

## Thermodynamics

Reference:

Any physical chemistry text book

See me for access to these texts:

Nicholls and Ferguson Bioenergetics 2 . Chapter 3

Cramer and Knaff Energy transduction in biological membranes. Chapter 1-2

Voet and Voet Biochemistry Chapter 2-3

Also look in your favorite Biochemistry; Physical Chemistry, or Organic Chemistry Books for the sections on Thermodynamics & the section on pK<sub>a</sub>'s

(N) from Nicholls Bioenergetics 2

(CK) from Cramer and Knaff Energy transduction in biological membranes

(VV) from Voet and Voet Biochemistry

### (VV) Energy conversion

1J = 1 kg/m/s<sup>2</sup> = 1CV (coulomb volt) = 1 Nm (newton meter)

1 cal heats 1 g of water from 14.5 to 15.5°

1 cal = 4.186 J                      1 kcal = 4.186 kJ

1 V = 23 kcal                      1 V=8000 cm<sup>-1</sup>

N= 6.023x10<sup>23</sup> objects (1 mole)

C = 6.241x10<sup>18</sup> electrons (1 coulomb)

F = N electrons = 96,494 C/mol = 96494/V/mol (faraday)

273.15 K = 0C°

k<sub>b</sub> = 1.3807 x 10<sup>-23</sup> J/K (Boltzmann's constant)

R = Nk<sub>b</sub> = 1.987 cal/K/mol = 8.3145 J/K/mol (gas constant)

(N) Systems are:

Can exchange

	Material	Energy
<b>Isolated</b>	no	no
<b>Closed</b>	no	yes
<b>Open</b>	yes	yes

In an open system you really can't solve any thermodynamic equations exactly because you don't get to equilibrium. But you can tell

How far a reaction is from equilibrium.

What the equilibrium mixture of reactants and products would be if the system is closed and allowed to come to equilibrium.

The maximum work the system can do as it moves towards equilibrium. This equals the minimum energy needed to put the system into its current state.

(CK) **Energy (E)** is a macroscopic, extensive property. Energy is a state function. Defines:

- 1) If a system can do work.
- 2) There is a unique amount of energy for a given state
- 3)  $\Delta E$  between 2 states is independent of the path
- 4) Energy is conserved (first law of thermodynamics)

2nd law

What is possible is not fully defined by the first law.

You can't cool a cold reservoir to make work This would use the energy of the heat -moving heat from a colder to hotter place and extracting some of this energy to do work. You can do work and move energy from a cold place to a hotter one (e.g. your refrigerator).

You can't transfer heat (Q) from one reservoir to another to extract energy for work (W) if both reservoir are at the same temperature.

You can always use work to make heat!

**Free energy-** Tells us which direction a process go will in?

A spontaneous process

is not just an increase in entropy.

is not just a decrease in enthalpy.

If the drive in the universe were to optimize only S or H what would equilibrium look like?

**Gibbs free energy-state function**

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

$$dG = -SdT + Vdp + \sum_{j=1}^M \mu_j dN_j \quad (\mu_j \text{ is the chemical potential})$$

Equilibrium is a balance between the conflicting requirements to maximize entropy and minimize energy. For example, stronger bonds are at lower (more favorable) enthalpy but fix the molecule more tightly reducing (making less favorable) the entropy.

$$E = W + Q$$

(the change in energy going from state 1 to 2 can be contributed by **work** (done on or done by) and by **heat** (put in or out))

work - changes in energy that involve coherent (non-random) molecular movement.

change in volume; (mechanical)

moving across a concentration gradient (chemiosmotic work-)

electrons moving between 2 different potentials (electrochemical work)

heat - result of random motions; heat always flows from higher to lower temperature.

$$H = E + PV \text{ Enthalpy}$$

Under conditions of constant pressure (changes in volume can yield work) then  $\Delta H$  is the absorption of heat at constant pressure

$$\Delta H = \Delta Q_p \text{ If no other work done}$$

$$W = P\Delta V + w' \text{ (w' is non-PV work)}$$

$$\Delta H = \Delta E + p\Delta V = q_p - w + P\Delta V = q_p + w'$$

measure in constant pressure calorimeter where  $w' = 0$

### Entropy

Is a measure of how a system can be arranged. All other things being equal (eg if all arrangements have the same enthalpy) the more ways the better.

$$S = k_b \ln W$$

$$\Delta S \geq q/T \text{ (heat transferred by a process at constant T) (dissolving salts)}$$

$$T\Delta S \geq q_p$$

(VV) How many ways can be arrange 4 balls in a box with 9 positions?

$$W = \frac{9 \cdot 8 \cdot 7 \cdot 6}{4 \cdot 3 \cdot 2 \cdot 1} = 126 \text{ 9 places for 1st; 8 for 2nd; 7 for 3rd; 6 for 4th}$$

$$\text{(so } W = 126; S \gg 2 \text{ cal/mol/K } \ln(126) = 9.7 \text{ cal/mol/K)}$$

$$W = \text{boxes!}$$

objects!

but there are only 4 ways to have all balls next to each other (do you agree?)

