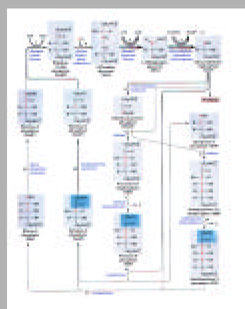
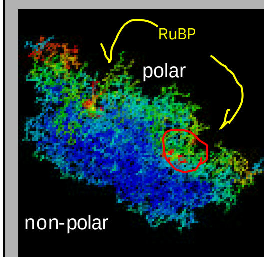
14: Calvin-Benson Cycle



Rubisco



- Photosynthesis: fixation of carbon using metabolic energy derived from photons
  - Light reactions: conversion of photons to ATP and NADPH equivalents
  - Dark reactions: direct incorporation of CO2 into carbonyl groups to make new sugar molecules (RuBP → 2GAP)

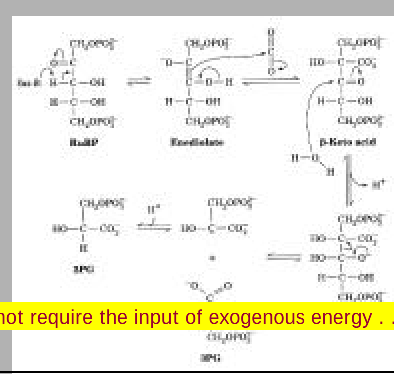
Rubisco reaction does not require the participation of any high-energy reactants

So why the dependence between light and dark reactions?

Light Reactions

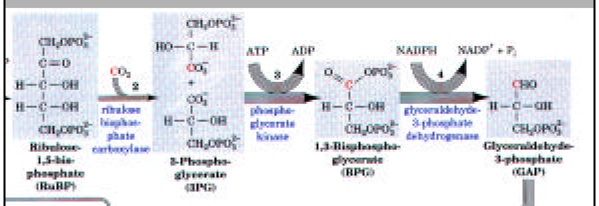
- PSI & PSII: 4e- excited by 8 photons
- $4Fd^- + 2NADP^+ + 2H^+ \rightarrow 4Fd + 2NADPH$
  - FNR requires FAD^+, which has a $\mathbf{E}^{o'} \sim 0.0V$
- Reaction Equivalents:
  - Oxidation of water by the OEC generates 4 H^+ in the interior for every 4 e- removed to $P680^+$.
  - Q-cycle transports 8 H^+ with those 4 e-
- ATP synthase stoichiometry:
  - 3 H^+ translocated to exterior per ADP → ATP
  - So 12 H^+ interior will yield 4 ATP
- NADPH has the energy equivalents of 3 ATP
- **TOTAL ENERGY YIELD: 10 ATP per $8h\nu$**
  - **4 ATP & 2 NADPH per $8h\nu$**

Dark Reactions: CO_2 fixation

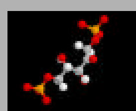


Does not require the input of exogenous energy . . . Why?

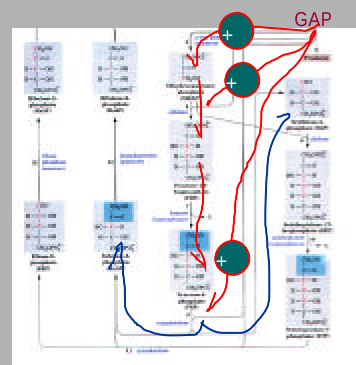
Calvin-Benson: Reaction Series 1



- Cummulative $\Delta G^{o'}$ = -17.1 kJ mol^{-1}

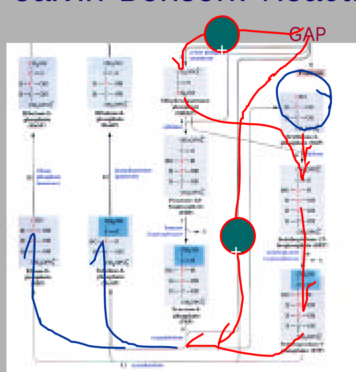


Calvin-Benson: Reaction Series 2



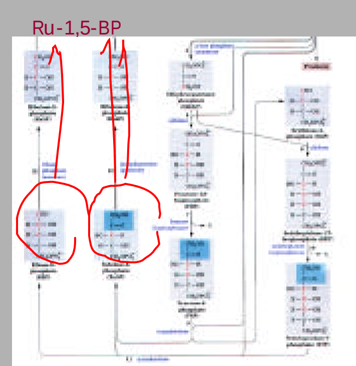
- C3 + C3 --> C6
- C6 + C3 --> C9
- C9 --> C4 + C5
- Σ $\Delta G^{o'}$
- -37.2 kJ mol^{-1}

