The Chloroplast Electron Transport Chain

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Contents

Note: this is the Chloroplast.ipynb notebook. The PDF version "The Chloroplast Electron Transport Chain" is available here.

This is a work in progress and needs more explanatory notes.

```
In [1]: ## Some useful imports
        import BondGraphTools as bgt
        import numpy as np
        import sympy as sp
        import matplotlib.pyplot as plt

        ## For reimporting: use imp.reload(module)
        import importlib as imp

        ## Stoichioometric analysis
        import stoich as st
        ##import hstoich as hst

        ## SVG
        import svgBondGraph as sbg

        ## Display (eg disp.SVG(), disp.
        import IPython.display as disp

        ## Data
        import phiData
        import redoxData
```

1 Introduction

Photosynthesis within plant chloroplasts is the basis of life on earth (Blankenship, 2015), (Nicholls and Ferguson, 2013).

Like the mitochondrion, the chloroplast has a membrane seperating an inner space (lumen) from an outer space (stroma). In the chloroplast, the lumen gains protons and is called the p-space, the stroma looses protons and is called the n-space. Thus geometrically, the lumen corresponds to the mitochondrial matrix and the stroma to the mitochondrial intermembrane space; but electrically the p-space is inside and the n-space outside - the reverse of the mitochondrial situation.

The chloroplast electron transport chain has 4 complexes.

1. Photosystem II (PII) which absorbs photons at 680nm and splits water releasing protons into the p-space and passing electrons to the plastoquinone(PQ)/plastoquine(PQH2) couple which absorbs protons from the n-space.

2. Cytochrome bf (Cyt) which passes electrons to the plastoquine/plastoquinone couple which releases two protons into the p-space. Electrons are passed to the plastocyanine couple (PcOx/PcRed). Two protons are pumped across the membrane.

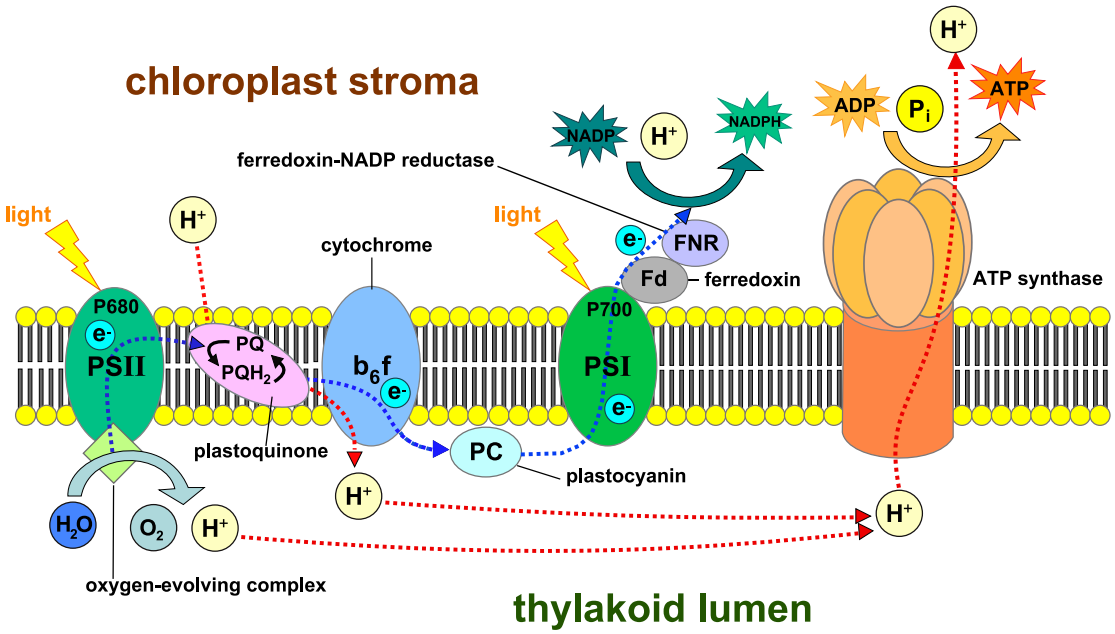
3. Photosystem I (PI) which absorbs photons at 700nm and transports electrons from the plastocyanine (PcRed/PcOx) couple to the ferredoxin (FdOx/FdRed) couple.

4. Feredoxin-NADP reductase which transfers electrons from the ferredoxin (FdRed/FdOx) couple to convert NADP to NADPH absorbing a proton from the n-space.

The following figure is: https://commons.wikimedia.org/wiki/File:Thylakoid_membrane_3.svg

In [2]:
```
# https://commons.wikimedia.org/wiki/File:Thylakoid_membrane_3.svg
disp.SVG("Thylakoid_membrane_3.svg")
```

Out[2]:



2 Photon Energetics

$$\phi_{photon} = \frac{N_{av} h c}{F \lambda} \tag{1}$$

$$\text{where } N_{av} = \text{Avogadro's number} \tag{2}$$

$$h = \text{Planck's constant} \tag{3}$$

$$c = \text{velocity of light} \tag{4}$$

$$F = \text{Faraday's constant} \tag{5}$$

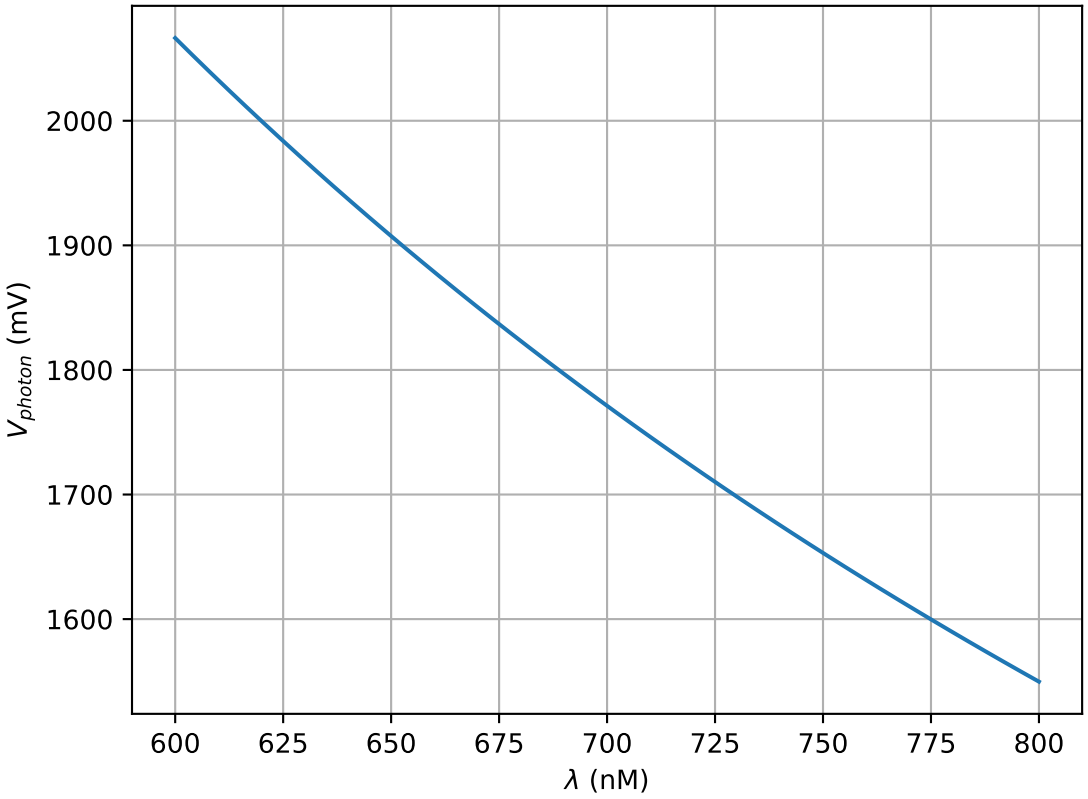
$$\text{and } \lambda = \text{wavelength} \tag{6}$$

For example:

$$\phi_{photon} = \begin{cases} 1.82V & \lambda = 680nm \\ 1.77V & \lambda = 700nm \end{cases} \tag{7}$$

In [3]: disp.SVG('V_photon.svg')

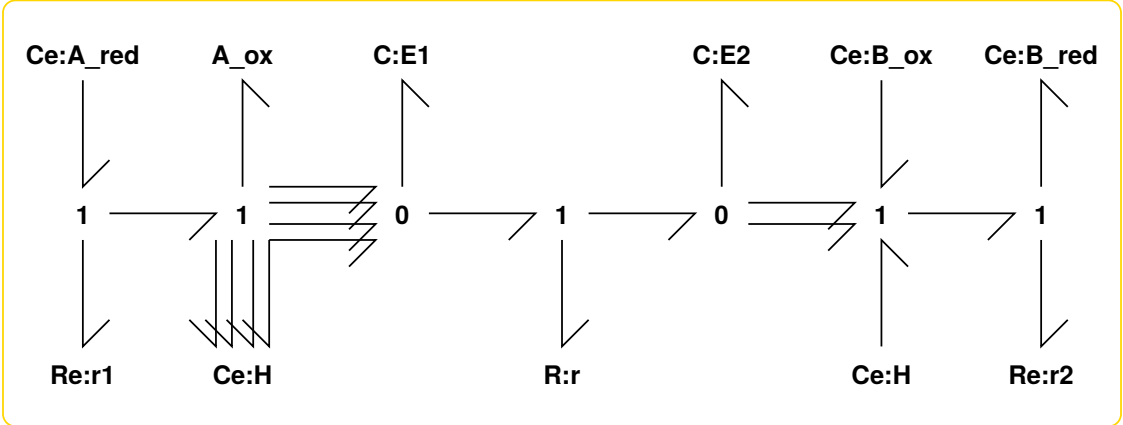
Out[3]:



3 Redox reactions

In [4]: disp.SVG('Redox_abg.svg')

Out[4]:



Redox reactions can be written as two half-reactions:

$$A_{red} \overset{r_1}{\rightleftharpoons} n_1 e_1^- + m_1 H_1^+ + A_{ox} \tag{8}$$

$$B_{ox} + n_2 e_2^- + m_2 H_2^+ \overset{r_2}{\rightleftharpoons} B_{red} \tag{9}$$

3.1 Redox potentials

Note that photon energies have been used for V_700 and V_680; this value is too large as the energy conversion is not direct. A model of this needs to be built. See, for example: (Blankenship and Prince, 1985)

```
In [5]: import redoxData
        imp.reload(redoxData)
        ## pH from BerTymStr 19.3
        pH_p = 4 # pH of p-space
        pH_n = pH_p + 3
        VpH = redoxData.VpH(pH_p - pH_n)
        V680 = redoxData.V_photon(wavelength=680)
        V700 = redoxData.V_photon(wavelength=700)
        print(VpH)
        print('V_pH =',int(1000*VpH),'mV')
        print('V_680 =',int(1000*V680),'mV')
        print('V_700 =',int(1000*V700),'mV')
```

```
0.18462115653058278
V_pH = 184 mV
V_680 = 1823 mV
V_700 = 1771 mV
```

```
In [6]: ## Convert redox potentials to species phi
        imp.reload(redoxData)
        phi_redox = redoxData.phi()
        phi_redox['Hn'] = redoxData.VpH(pH_n)
        phi_redox['Hp'] = redoxData.VpH(pH_p)

        ## The correct photon potentials need sorting out
        ## The raw valyes used here are an overestimate. See BlaPri85
        phi_redox['P680'] = V680
        phi_redox['P700'] = V700
        #phi_redox['P680'] = phi_redox['P680+']
        #phi_redox['P700'] = phi_redox['P700+']

        ## The membrane potential is said by some to be zero. (check this)
        phi_redox['dV'] = VpH
```

