

Calculating Γ^* used by e-Photosynthesis

Use a custom function to find temperature-corrected V_{cmax} and V_{omax} rate constants:

```
% Import enzyme data
Edata = importdata('Einput7.txt');
%Vcmax = Edata.data(1,1); % Original Vmax file
Vcmax_rice = Edata.data(1,1)*0.96; % Multiply by optimal scaling factor for rice
% Call the function to calculate PsV1 and PrV111 values at different
% temperatures
WeatherTemp = 28.9310407291759; %Avg rice Tleaf
[PsV1_Tp,PrV111_Tp,Ru_Act_Tp] = find_Rubisco_params(Vcmax_rice,WeatherTemp)
```

```
PsV1_Tp = 4.6687
PrV111_Tp = 1.1205
Ru_Act_Tp = 0.9389
```

```
[PsV1_25,PrV111_25,Ru_Act_25] = find_Rubisco_params(Vcmax_rice,25)
```

```
PsV1_25 = 3.6966
PrV111_25 = 0.8872
Ru_Act_25 = 0.9627
```

```
[PsV1_35,PrV111_35,Ru_Act_35] = find_Rubisco_params(Vcmax_rice,35)
```

```
PsV1_35 = 6.0709
PrV111_35 = 1.4570
Ru_Act_35 = 0.8191
```

According to Zhu et al. (2007), PsV1 and PrV111 are expressed in units of $\mu\text{mol m}^{-2} \text{s}^{-1}$ or $\text{mmol L}^{-1} \text{s}^{-1}$.

To calculate Γ^* being used in e-Photosynthesis, we need to define a few constants:

```
% Gas solubilities at 25C and 35C
CO2_25_sol = 0.034; %mol L -1 bar -1
O2_25_sol = 0.0013; %mol L -1 bar -1 - Hermida-Carrera (2016) = 0.0013, von
Caemerrer (2000) = 0.00126
CO2_35_sol = 0.0262; %mol L -1 bar -1 - Hermida-Carrera et al (2016)
O2_35_sol = 0.0011; %mol L -1 bar -1 - Hermida-Carrera et al (2016)

% Gas mole fractions/ partial pressures
CO2_mol = 0.0004; % Atmospheric CO2 concentration (0.04%) converted to mol/L
O2_mol = 0.21; % Atmospheric O2 concentration (21%) converted to mol/L
O2_gas = 210 * 1e3; % Atmospheric O2 partial pressure converted from mbar to
ubar (x 10^3) or mol fraction of 0.21 x 10^6 = 210,000 umol mol-1

% Enthalpy of dissolution
CO2_Dsol = 2000; % J/mol
O2_Dsol = 1700; % J/mol

% Temperature response
Tp = 28.9310407291759; % Average temp in C of measurements from gas exchange
```

```
R = 8.314; % Ideal gas constant in J K-1 mol-1
```

Import Rubisco Michaelis-Menten parameter data from Carmen's file:

```
% Specify the file path and name
file_path_kinetics = 'C:\Users\vijayak2\OneDrive - Lancaster
University\Code\Rice\IRRI_data\msuRACiFit\third\Data\Rubisco_kinetics_Oryza_sativa.x
lsx'; % Replace with your file path
opts = detectImportOptions(file_path_kinetics);
% Specify the range of headers
opts.VariableNamesRange = 'A1:BC1';
% Specify the range of data values
opts.DataRange = 'A2:BC5';
% Use the original column headers as table variable names
opts.VariableNamingRule = 'preserve';
% Import the data as a table
Rubisco_kinetics = readtable(file_path_kinetics,opts);
```

Take the means of the c and dHa columns for K_c and K_{cair} from Rubisco_kinetics:

```
c_Kc = mean(rmmissing(table2array(Rubisco_kinetics(:, 14)))); % Hermida-
Carrera et al (2016); Oryza sativa Kc c, dimensionless
dHa_Kc = mean(rmmissing(table2array(Rubisco_kinetics(:, 15)))); % Hermida-
Carrera et al (2016); Oryza sativa Kc dHa, kJ mol -1
c_Kcair = mean(rmmissing(table2array(Rubisco_kinetics(:, 24)))); % Hermida-
Carrera et al (2016); