1.1 Thermodynamics

Biophysics

Outline

- Reminders from thermodynamics 1st year
  - Nomenclature, concepts, relevant magnitudes and equations
- Thermodynamics in biology
  - Metabolic processes, Binding and recognition, Macromolecular stability
- From the macroscopic to the microscopic view.
  - Statistical thermodynamics
  - Ideal gases theory. Temperature, pressure, …
  - The concept of ensemble of states
  - Boltzmann distributions

Thermodynamics

- Thermodynamics is the study of the effects of **work**, **heat**, and **energy** on a system

- Thermodynamics is only concerned with **macroscopic** (large-scale) changes and observations

Concepts and nomenclature

Open, closed, isolated Systems

- Biological Systems are actually open, but at laboratory level they are considered closed.
- System + Environment = Universe

Energy

- Capability to produce work on any kind (mechanical, electrical, chemical, ...)

Temperature

- Measure of "heat content"

Heat (q), Work (w)

- Ways to transfer energy (ex, from Closed Systems to/from the Environment)
- Heat and work depend on the process

State funcions

- Any magnitude that DOES NOT depend on the process, only on initial and final STATES

Concepts and nomenclature

Internal energy (E)

- The energy "contained" in the system, no matter its nature.
- Ex. Potential, Kinetic, Chemical.
- At closed Systems ΔE corresponds to heat exchanged at "constant volume" (q_V)

Enthalpy (H)

- The total "heat" contained in the system ($H = E + PV$)
- At closed systems ΔH corresponds to heat exchanged at "constant pressure" (q_P)
- ΔH is the energy that matters "in solution", the usual biochemical experiment

1st Thermodynamics principle $\quad \Delta E = q + w$

E and H are State functions!!

Concepts and nomenclature

Reversible (in equilibrium) and irreversible (spontaneous) processes

- A process is considered reversible when can be (infinitesimally) reversed without significant change in the thermodynamic properties of the system and environment
- Another way to say that the System and the environment are "in equilibrium"

Entropy (S)

- The entropy is a State Function defined as q_{rev}/T
- Entropy of the Universe is always ≥ 0 (2nd principle of thermodynamics)
- Universe $\Delta S = 0$ for reversible processes and $\Delta S > 0$ for irreversible ones.

Gibbs free energy.

- The available energy to make work (on any kind) ΔG
- $\Delta G = 0$ for reversible processes and $\Delta G < 0$ for irreversibles ones
- $\Delta G > 0$ indicates thay the opposite reaction is spontaneous.

(Bio)Chemical processes

$$S \rightarrow P$$

- Chemical processes imply changes in the relative amounts (concentrations) of the components of the system

- In Biology we work "in solution", then P and V remain constant

- ΔH, ΔS, ΔG are the usual relevant functions

- Values at 1M concentration of all reactants are taken as the "reference" values ΔH^o, ΔS^o, ΔG^o
  - This values should be corrected with the actual concentrations.

- Reactions proceed in the direction of decreasing ΔG
  - Ex. ATP + H_2O -> ADP + P (ΔG^o = -28 KJ/mol)

- This DOES NOT imply that the reaction is actually produced at a reasonable rate!! Kinetics is not included here.

Transition state (‡)