Calvin-Benson: Reaction Series 3



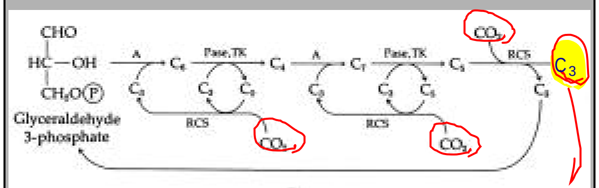
- C3 + C4 --> C7
- C7 + C3 --> C10
- C10 --> C5 + C5
- Σ $\Delta G^{o'}$
- -43.1 kJ mol^{-1}

Calvin-Benson: Reaction Series 4



- Regenerate the initial reactant:
- Ru-1,5-BP
- Σ $\Delta G^{o'}$
- -18.1 kJ mol^{-1}

Calvin-Benson: Summary



GAP

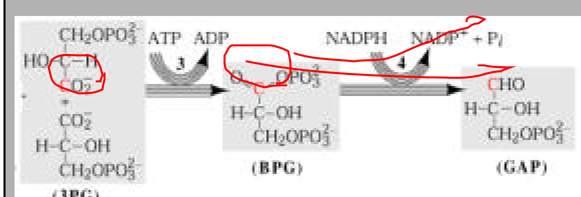
- Functions as a network of reactions rather than a pathway of reactions.

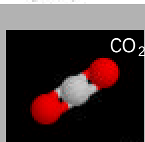
Summary Reaction

- Start: $3\ CO2 + 9\ ATP + 6\ NADPH$
- Finish: $GAP + 9\ ADP + 6\ NADP^+ + 8\ P_i$

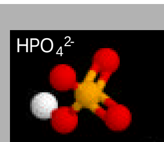
$9\ PO_3^{2-} = 1\ PO_3^-$ (in GAP) $+ 8\ H_2PO_4^-$

Carbonyl Electrons

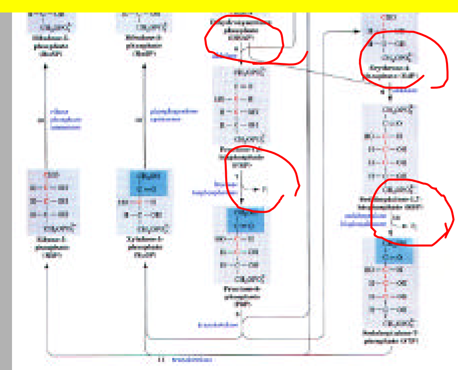




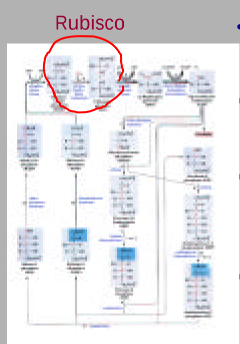
Each dephosphorylation results in the loss of electron energy associated with the carbonyl group oxygen



Why the negative ΔGs?



Calvin-Benson: Biosynthesis

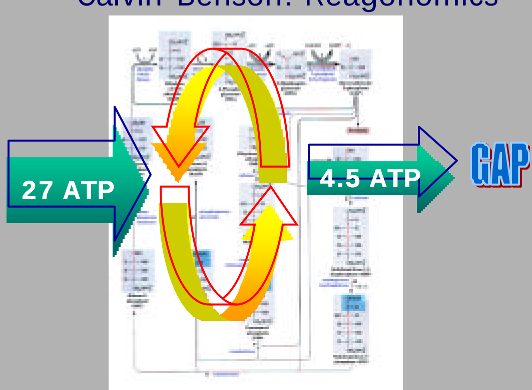


- Calvin Benson Cycle requires a high energy input because it is a biosynthetic (anabolic) pathway
- 90% of the energy input into the cycle is for the conversion of 3PG to GAP
- Yet only 16% of the total energy input will be exported as biosynthetic building blocks (GAP)
- What's wrong with this picture?

