

Simple Calculations in Bioenergetics

*(Ian West's footnotes to Keith
Garlid's lecture course
22 April 2004)*

Peter Dennis Mitchell -- 1978



Glynn House from the south east - 1987



Glynn House from the west - 1987



The Glynn team in 1978

Roy Mitchell, Alan Jeal, Robert Harper, Stephanie Key, ? Jennifer Moyle, PDM



The Glynn team 1987



Energy units and conversion factors

$$F = 96,485 \text{ Coulomb/equiv}$$

$$R = 8.314 \text{ Joules/deg}$$

$$1 \text{ calorie} = 4.184 \text{ Joule}$$

$$\text{Log}_e x (= \text{Ln } x) = 2.303 \text{ Log}_{10} x$$

(Ln 10 = 2.303)

$$RT/F = 25.688 \text{ at } 25^\circ \text{ C } (298.14^\circ \text{ K})$$

$$2.303 RT/F = 59.15 \text{ at } 25^\circ \text{ C}$$

$$C = A \text{ s}$$
$$\text{volt} = \text{J/C}$$

Energy units and conversion factors

$$F = 96,485 \text{ Coulomb/equiv}$$

$$R = 8.314 \text{ Joules/deg}$$

$$1 \text{ calorie} = 4.184 \text{ Joule}$$

$$\text{Log}_e x (= \text{Ln } x) = 2.303 \text{ Log}_{10} x$$

(Ln 10 = 2.303)

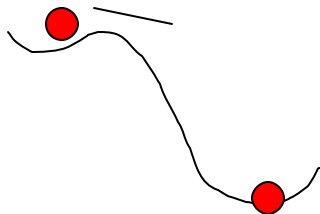
$$RT/F = 25.688 \text{ at } 25^\circ \text{ C } (298.14^\circ \text{ K})$$

$$2.303 RT/F = 59.15 \text{ at } 25^\circ \text{ C}$$

$$\text{C} = \text{A s}$$
$$\text{volt} = \text{J/C}$$

Energy and Free Energy

- Energy, same units as work (e.g. force x distance)
unit = Joule,
dimensional units = $\text{kg m}^2 \text{s}^{-2}$
- Gibbs' Free energy (G) = ? $H - T ? S$
- ? G (in going from state 1 to state 2) is
 - the work done **on** the system,
 - the (free) energy gained **by** the system,
 - maximum work that could be got from the system if you went **reversibly** back from state 2 to state 1
 - is **positive** if positive work is done **on** the system and the system **gains Energy**
 - is negative if the system loses free energy and “falls” into an “energy well”



Work



Units = $\text{kg m}^2 \text{s}^{-2}$

E.g.

Force (kg m s^{-2}) . ? **distance** (m)

Pressure ($\text{kg m}^{-1} \text{s}^{-2}$) . ? **volume** (m^3)

volt ($\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$). ? **Coulomb** (A s)

? **volt** ($\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$). **Coulomb** (A s)

In general it is the product of an

Intensive quantity and an *Extensive* one

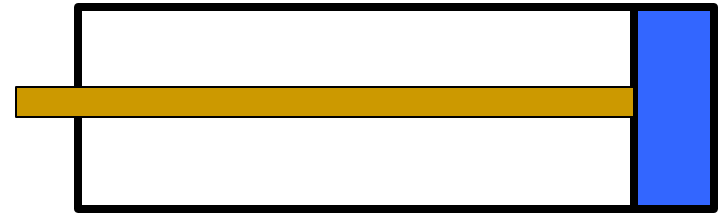
Simple examples of work -- P ? V

State 1



$$P_1 V_1$$

State 2



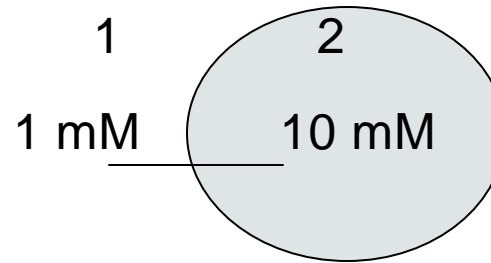
$$P_2 V_2$$

$$P = nRT/V$$

$$\begin{aligned} \text{Work done on the system} &= - \int_1^2 P dV = - \int_1^2 nRT dV/V = -nRT \int_1^2 dV/V \\ &= -(nRT \ln V_2 - nRT \ln V_1) \\ &= (nRT \ln c_2 - nRT \ln c_1) \\ &= RT \ln (c_2/c_1) \text{ per mol} \end{aligned}$$

$$\text{So, } \Delta G_{1 \rightarrow 2} = 2.303 RT \log (c_2/c_1) \text{ per mol} \text{ ----- (1)}$$

What then is the work done on the system (at 25 °C) when ?



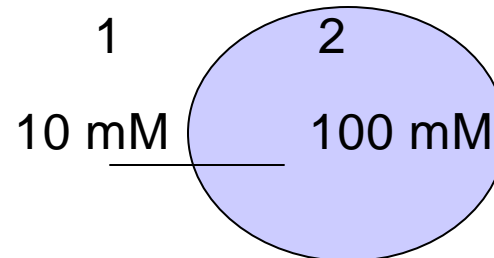
we transfer 1 mole of sucrose from 1 mM to 10 mM

”

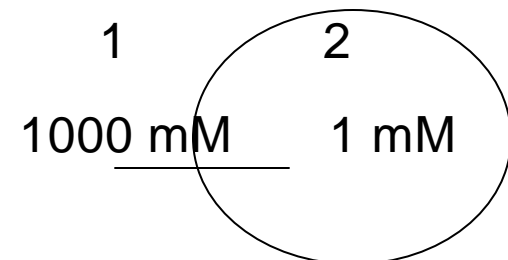
”

”

10 mM to 100 mM



we transfer 1 mole of X from 1000 mM to 1 mM

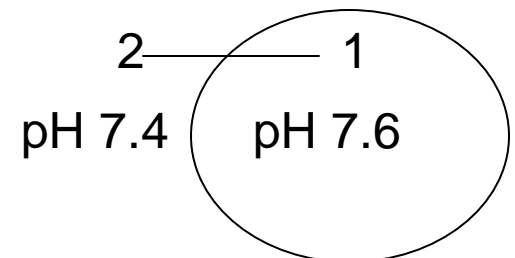


? $G_1?_2 = 2.303 RT \text{ Log } (c_2/c_1)$ per mol
 $2.303 RT = 5708 \text{ J/mol}$
 $R = 8.314 \text{ Joules/deg}$
 $F = 96,485 \text{ Coulomb/equiv}$
 $2.303 RT/F = 59.15 \text{ at } 25^\circ \text{ C } (298.14^\circ \text{ K})$

What is the work done on the system (at 25 °C) when, in the absence of ???

1. We transfer 1 mole of H^+ from pH 8 to pH 7
2. We transfer 1 mole of H^+ from pH 8.5 to pH 7.5
3. We transfer 1 mole of H^+ from pH 7.5 to pH 1.5
(as does the acid pump in the stomach)
4. We transfer 1 mole of H^+ from mitochondrial matrix (pH 7.6) to cytoplasm (pH 7.4)

(Note that $\text{Log } 2$ is 0.3010; we are doubling the $[H^+]$)

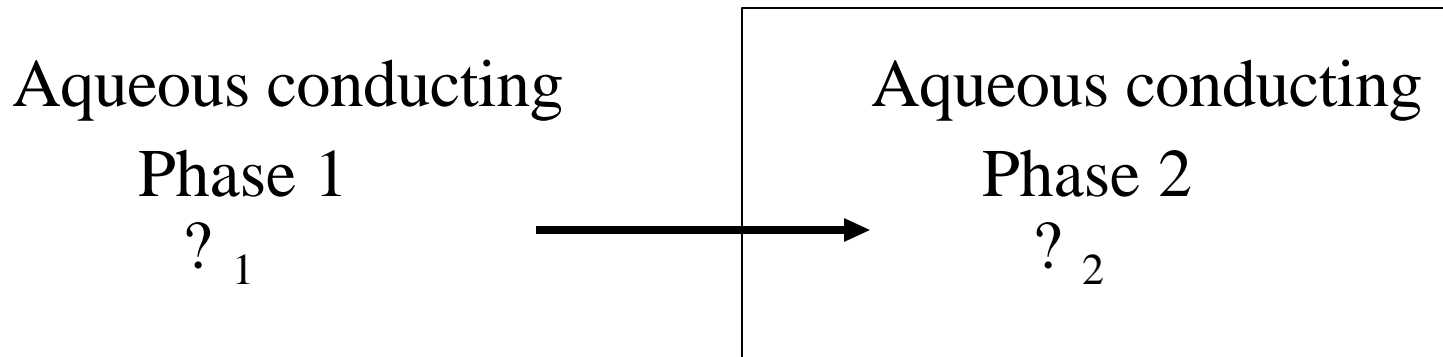


Simple examples of work – ‘charge’ . ??