4 Bond graph description

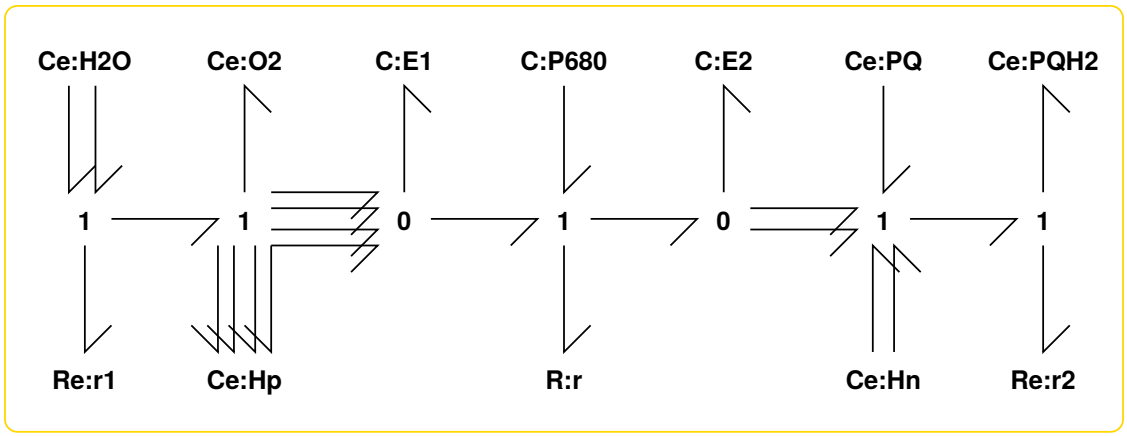
The four complexes are represented by svg graphics which are automatically converted into BondGraphTools format.

The stoichiometric toolbox is then used to generate the pathway-reduced equation for the complex.

4.1 Complex PII -- Photosystem II

In [7]:
```
disp.SVG('PII_abg.svg')
```

Out[7]:



In [8]:
```
imp.reload(sbg)
sbg.model('PII_abg.svg',convertR=True,convertCe=True,quiet=True)
import PII_abg
```

In [9]:
```
## Stoichiometry
imp.reload(st)
sPII = st.stoich(PII_abg.model(),quiet=True)
chemostats = ['H2O','O2','PQ','PQH2','Hn','Hp','P680']
scPII = st.statify(sPII,chemostats=chemostats)
spPII = st.path(sPII,scPII)
## All reactions
disp.Latex(st.sprintrl(sPII,chemformula=True))
```

Out[9]:

$$E_1 + P_{680} \overset{r}{\rightleftharpoons} E_2 \tag{10}$$

$$2\,H_2O \overset{r_1}{\rightleftharpoons} 4\,E_1 + 4\,Hp + O_2 \tag{11}$$

$$2\,E_2 + 2\,Hn + PQ \overset{r_2}{\rightleftharpoons} PQH_2 \tag{12}$$

In [10]:
```
## Pathway reaction
disp.Latex(st.sprintrl(spPII,chemformula=True))
```

Out[10]:

$$4\,P_{680} + 2\,H_2O + 4\,Hn + 2\,PQ \xrightleftharpoons{pr_1} 4\,Hp + O_2 + 2\,PQH_2 \tag{13}$$

In [11]:
```
## Compute net redox potential
RP_PII = (
            - redoxData.EpH('O2/2H2O',pH=pH_p)
            + V680
            + redoxData.EpH('PQ/PQH2',pH=pH_n)
          )

print(redoxData.EpH('O2/2H2O',pH=pH_p))
print(redoxData.E('P680+/P680*'))
print(redoxData.E7('PQ/PQH2'))
print(redoxData.EpH('PQ/PQH2',pH=pH_n))
#print(RP_PII)
print('RP_PII =',int(1000*RP_PII), 'mV')
```

```
1.0006211565305827
0.8
0
0.0
RP_PII = 822 mV
```

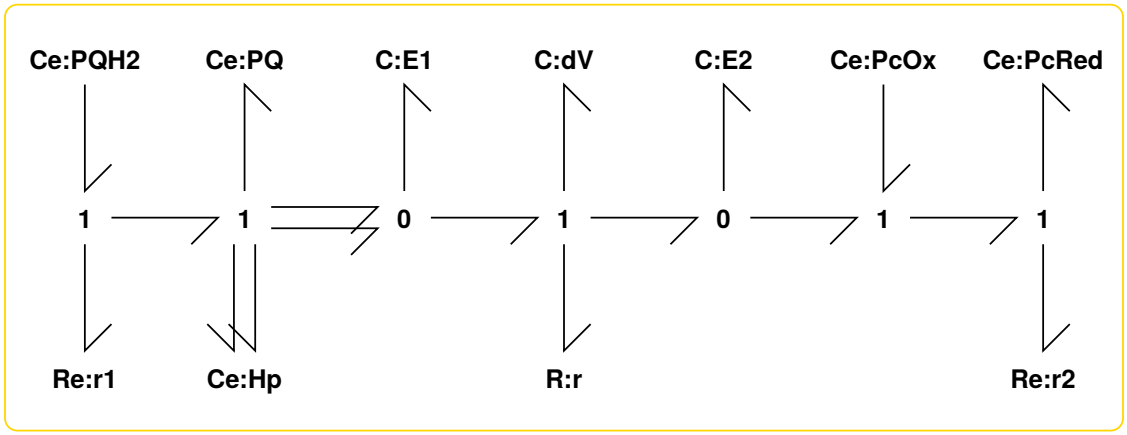
In [12]:
```
## Compute the reaction potential Phi
phi = phiData.phi_species(phi_redox,spPII['species'])
Phi_PII_ = -spPII['N'].T@phi
Phi_PII = Phi_PII_[0][0]
print('Phi_PII =',int(1000*Phi_PII), 'mV')
print('Ratio =',(Phi_PII/RP_PII))
```

```
Phi_PII = 3290 mV
Ratio = 4.0
```