Notes:

- Why not fix CO_2 into 3PG and then shunt it into glycolysis? Why invest so much energy into producing GAP?
  - The energy investment in GAP is to regenerate the reaction constituents. Only 16% of the energy input goes into GAP export; the rest serves to reconstruct the RuBP substrate. If 3PG was catabolized in glycolysis, the dark reactions would not be cyclical.

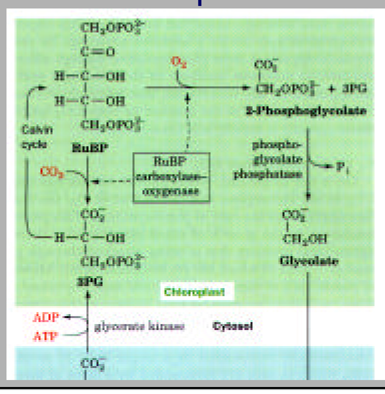
Calvin-Benson: Reagonomics



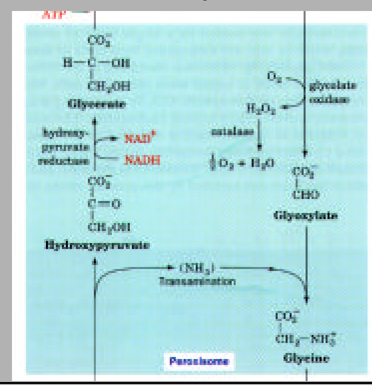
Photorespiration

- The CB Cycle requires a large input of energy
- Rubisco is not 100% at selecting CO_2 from O_2
- The incorporation of O_2 imposes additional energy costs on the cycle
- It's a metabolite recycling cost that requires a decarboxylation event
- For terrestrial organisms, the problem is severe:
  - $[CO_2]$ in air=0.035% $[O_2]$ in air=21%
- For aquatic organisms,
  - the ratio $pCO_2:pO_2$ is 1/24.

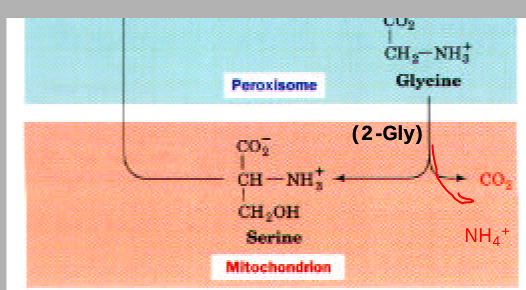
Photorespiration:1



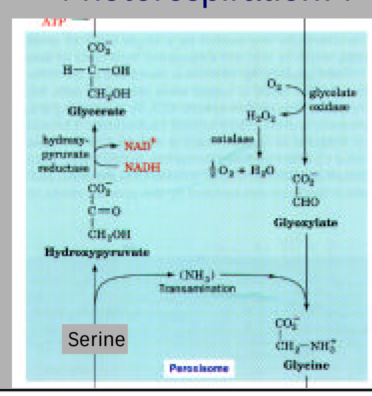
Photorespiration:2



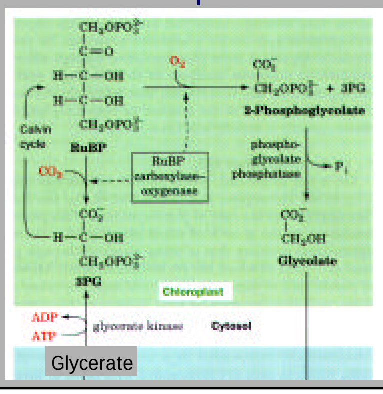
Photorespiration:3



Photorespiration:4



Photorespiration:5



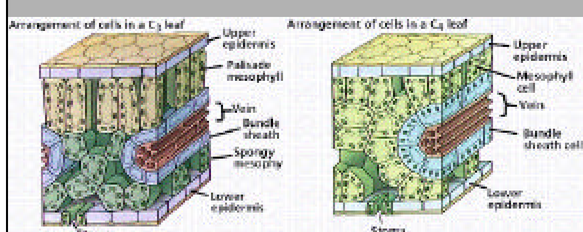
Photorespiration:

- In addition to the low efficiency of energy output by the Calvin-Benson cycle, the less than ideal specificity of Rubisco for CO_2 means that for every O_2 it incorporates, yet an additional 4 ATP have to be spent in recycling the glyoxylate to 3PG.
- PLUS another 12 ATP equivalents are lost during the decarboxylation of a CO_2 that had been previously fixed

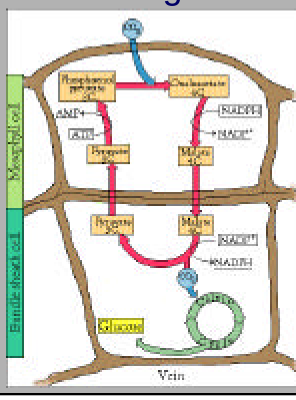
C3 and C4

- BUT, apparently in the plant kingdom, photosynthetic efficiencies using 3-carbon sugars just aren't low enough, so some plants expend even more energy using a 4-carbon intermediate pathway.

