_{\text{opt}} = -kT \ln Q$$

Details

Sequence properties ❓

Free energy:		-23.01 kcal/mol ❓
Base	Number	%
A	4	14.3 ❓
C	10	35.7 ❓
G	10	35.7 ❓
U	4	14.3 ❓
Other	0	0.0 ❓

Sequence/structure properties ❓

Free energy:	-23.00 kcal/mol ❓
Probability:	0.988 ❓
Ensemble defect:	0.0 nt ❓
Normalized ensemble defect:	0.1 % ❓
Nucleotides:	28 nt ❓

The End

Questions :) ?

References

1. Molecular Driving Forces, text book, Dill et al.
2. Entropy and Partial Differential Equations, text book, C. Evans `https: //math.berkeley.edu/~evans/entropy.and.PDE.pdf`
3. `https://en.wikipedia.org/wiki/Nucleic_acid_ thermodynamics`