4.2 Complex Cyt -- Cytochrome bf

In [13]:
```
disp.SVG('Cyt_abg.svg')
```

Out[13]:



In [14]:
```
sbg.model('Cyt_abg.svg',convertR=True,convertCe=True,quiet=True)
import Cyt_abg
imp.reload(Cyt_abg)
```

Out[14]:
```
<module 'Cyt_abg' from '/home/peterg/WORK/Research/SystemsBiology/Notes/2019/Chloroplas
```

In [15]:
```
## Stoichiometry
sCyt = st.stoich(Cyt_abg.model(),quiet=True)
chemostats = ['PQ','PQH2','PcOx','PcRed','Hp','dV']
scCyt = st.statify(sCyt,chemostats=chemostats)
spCyt = st.path(sCyt,scCyt)
disp.Latex(st.sprintrl(sCyt,chemformula=True))
```

Out[15]:

$$E_1 \overset{r}{\rightleftharpoons} E_2 + dV \tag{14}$$

$$PQH_2 \overset{r_1}{\rightleftharpoons} 2\,E_1 + 2\,Hp + PQ \tag{15}$$

$$E_2 + PcOx \overset{r_2}{\rightleftharpoons} PcRed \tag{16}$$

In [16]:
```
disp.Latex(st.sprintrl(spCyt,chemformula=True))
```

Out[16]:

$$PQH_2 + 2\,PcOx \overset{pr_1}{\rightleftharpoons} 2\,dV + 2\,Hp + PQ + 2\,PcRed \tag{17}$$

In [17]:
```
## Compute net redox potential
RP_Cyt = (- redoxData.EpH('PQ/PQH2',pH=pH_p)
          - redoxData.VpH(pH_p - pH_n)
          + redoxData.E('PcOx/PcRed')
         )

print(RP_Cyt)
print('RP_Cyt =',redoxData.mV(RP_Cyt), 'mV')
```

```
0.010757686938834443
RP_Cyt = 11 mV
```

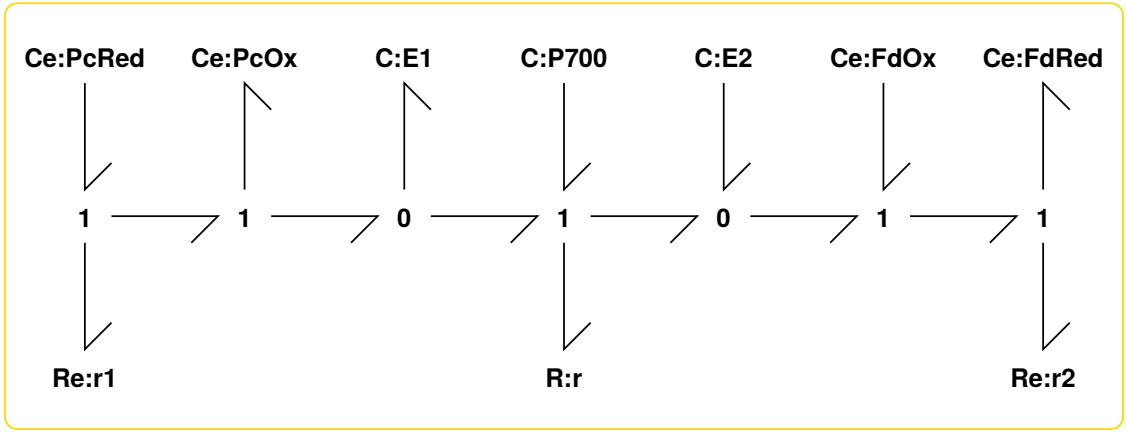
```
In [18]: ## Compute the reaction potential Phi
         phi = phiData.phi_species(phi_redox,spCyt['species'])
         Phi_Cyt_ = -spCyt['N'].T@phi
         Phi_Cyt = Phi_Cyt_[0][0]
         print('Phi_Cyt =',redoxData.mV(Phi_Cyt), 'mV')
         print('Ratio =', int(Phi_Cyt/RP_Cyt))
```

```
Phi_Cyt = 22 mV
Ratio = 2
```