C3 and C4 plants

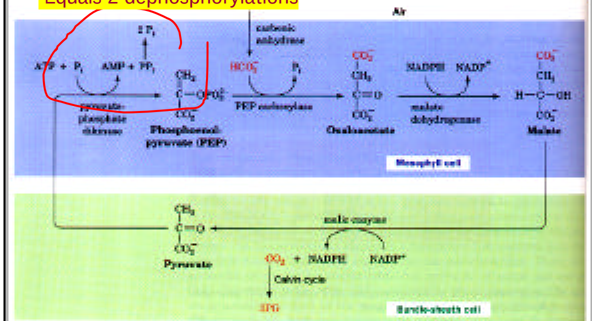


C4 Diagram



C4 Pathway: Hatch-Slack

Equals 2 dephosphorylations

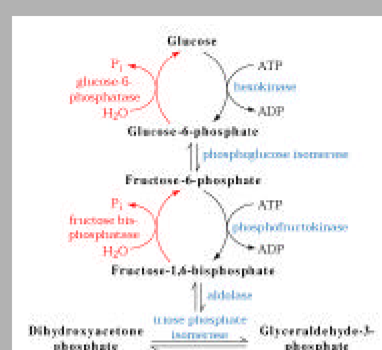


For every CO2 fixed, an additional 2 ATP are required

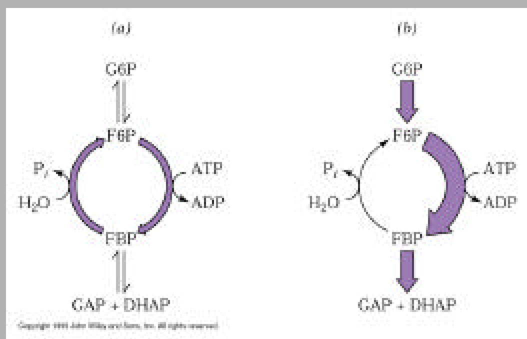
Photosynthetic Energy Balance

- **PSI & PSII:**
  - TOTAL ENERGY YIELD: 10 ATP per 8hn
- **It takes 27 ATP equivalents to turn the CB cycle.**
- **24 photons to generate 1 GAP for use in biosynthetic activities**

