

Thermodynamics

Outline

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 - Definitions and conventions
- II. Free energy
 - Relation to concentration
 - Relation to equilibrium constant
- III. Coupling reactions

I. The Laws of Thermodynamics

Energy exists in many different forms, e.g. kinetic, potential, heat, chemical, etc. It is often useful to think of energy as heat or the ability to do work.

First law: The total amount of energy in the Universe is constant.

$$\Delta E = q + w \quad \Delta E = \text{change in internal energy} \quad q = \text{heat} \quad w = \text{work}$$

$$q > 0 \text{ system absorbs heat} \quad w > 0 \text{ work done on system}$$

Let's use electrostatic energy as an example for how to think of energy as the ability to do work. We can calculate the energy stored in a system composed of a positive and a negative charge separated by a defined distance. This energy of interaction is designated U . Let's calculate U for a sodium ion and a chloride ion separated by distance R in a vacuum. The energy of the system can be determined by how much work is done by bringing the ions from an infinite separation to distance R apart. From Coulomb's law we can calculate the attractive force between the ions some arbitrary distance r apart:

$$F = k \frac{q_1 q_2}{r^2}$$

Now we recall that work is force applied over distance $w = F r$. Since the force changes with distance we must integrate and $w = \int F dr$. The integration goes from our reference conditions (infinite separation) to our final state, R :

$$U = \int_{\infty}^R F dr = \int_{\infty}^R k \frac{q_1 q_2}{r^2} dr = k \frac{q_1 q_2}{R}$$

It is important to distinguish work and energy from force. The force between the ions varies by $1/r^2$; however, the energy differs by $1/r$.

E for a molecule could be defined as the difference in energy of isolated nuclei and electrons and the assembled molecule. This is impractical. Instead measure ΔE , the difference between the molecule and a set of reference molecules, for example, the products of combustion in a bomb calorimeter ($\Delta E = E_f - E_r$). The state of the chemical (eg. temperature, phase, pressure, etc.) also contributes to ΔE . A standard state has been defined: $T = 25^\circ\text{C}$; $P = 1 \text{ atm}$; $\text{conc} = 1 \text{ molar}$.

Second law: The entropy of the Universe is increasing.

Entropy S is a measure of disorder:

$$S = k \ln W \quad k = \text{the Boltzmann constant } [R/N_A] \quad \text{and } W = \text{the number of configurations of the state with equivalent amounts of energy.}$$

II. Free energy

Free energy determines relative favorability of chemical processes at constant pressure. ΔG , $G_{\text{final}} - G_{\text{initial}}$, is a measure of the theoretical maximum amount of work that can be produced when the system goes from the initial to the final state. It can be shown that:

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

In biochemistry we are most often concerned with the free energy of a chemical in solution. The free energy of species i will have contributions from its intrinsic free energy and from its concentration. For this reason we define a standard free energy, which is the total free energy of i in a 1 mol/L solution. If a solution has a concentration different than 1 M, the actual free energy of i is given by:

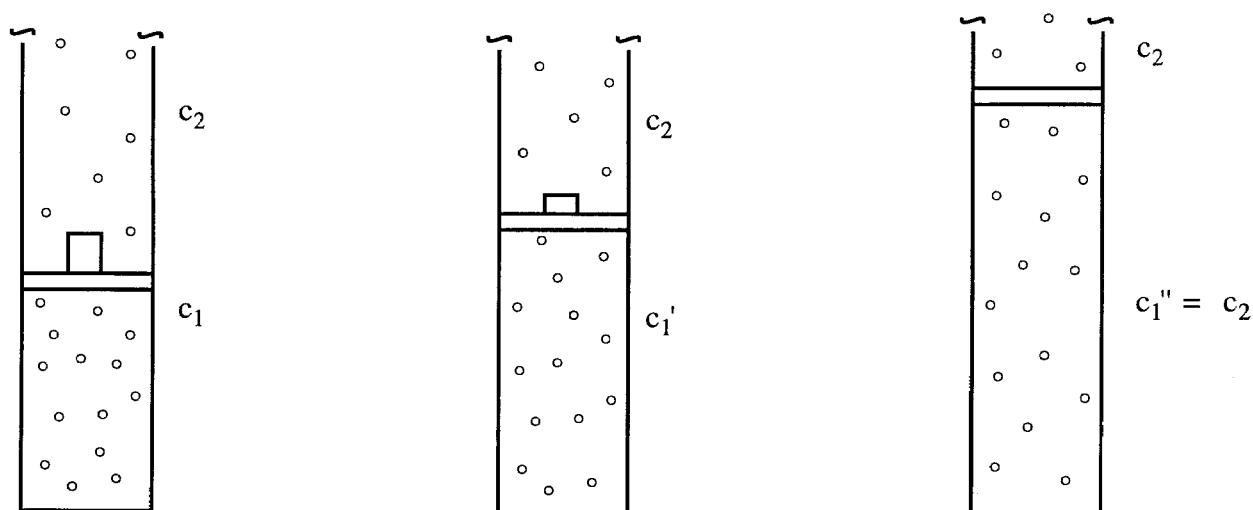
$$G_i = G_i^\circ + RT \ln [i]$$

For aqueous hydrogen ions and hydroxyl ions in biochemical reactions, 1 M is not practical. Biochemists often use a different standard free energy, ΔG° , which uses pH 7.0 as the standard state for H^+ and OH^- . Keep an eye out for that prime.