4.3 Complex PI -- Photosystem I

```
In [19]: disp.SVG('PI_abg.svg')
```

Out[19]:




```
In [20]: sbg.model('PI_abg.svg',convertR=True,convertCe=True,quiet=True)
         import PI_abg
```

```
In [21]: ## Stoichiometry
         sPI = st.stoich(PI_abg.model(),quiet=True)
         chemostats = ['PcOx','PcRed','FdOx','FdRed','P700']
         scPI = st.statify(sPI,chemostats=chemostats)
         spPI = st.path(sPI,scPI)
         disp.Latex(st.sprintrl(sPI,chemformula=True))
```

Out[21]:

$$E_1 + P_{700} \overset{r}{\rightleftharpoons} E_2 \tag{18}$$

$$PcRed \overset{r_1}{\rightleftharpoons} E_1 + PcOx \tag{19}$$

$$E_2 + FdOx \overset{r_2}{\rightleftharpoons} FdRed \tag{20}$$

```
In [22]: disp.Latex(st.sprintrl(spPI,chemformula=True))
```

Out[22]:

$$P_{700} + FdOx + PcRed \overset{pr_1}{\rightleftharpoons} FdRed + PcOx \tag{21}$$

```
In [23]: ## Compute net redox potential
         RP_PI = (
                 - redoxData.E('PcOx/PcRed')
                 + V700
                 + redoxData.E('FdOx/FdRed')
                 )

         #print(RP_PI)
         print('RP_PI =',redoxData.mV(RP_PI), 'mV')
```

```
RP_PI = 961 mV
```

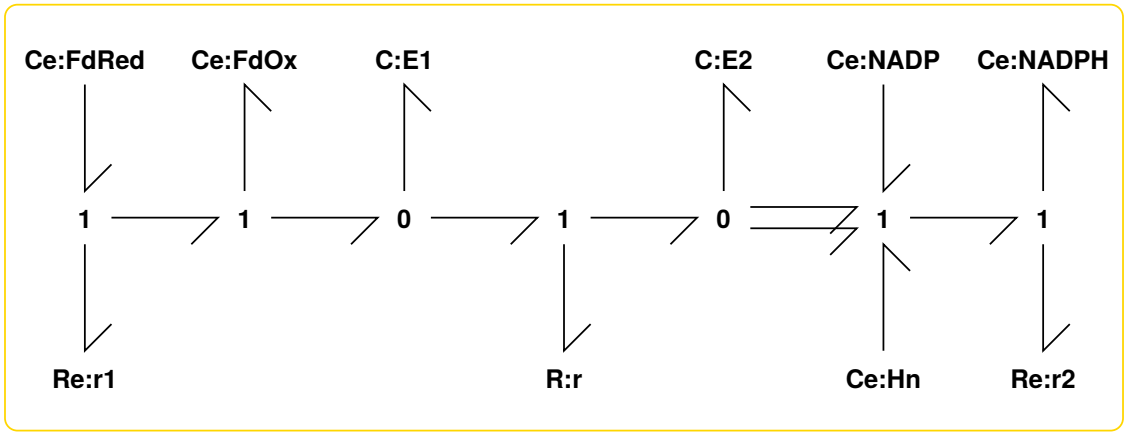
```
In [24]: ## Compute the reaction potential Phi
         phi = phiData.phi_species(phi_redox,spPI['species'])
         Phi_PI_ = -spPI['N'].T@phi
         Phi_PI = Phi_PI_[0][0]
         print('Phi_PI =',redoxData.mV(Phi_PI), 'mV')
         print('Ratio =', int(round(Phi_PI/RP_PI)))
```

```
Phi_PI = 961 mV
Ratio = 1
```