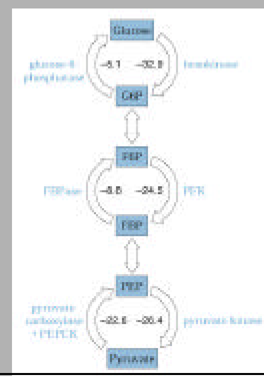
Gluconeogenesis



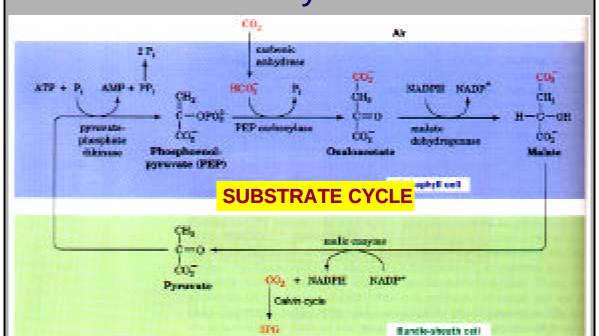
Substrate Cycle



Glycolytic Substrate Cycles



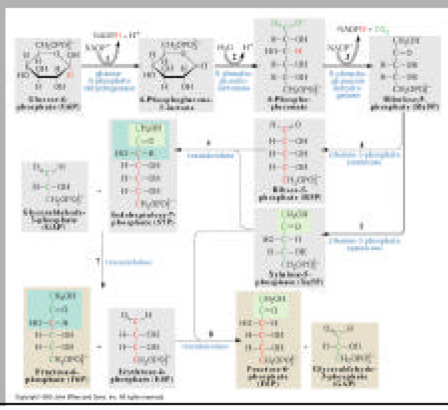
C4 Cycle



Pentose Phosphate Pathway

- NADPH is used for reductive biosynthesis
  - Fatty acid synthesis
- NADH use primarily for oxidative phosphorylation
  - ATP synthesis
- Intracellular concentrations:
  - [NAD+]/[NADH] = 1000; favors metabolite oxidation
  - [NADP+]/[NADPH] = 0.01; favors synthetic reduction
- Similar metabolic landscape as in the CB cycle

Hexose Monophosphate Shunt



Summary Equation

$3G6P + 6NADP^+ + 3H_2O$

$\Downarrow$

$6NADPH + 6H^+ + 3CO_2 + 2F6P + GAP$

Summary Equation

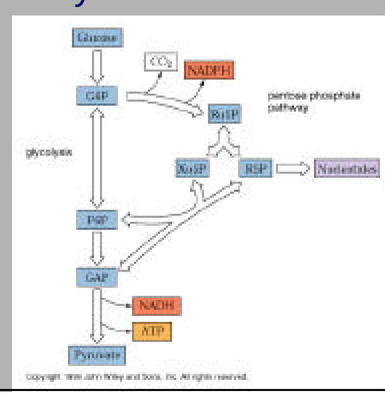
$3G6P + 6NADP^+ + 3H_2O \rightarrow 6NADPH + 6H^+ + 3CO_2 + 2F6P + GAP$

6NADH + 6ATP

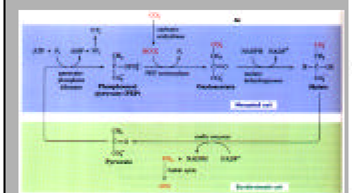
5NADH + 5ATP

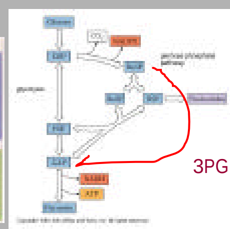
Difference is in the complete oxidation of carbon to CO_2

PPP synthesis of nucleotides



Early metabolic scheme ??





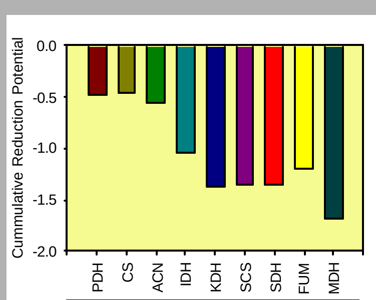
Carbon Cycle Summary

Why is CO_2 so chemically important ?

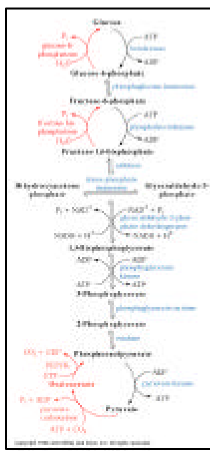
$ACOA + 3NAD^{+} + GDP/P_i + 2H_2O \rightarrow 2CO_2 + 3NADH/H^{+} + GTP$

- Summary equation is the same from any starting point in the cycle (which is why it is a cycle).
- The TCA cycle is a series of energy transfer reactions.
- The primary chemical modification is the conversion of
  $CH_3CH{=}0 + H_20 \rightarrow 2CO_2$
- Essentially this could be called the carbonyl cycle because of the importance of this carbon group in determining the overall energetics of the chemical reactions.

Net change in reduction potential



- Total drop in reduction potential through the TCA cycle is –1.1 V (equivalent to photosystem *e-* transfers)



Gluconeogenesis

Why can't glycolysis
Be reversed to fix CO2?

Reductive TCA cycle ???

C=O bond has high *e*- energy

- In a sense, the forward direction of the TCA cycle is an electron transfer scheme in which the carbonyl group provides the 'electron-excitation' event to influence chemical interactions.
  - Destabilizing force for bond reformation
- The reverse direction, would require a significant level of energy input to overcome the necessary +1.1 V change in reduction potentials.
- In metabolism, C-C bonds can rarely be broken without the direct participation of an adjoining carbonyl group.
- Ex: Glutaraldehyde $CH_3CH=0$; Formaldehyde $H_2C=O$.