Why is free energy proportional to the logarithm of the concentration? Let's enter the world of ideal gases, frictionless pistons, infinite volumes,... and find out.

Consider a very tall cylinder filled with a solution of an ideal solute and containing a piston composed of a dialysis membrane. The membrane piston can move without friction up and down the cylinder and is freely permeable to water; however, the solute cannot pass through it. If the concentration of the solute is not the same on both sides of the piston, then there is osmotic pressure (π) across the piston. The pressure is determined by $\pi = (c_1 - c_2) RT$, where c_1 and c_2 are the concentrations below and above the piston. The volume of the solution above the piston is so large that movements of the piston will only change the concentration of the solution below the piston. The system is set up initially with the concentration below the piston at 1 mol/L (the standard state) and the concentration

above the piston is the final concentration (which is lower than 1 M), whose free energy we want to determine. A weight rests on the piston which exactly counteracts the osmotic pressure. We will calculate how much work is done to reversibly raise the piston to a position where the concentrations are the same above and below it:



The piston is moved by slowly reducing the weight on the membrane. When the weight is reduced, the osmotic pressure pushes the membrane up, increasing the volume of the lower chamber and reducing its concentration and thus the osmotic pressure. The lower osmotic pressure is now countered by the reduced weight and a new equilibrium is established. The process can be considered reversible if the weight is reduced by sufficiently small increments such that system is always at equilibrium. The procedure is continued until there is no weight left, at which point the concentration below the piston is equal to that above it.

The solution does work as the weight is pushed, thus by our convention $w < 0$. Since the weight equals the osmotic pressure, the amount of work done is $w = - \int \pi ds$, where s is the distance that the weight has moved. In the cylinder, the distance that the weight moves is directly proportional to the change in volume, thus $w = - \int \pi dV$. Using the definitions of osmotic pressure π and concentration c :

$$\pi = cRT = \frac{nRT}{V}$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \left[\frac{c_1}{c_2} \right]$$

Since c_1 is the standard condition, 1 M, and we want to know the work associated with one mole of i at concentration c_2 $w = RT \ln [i]$. The free energy associated with i at a nonstandard concentration is:

$$G = G_i^\circ + w = G_i^\circ + RT \ln [i] \quad [\text{Remember, the work was done by the system so the system energy content decreases}]$$

With this equation it is now a simple matter to derive the relationship between the equilibrium constant of a reaction and the free energy change associated with it.



At equilibrium $\Delta G = 0$. Substitute the expression for free energy

$$0 = x\{G_X^\circ + RT \ln [x]\} + z\{G_Z^\circ + RT \ln [z]\} - a\{G_A^\circ + RT \ln [a]\} - b\{G_B^\circ + RT \ln [b]\}$$

Now gather the standard free energy terms and the ln terms:

$$0 = xG_X^\circ + zG_Z^\circ - aG_A^\circ - bG_B^\circ + RT[\ln\{[x]^x\} + \ln\{[z]^z\} + \ln\{[a]^a\} + \ln\{[b]^b\}]$$

$$\Delta G^\circ = -RT \ln \left[\frac{[x]^x [z]^z}{[a]^a [b]^b} \right] = -RT \ln K_{eq}$$

where ΔG° = the standard free energy change of the reaction.

III. Coupling reactions

Imagine a sequence of reactions:



Suppose we know the equilibrium constant for each individual process:

$$K_1 = [B] / [A] \quad \text{and} \quad K_2 = [C] / [B]$$

It is trivial to see that the equilibrium constant for the overall equilibrium between A and C is the product of the individual rate constants.

Coupled reactions are no different. A specific example:

		K_{eq}	ΔG°
ATP	\rightarrow ADP + P _i	1.38×10^5	-7.3 kcal/mol
P _i + Glucose	\rightarrow Glucose-6-phosphate	4.74×10^{-3}	3.3 kcal/mol
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ATP + Glucose	\rightarrow ADP + Glucose-6-phosphate	6.56×10^2	-4.0 kcal/mol

The free energy changes in coupled or sequential reactions can also be considered. Since free energy is proportional to the logarithm of the equilibrium constant, then the free energies of the coupled reactions are added. Make certain that each reaction is considered in the direction that it occurs in the coupled process.