4.4 Complex Fer -- Feredoxin-NADP reductase

```
In [25]: disp.SVG('Fer_abg.svg')
```

Out[25]:




```
In [26]: sbg.model('Fer_abg.svg',convertR=True,convertCe=True,quiet=True)
         import Fer_abg

In [27]: ## Stoichiometry
         sFer = st.stoich(Fer_abg.model())
         chemostats = ['FdRed','FdOx','NADP','NADPH','Hn']
         scFer = st.stoich(Fer_abg.model(),chemostats=chemostats)
         spFer = st.path(sFer,scFer)
         disp.Latex(st.sprintrl(sFer,chemformula=True))

Swapping Re:r for two Sf in Fer
Swapping Re:r1 for two Sf in Fer
Swapping Re:r2 for two Sf in Fer
Swapping Re:r for two Sf in Fer
Swapping Re:r1 for two Sf in Fer
Swapping Re:r2 for two Sf in Fer
```

Out[27]:

$$\mathrm{E_1} \overset{\mathrm{r}}{\rightleftharpoons} \mathrm{E_2} \tag{22}$$

$$\mathrm{FdRed} \overset{\mathrm{r_1}}{\rightleftharpoons} \mathrm{E_1} + \mathrm{FdOx} \tag{23}$$

$$2\,\mathrm{E_2} + \mathrm{Hn} + \mathrm{NADP} \overset{\mathrm{r_2}}{\rightleftharpoons} \mathrm{NADPH} \tag{24}$$

```
In [28]: disp.Latex(st.sprintrl(spFer,chemformula=True))
```

Out[28]:

$$2\,\mathrm{FdRed} + \mathrm{Hn} + \mathrm{NADP} \overset{\mathrm{pr_1}}{\rightleftharpoons} 2\,\mathrm{FdOx} + \mathrm{NADPH} \tag{25}$$

```
In [29]: ## Compute net redox potential
         RP_Fer = (
                 - redoxData.E('FdOx/FdRed')
                 + redoxData.EpH('NADP/NADPH',pH_n)
                 )

         #print(RP_Fer)
         print('RP_Fer =',int(1000*RP_Fer), 'mV')
```

```
RP_Fer = 105 mV
```

```
In [30]: ## Compute the reaction potential Phi
         phi = phiData.phi_species(phi_redox,spFer['species'])
         Phi_Fer_ = -spFer['N'].T@phi
         Phi_Fer = Phi_Fer_[0][0]
         print('Phi_Fer =',int(1000*Phi_Fer), 'mV')
         print('Ratio =', int(Phi_Fer/RP_Fer))
```

```
Phi_Fer = 212 mV
Ratio = 2
```

5 The Electron Transport Chain

The overall model is described a bond graph tools file:

```
In [31]: ## File ETC_abg.py

         import BondGraphTools as bgt
         import PII_abg
         import Cyt_abg
         import PI_abg
         import Fer_abg

         def model():
             """
             Model of chloroplast electron transport chain
             """

             ETC = bgt.new(name='ETC')    # Create system
             PII = PII_abg.model()
             Cyt = Cyt_abg.model()
             PI = PI_abg.model()
             Fer = Fer_abg.model()
             bgt.add(ETC,PII,Cyt,PI,Fer)

             return ETC
```

5.1 Unify species in stoichiometric matrix using stoich.unify()

```
In [32]: import ETC_abg
```

The connections are made by listing the species in common between the four components PII, Cyt, PI and Fer.

```
In [33]: ## Stoichiometry
         common = ['PQ','PQH2','PcOx','PcRed','FdOx', 'FdRed','Hn','Hp']
         model = ETC_abg.model()
         s = st.stoich(model,quiet=True)
         st.unify(s,common) # Unify using stoichiometry

         ## Pathway analysis
         chemostats = ['H2O','O2','NADP','NADPH','Hp','Hn','P680','P700','dV']
         sc = st.statify(s,chemostats=chemostats)
         sp = st.path(s,sc)
```

```
In [34]: disp.Latex(st.sprintrl(s,chemformula=True))
```