Free energy, G

$\Delta G^{\ddagger}_{S \rightarrow P}$

$\Delta G^{\ddagger}_{P \rightarrow S}$

$\Delta G'^o$
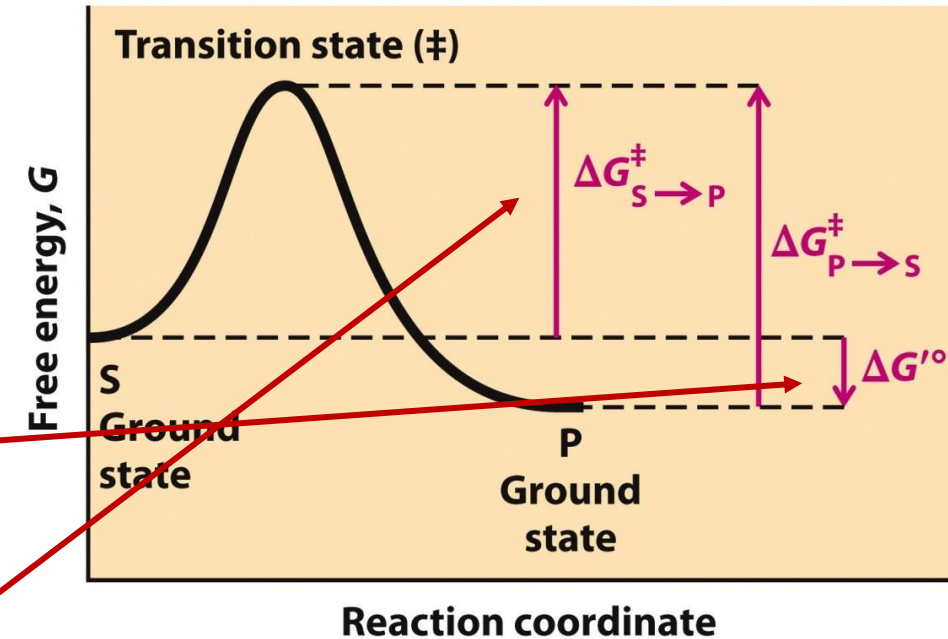
S Ground state

P Ground state

Reaction coordinate

Figure 6-2
Lehninger Principles of Biochemistry, Fifth Edition
© 2008 W. H. Freeman and Company

ΔX? & Units

In general thermodynamics functions are always "relative" ΔE, ΔH, ΔS, ΔG

- Only T and S may have absolute values (lim ΔS = 0 when T→ 0K)
- We use "ΔΔG" to express differences among processes
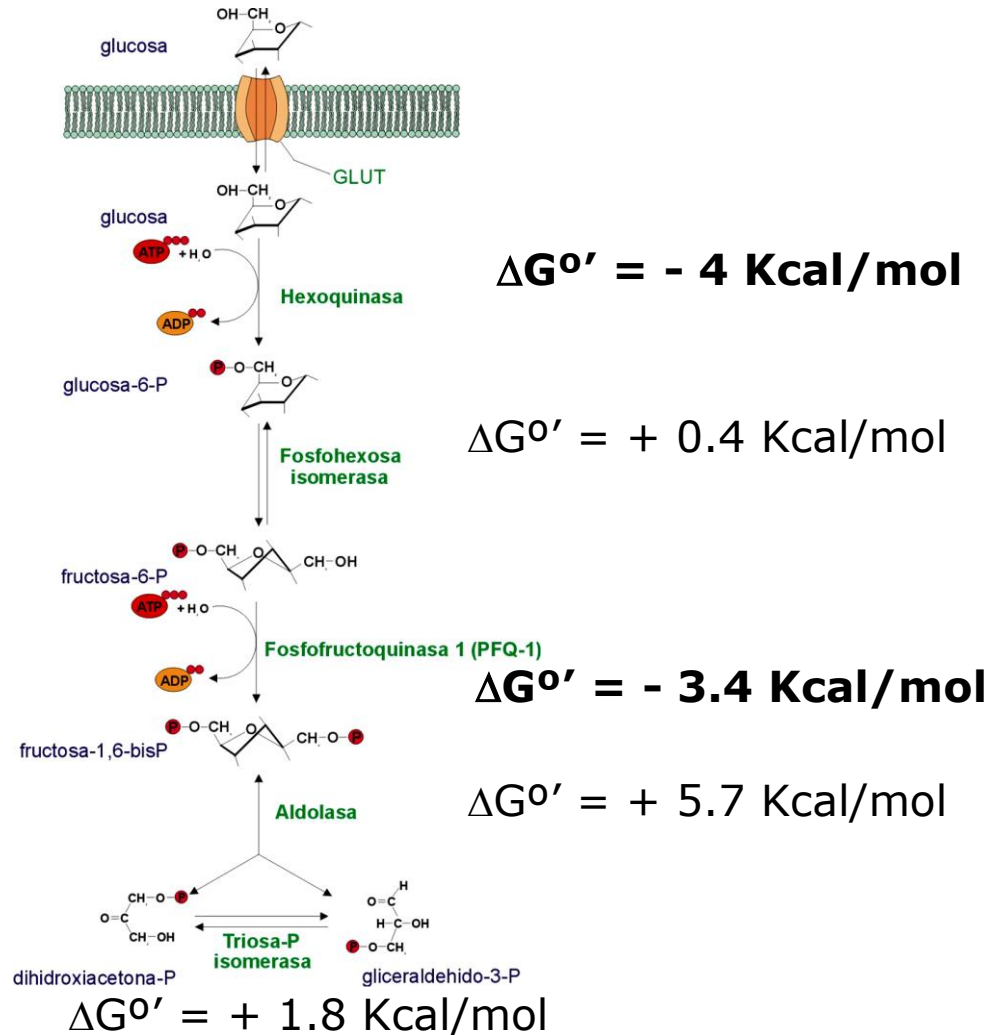
Most thermodynamics magnitudes are "energies"