Work done = **Coulomb** (A s) . ? **volt** (kg m² s⁻³ A⁻¹)

If we count the charges in equivalents or moles instead of coulombs we get more joules as there are 96,485 C/Equiv

If our ion has valency z then a mol carries zF coulomb

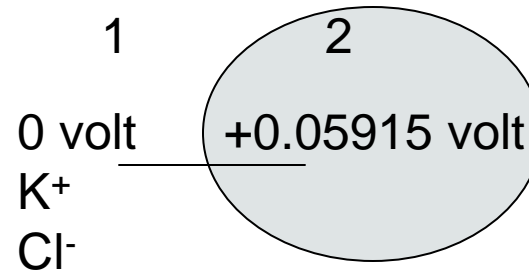


Work done on (gained by) the system--

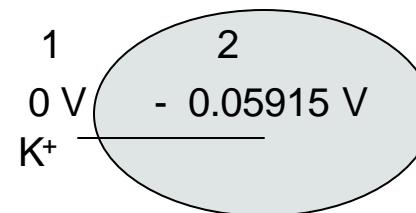
$$? G_{1? 2} = zF?? = zF (?_2 - ?_1) \text{ -----(2)}$$

What is the electrical work done on the system when
(at 25 °C – but it does not matter) --

$F = 96,485$ Coulomb/equiv
 $R = 8.314$ Joules/deg
 $2.303 RT/F = 0.05915$ at 25 °C (298.14 °K)



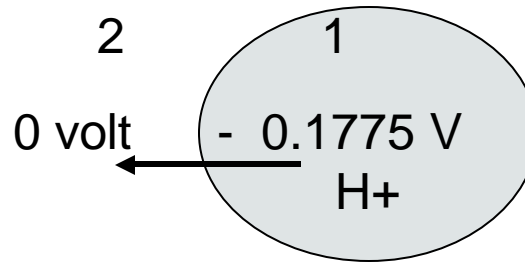
- we transfer 1 mole of K⁺ from phase 1 (at 0 volts – reference phase) to phase 2 at + 0.05915 volts (59.15 mV) ?
- we transfer 1 mole of Cl⁻ from phase 1 (at 0 volts) to phase 2 at + 0.05915 V?



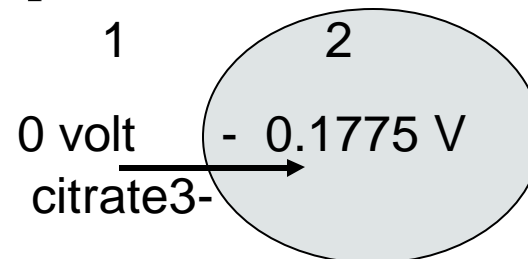
- we transfer 1 mole of K⁺ from phase 1 (at 0 volts) to cytoplasm at - 59.15 mV?

What now is the electrical work done on the system when --

$F = 96,485$ Coulomb/equiv
 $R = 8.314$ Joules/deg
 $2.303 RT/F = 0.05915$ at 25°C (298.14°K)



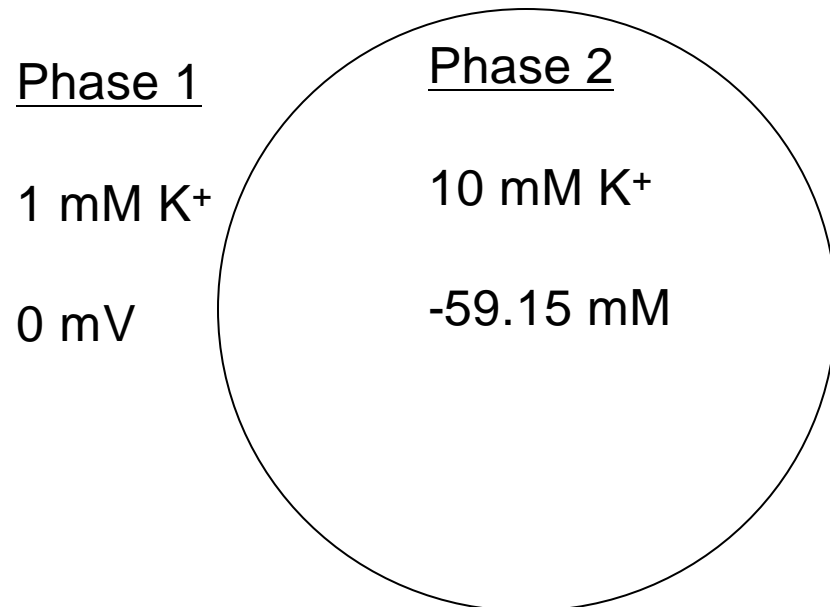
- we pump 1 mole of H^+ from matrix at -177.5 mV to the cytoplasm at 0 mV (reference phase) (noting that $177.5 = 3 \times 59.15$) ?
- we similarly pump 10 mole of H^+ ?
- we pump 1 mole of Ca^{2+} from matrix at -177.5 mV to the cytoplasm (at 0 mV)?
- we transfer 1 mole of citrate^{3-} from cytoplasm to matrix at -177.5 mV



What if work is done against concentration (osmotic) forces and electrical forces..