Out[34]:

$$E_1 + P_{680} \overset{r}{\rightleftharpoons} E_2 \tag{26}$$

$$2\,H_2O \overset{r_1}{\rightleftharpoons} 4\,E_1 + 4\,Hp + O_2 \tag{27}$$

$$2\,E_2 + 2\,Hn + PQ \overset{r_2}{\rightleftharpoons} PQH_2 \tag{28}$$

$$E_1 \overset{r}{\rightleftharpoons} E_2 + dV \tag{29}$$

$$PQH_2 \overset{r_1}{\rightleftharpoons} 2\,Hp + PQ + 2\,E_1 \tag{30}$$

$$E_2 + PcOx \overset{r_2}{\rightleftharpoons} PcRed \tag{31}$$

$$E_1 + P_{700} \overset{r}{\rightleftharpoons} E_2 \tag{32}$$

$$PcRed \overset{r_1}{\rightleftharpoons} PcOx + E_1 \tag{33}$$

$$E_2 + FdOx \overset{r_2}{\rightleftharpoons} FdRed \tag{34}$$

$$E_1 \overset{r}{\rightleftharpoons} E_2 \tag{35}$$

$$FdRed \overset{r_1}{\rightleftharpoons} FdOx + E_1 \tag{36}$$

$$Hn + 2\,E_2 + NADP \overset{r_2}{\rightleftharpoons} NADPH \tag{37}$$

```
In [35]: disp.Latex(st.sprintrl(sp,chemformula=True))
```

Out[35]:

$$4\,P_{680} + 2\,H_2O + 6\,Hn + 4\,P_{700} + 2\,NADP \overset{pr_1}{\rightleftharpoons} 8\,Hp + O_2 + 4\,dV + 2\,NADPH \tag{38}$$

```
In [36]: ## Compute the reaction potential Phi
         phi = phiData.phi_species(phi_redox,sp['species'])
         Phi_ETC_ = -sp['N'].T@phi
         Phi_ETC = Phi_ETC_[0][0]
         print('Phi_ETC =',int(1000*Phi_ETC), 'mV')
         #print('Ratio =', int(Phi_Fer/RP_Fer))
```

```
Phi_ETC = 7602 mV
```

5.2 Unify species in model using modular.unify()

```
In [37]: imp.reload(bgt)
         import modular
         imp.reload(modular)
         imp.reload(st)
         model = ETC_abg.model()
         common = ['PQ','PQH2','PcOx','PcRed','FdOx', 'FdRed','Hn','Hp']
         modular.unify(model,common,quiet=True)
         s = st.stoich(model,quiet=True)
         #disp.Latex(st.sprintl(s,'N'))
         #disp.Latex(st.sprintrl(s))
```

```
In [38]: chemostats = ['H2O','O2','NADP','NADPH','Hp','Hn','P680','P700','dV']
         sc = st.statify(s,chemostats=chemostats)
         sp = st.path(s,sc)
         disp.Latex(st.sprintrl(sp,chemformula=True))
```

Out[38]:

$$4\,P_{680} + 2\,H_2O + 4\,P_{700} + 2\,NADP + 6\,Hn \xrightleftharpoons{pr_1} O_2 + 4\,dV + 2\,NADPH + 8\,Hp \qquad (39)$$

```
In [39]: ## Compute the reaction potential Phi
         phi = phiData.phi_species(phi_redox,sp['species'])
         Phi_ = -sp['N'].T@phi
         Phi= Phi_[0][0]
         print('Phi =',redoxData.mV(Phi), 'mV')
```

```
Phi = 7603 mV
```

References

Robert E. Blankenship. *Molecular mechanisms of photosynthesis*. Wiley Blackwell, Oxford, 2015.

Robert E. Blankenship and Roger C. Prince. Excited-state redox potentials and the z scheme of photosynthesis. *Trends in Biochemical Sciences*, 10(10):382 – 383, 1985. ISSN 0968-0004. doi:10.1016/0968-0004(85)90059-3.

David G Nicholls and Stuart Ferguson. *Bioenergetics 4*. Academic Press, Amsterdam, 2013.