- Joules (J) "The Work done by 1 Newton of force displaced 1m " $J = N.m = kg.m^2.s^{-2}$
- Calories (cal) = 4.184 J "Many definitions" with minor differences
- Most usually expressed as KJ or Kcal
- Other
  - eV (1.602 10^{-19} J) Used in spectroscopy and quantum chemistry
  - atm.liter Used in ideal gas theory (Remember H = E + PV so PV is an "energy")
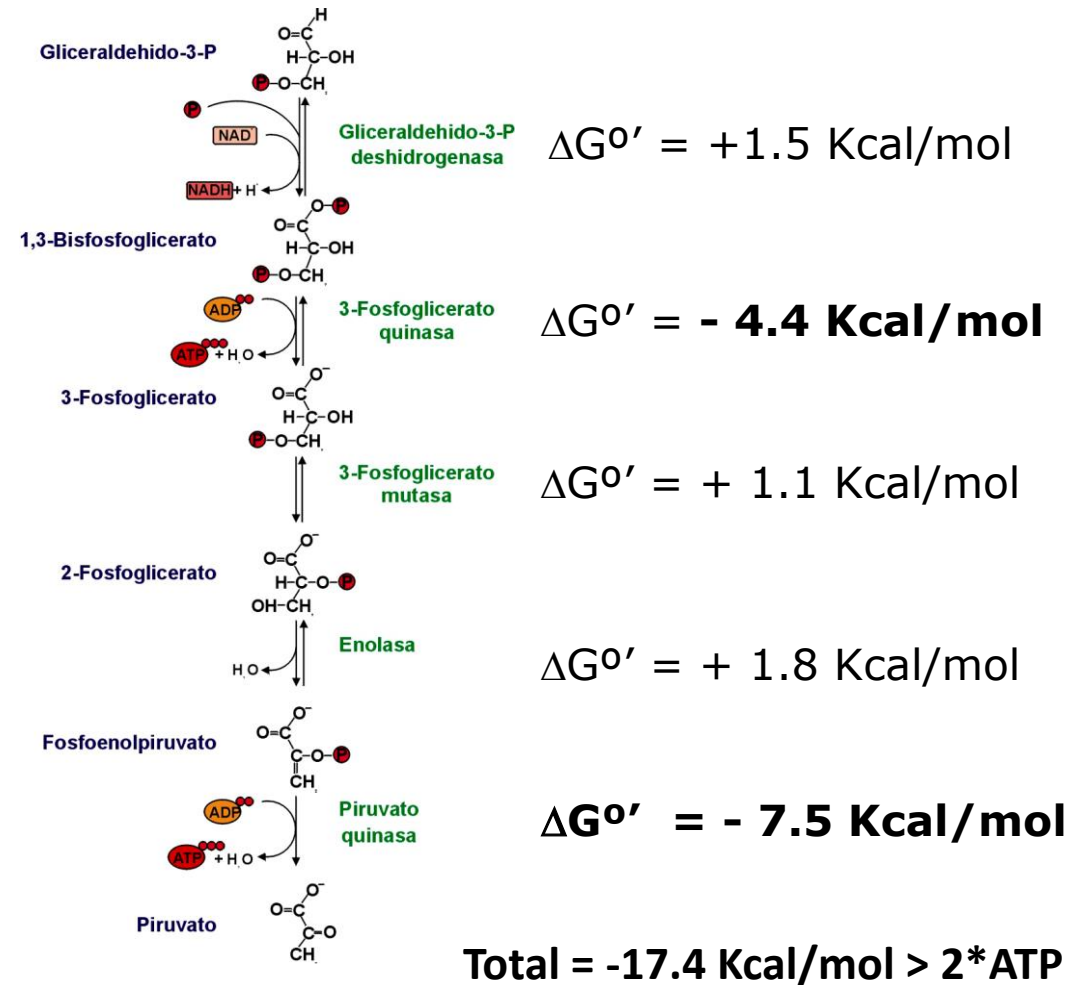
Temperature. K (Kelvin)