We simply add the work terms together.

Consider the work done in transferring 1 mol of K^+ at $25^\circ C$ as in the picture.



$F = 96,485$ Coulomb/equiv
 $R = 8.314$ Joules/deg
 $2.303 RT/F = 0.05915$ at $25^\circ C$ ($298.14^\circ K$)

When work is done against concentration (osmotic) forces and electrical forces.

We simply add the work terms together. So let us

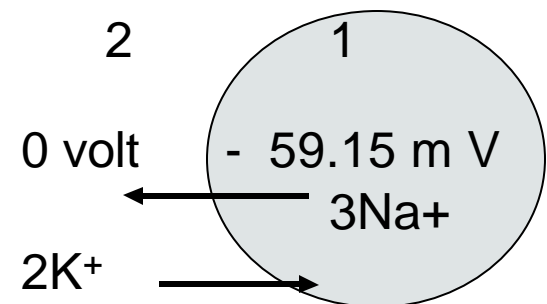
-- calculate the pumping work done by the Na^+/K^+

ATPase supposing it transfers 2 mol K^+ from plasma (5 mM) to cytoplasm (140 mM) and 3 mol Na^+ from cytoplasm (14 mM) to plasma (140 mM) against a membrane potential of - 59.15 mV.

$$F = 96,485 \text{ Coulomb/equiv}$$

$$R = 8.314 \text{ Joules/deg}$$

$$2.303 RT/F = 0.05915 \text{ at } 25^\circ \text{ C } (298.14^\circ \text{ K})$$





Chemical Work

Suppose B? A reaction occurs spontaneously. (? G negative)

Therefore A? B obviously requires work (? G positive)

How much work?

Note [a] it is a characteristic of the reaction, and [b] it depends on concentration of A and B

So lets talk about *standard* ? G^o when substrates are at *standard* concentrations (1 molar; except for 1 atmos for gasses, 55 M for water, 10⁻⁷M for H⁺). In that case:-

$$\Delta G = \Delta G^{\circ}$$

But if A=0.1 M, and B=10 M, we must do extra work on A and B

$$\Delta G = \Delta G^{\circ} + 2.3 RT \log 1/[A] + 2.3 RT \log [B]$$

$$\Delta G = \Delta G^{\circ} + 2.3 RT \log 1/0.1 + 2.3 RT \log 10$$

$$\Delta G = \Delta G^{\circ} + 2.3 RT \log [B] / [A]$$

Chemical Work (continued)

More generally, for $aA + bB \rightarrow cC + dD$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Let us try to calculate the ΔG per mole for ATP synthesis in the cytoplasm supposing $\Delta G^{\circ'} = + 30,600$ Joules / mol; $[ADP] = 0.1\text{mM}$, $[P_i] = 0.1\text{mM}$, $[ATP] = 5 \text{ mM}$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Chemical Work (continued)

More generally, for $aA + bB \rightarrow cC + dD$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Let us try to calculate the ΔG per mole for ATP synthesis in the cytoplasm supposing $\Delta G^{\circ'} = + 30,600$ Joules / mol; $[ADP] = 0.1\text{mM}$, $[P_i] = 0.1\text{mM}$, $[ATP] = 5 \text{ mM}$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log \left(\frac{[ATP]}{[ADP][P_i]} \right)$$

$$\Delta G = \Delta G^{\circ'} + 2.3 RT \log (0.005/0.0001 \times 0.0001)$$

Chemical Work (continued)

More generally, for $aA + bB \rightarrow cC + dD$

$$\Delta G = \Delta G^\circ + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Let us try to calculate the ΔG per mole for ATP synthesis in the cytoplasm supposing $\Delta G^\circ = +30,600$ Joules / mol; $[ADP] = 0.1$ mM, $[P_i] = 0.1$ mM, $[ATP] = 5$ mM; $T = 25$ °C

$$\Delta G = \Delta G^\circ + 2.3 RT \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right) \qquad \Delta G =$$

$$\Delta G^\circ + 2.3 RT \log \left(\frac{[ATP]}{[ADP][P_i]} \right)$$

$$\Delta G = \Delta G^\circ + 2.3 RT \log (0.005 / 0.0001 \times 0.0001)$$

As $\log 2 = 0.3010$; $\log 5$ must be 0.6990 ; and $\log 5 \times 10^5 = 5.699$

$$\Delta G = +30,600 + 32,530 = 63,130 \text{ Joules per mol}$$

So; can 3 H⁺ make 1 ATP? or do we need 4 H⁺/ATP ?