(VV)  $\Delta G = q_p - T\Delta S - w'$  where  $w'$  is non-PV (Pressure x  $\Delta$ Volume) work

$$T\Delta S \geq q_p$$

$$\Delta G \geq w' \Delta G \text{ is the maximum work that can be done}$$

## THIS IS THE STUFF YOU REALLY NEED TO KNOW

### Different forms of energy

Light energy (for  $\lambda$  in nm)

$$\Delta G = Nh\nu = \frac{Nhc}{\lambda} = 28667 \text{ kcal/mol} / \lambda = 1246.4 \text{ eV} / \lambda$$

$$860 \text{ nm} \rightarrow 33.33 \text{ kcal/mol} \rightarrow 1.45 \text{ eV}$$

$$h = 6.6 \times 10^{-27} \text{ erg} \cdot \text{sec}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$1 \text{ erg} = 1.44 \times 10^{13} \text{ kcal/mol}$$

A chemical reaction (see below)

$$\Delta G = \Delta G^\circ + RT \ln [P]/[R]$$

A chemical reaction which involves the transfer of electrons

$$E = E^\circ + RT/nF \ln D_{ox}/D_{red}$$

$$\Delta G^\circ = -nF\Delta E^\circ = -nF\Delta V$$

A concentration gradient across a membrane

$$\Delta G = RT \ln [in]/[out] \quad \text{For any molecule - charged or neutral.}$$

The electrical potential across a membrane given the concentration gradient of ions.

$$\Delta V = \Delta \Psi = RT/F \ln \frac{\sum_{\text{cations}} [\text{conc}]_{out} + \sum_{\text{anions}} [\text{conc}]_{in}}{\sum_{\text{cations}} [\text{conc}]_{in} + \sum_{\text{anions}} [\text{conc}]_{out}}$$

The energy of an ion concentration gradient

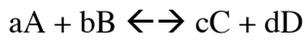
$$\Delta G = RT \ln \frac{[\text{conc}]_{in}}{[\text{conc}]_{out}} + nF\Delta V$$

Mechanical work

$$W = F\Delta s \quad (\text{force} \times \text{displacement in the direction of the force})$$

$$W = \tau\Delta\sigma \quad (\text{torque} \times \text{angular displacement})$$

(CK) For a reaction



$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{ratio of products and reactants at equilibrium}$$

$$K_{eq} = e^{-\Delta G^\circ / RT} = 10^{-\Delta G^\circ / 1.36 \text{kcal / mole}}$$

$$\Delta G^\circ = -(RT) \ln K_{eq} = -(2.303RT) \log K_{eq}$$

$$\Delta G = \Delta G^\circ + (RT) \ln \frac{[\text{products}]}{[\text{reactants}]}$$

$$\Delta G = \Delta G^\circ + (2.303RT) \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$\Delta G = \Delta G^\circ + (1.36 \text{kcal / mole}) \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$\Delta G = \Delta G^\circ + (58 \text{meV}) \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{products}]}{[\text{reactants}]}$$
$$= RT (-\ln K_{eq} + \ln \frac{[\text{products}]}{[\text{reactants}]})$$

**Now at equilibrium**  $[\text{products}]/[\text{reactants}] = K_{eq}$  so **G = 0**

i.e.  $\Delta G = RT (-\ln K_{eq} + \ln \frac{[\text{products}]}{[\text{reactants}]}) = RT (-\ln K_{eq} + \ln K_{eq})$

Two views of  $\Delta G^\circ$ :

(1)  $\Delta G^\circ$  is the energy needed to move the system from equilibrium to the standard state (i.e the energy of the standard state).

The default standard state has all concentrations at 1 (1 Mole/liter; 1 atmosphere are common). The solvent concentration is for the pure liquid. e.g. water will be at 55.5M.

$$\Delta G = \Delta G^\circ + (1.36 \text{ kcal / mol}) \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$= \Delta G^\circ + 1.36 \text{ kcal / mol} \log \frac{[1]}{[1]}$$

$$= \Delta G^\circ + 0$$

However, you can define the standard state in any way that is convenient. (see section on acids and bases for how to define a  $\Delta G^\circ$  at pH 7 as is standard in many biochemistry tables.

(2)  $\Delta G$  at equilibrium is 0; but  $\Delta G^\circ = -1.36 \text{ kcal/mol}(\log K_{eq})$ . Written in this way  $\Delta G^\circ$  tells us about the relative energy of the reactants and products.

$\Delta G^\circ$  is positive if there is more reactant in the mixture at equilibrium and negative if there more product.

If a reaction has a positive  $\Delta G^\circ$  for  $A \rightarrow B$  then it has a negative  $\Delta G^\circ$  for  $B \rightarrow A$ .