Entropy J/K

Most magnitudes are extensive (depends on the amount), so they are expressed "per mol": J/mol, Kcal/mol, KJ/mol.K …
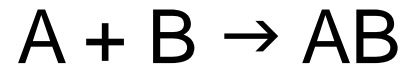
Thermodynamics in biology. Metabolism

$\Delta G^{o\prime} = - 4$ Kcal/mol

$\Delta G^{o\prime} = + 0.4$ Kcal/mol

$\Delta G^{o\prime} = - 3.4$ Kcal/mol

$\Delta G^{o\prime} = + 5.7$ Kcal/mol

$\Delta G^{o\prime} = + 1.8$ Kcal/mol

X2

$\Delta G^{o\prime} = +1.5$ Kcal/mol

$\Delta G^{o\prime} = - 4.4$ Kcal/mol

$\Delta G^{o\prime} = + 1.1$ Kcal/mol

$\Delta G^{o\prime} = + 1.8$ Kcal/mol

$\Delta G^{o\prime} = - 7.5$ Kcal/mol

Total = -17.4 Kcal/mol > 2*ATP

Thermodynamics in biology. Binding

ΔG_{bind}

$$A + B \rightarrow AB$$

$$K_{bind} = \frac{[AB]}{[A][B]}$$

$$\Delta G_{bind} = -RT \ln K_{bind}$$

Saturation degree

Y

1

0.5

$$Y = \frac{AB}{Atotal} = \frac{B}{K_D + B}$$
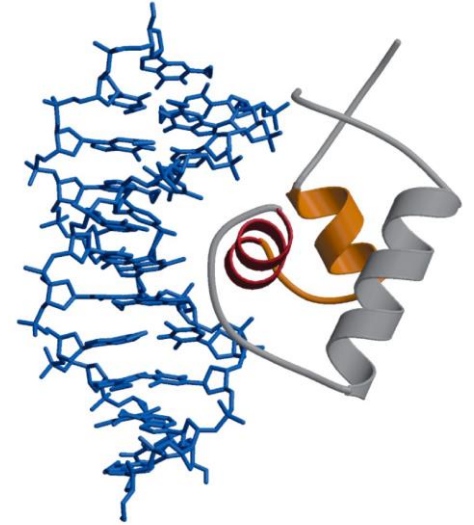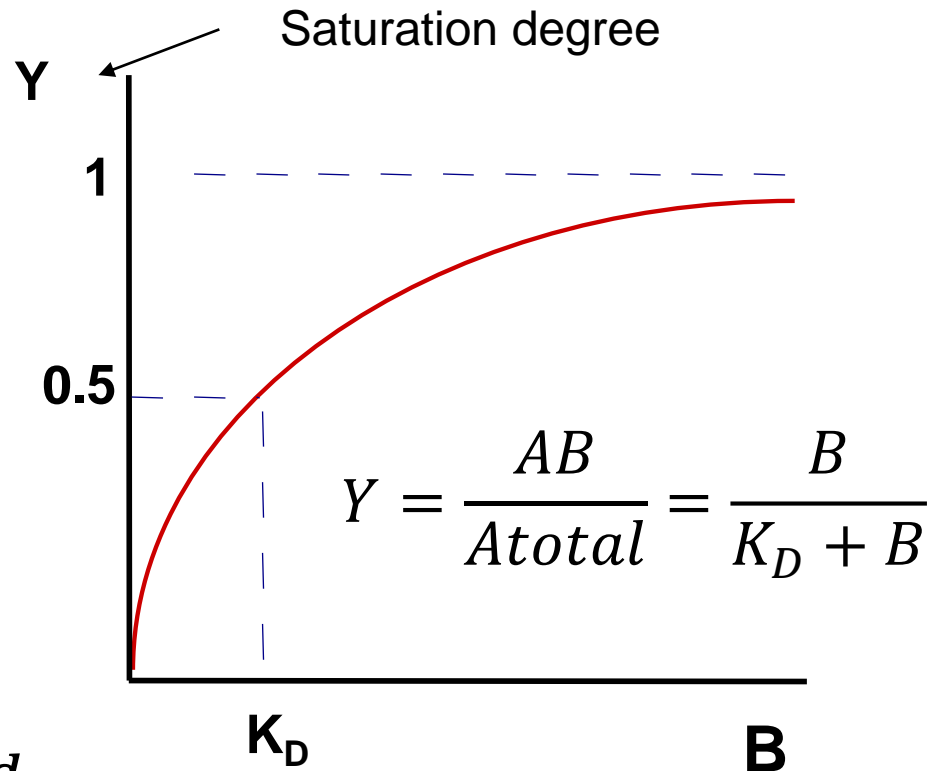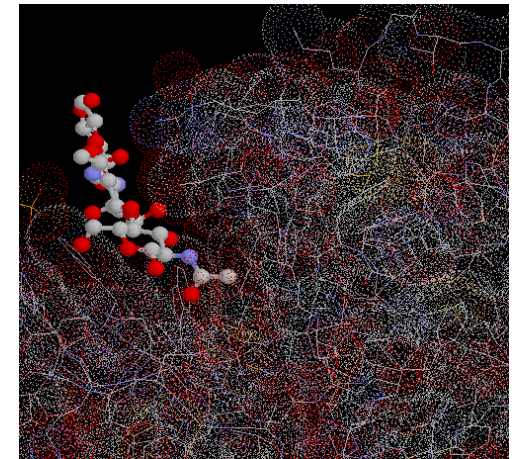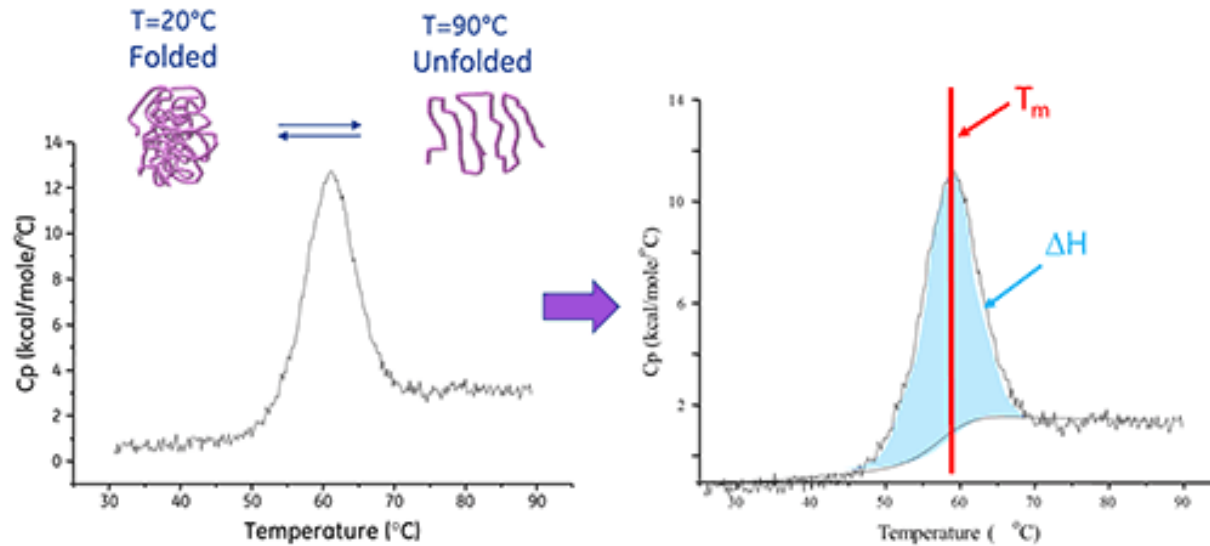
K_D

B

Figure 28-11a
Lehninger Principles of Biochemistry, Fifth Edition
© 2008 W. H. Freeman and Company

Thermodynamics in biology. Folding/unfolding

$$\Delta H(T) = \Delta H_m + \Delta C_P(T - T_m)$$

$$\Delta S(T) = \frac{\Delta H_m}{T_m} + \Delta C_P \ln\left(\frac{T}{T_m}\right)$$