If

$K_{eq} = 0.01$	$\Delta G^\circ = 2 * 1.36 \text{ kcal/mol} = 2 * 58 \text{ eV}$
$K_{eq} = 0.1$	$\Delta G^\circ = 1.36 \text{ kcal/mol} = 58 \text{ eV}$
$K_{eq} = 1$	$\Delta G^\circ = 0$
$K_{eq} = 10$	$\Delta G^\circ = -1.36 \text{ kcal/mol} = -58 \text{ eV}$
$K_{eq} = 100$	$\Delta G^\circ = -2 * 1.36 \text{ kcal/mol} = -2 * 58 \text{ eV}$

If  $\Delta G^\circ = 2.72 \text{ kcal/mol}$  then at equilibrium  $[\text{reactants}] = 0.01 * [\text{products}]$

If  $\Delta G^\circ = 1.36 \text{ kcal/mol}$  then at equilibrium  $[\text{reactants}] = 0.1 * [\text{products}]$

If  $\Delta G^\circ = 0 \text{ kcal/mol}$  then at equilibrium  $[\text{reactants}] = [\text{products}]$

If  $\Delta G^\circ = -1.36 \text{ kcal/mol}$  then at equilibrium  $[\text{reactants}] = 10 * [\text{products}]$

If  $\Delta G^\circ = -2.72 \text{ kcal/mol}$  then at equilibrium  $[\text{reactants}] = 100 * [\text{products}]$

For example  $\text{ADP} + \text{P}_i = \text{ATP}$   $K_{\text{eq}}=10^{-5}$  at pH 7.0

This means

1) The standard free energy of this reaction is:

$$\Delta G^\circ = (-1.36 \text{ kcal/mol}) \log K_{\text{eq}} = (-1.36 \text{ kcal/mol}) \log 10^{-5} = 6.8 \text{ kcal/mol}$$

The free energy ( $\Delta G$ ) is 0 when  $[\text{P}]/[\text{R}]=10^{-5}$

$$\Delta G = 6.8 + 1.36 \log 10^{-5} = 0 \text{ kcal/mol}$$

2) If you had 1M of ADP and 1M of  $\text{P}_i$  and 1M of ATP at pH 7 the system would be out of equilibrium. The free energy available to do work is:

$$\Delta G = \Delta G^\circ + (1.36 \text{ kcal/mol}) \log [1]/[1][1] = + 6.8 \text{ kcal/mol}$$

3) If you have  $10^{-2}\text{M}$   $\text{P}_i$  the equilibrium ratio of  $\text{ATP}/\text{ADP} = 10^{-7}$  since

$$K_{\text{eq}}=10^{-5} = \text{ATP}/(\text{ADP} * \text{P}_i)$$

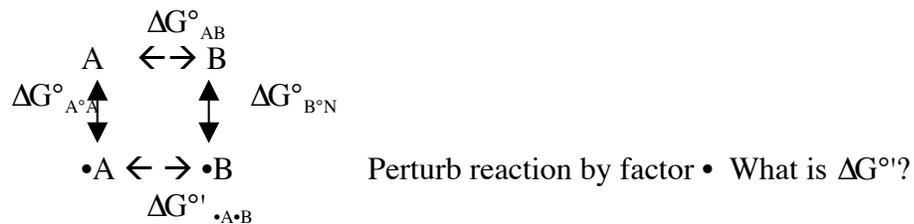
4) However,  $\text{ATP}/\text{ADP} = 10^3$  in the cell. How much work must be done to achieve this concentration ratio (if there is  $10^{-2}\text{M}$   $\text{P}_i$ )?

$$\begin{aligned} \Delta G &= \Delta G^\circ + (1.36 \text{ kcal/mol}) \log [\text{ATP}]/[\text{ADP}][\text{P}_i] \\ &= 6.8 \text{ kcal/mol} + 1.36 \log [10^3]/10^{-2} = 13.6 \text{ kcal/mol} \end{aligned}$$

We will discuss how the cell finds the energy to maintain this condition so far out of equilibrium when we learn about how the ATPase protein works.

The thermodynamic box.

Suppose I have a reaction that



If  $A \leftrightarrow \bullet A$  is changed by  $A$  kcal/mol =  $\Delta G^{\circ}_A$

If  $B \leftrightarrow \bullet B$  is changed by  $B$  kcal/mol =  $\Delta G^{\circ}_B$

$$\Delta G^{\circ'} = \Delta G^{\circ} - \Delta G^{\circ}_A + \Delta G^{\circ}_B$$

This comes from the assumption that the free energy moving around the box eg from A back to A has to be zero.

So if A is stabilized by  $\bullet$  by a smaller amount than B is then  $\Delta G^{\circ'}$  is more negative than  $\Delta G^{\circ}$

Remember the  $\Delta G^{\circ}_{AB}$  for  $A \rightarrow B$  is equal to  $-\Delta G^{\circ}_{BA}$  for  $B \rightarrow A$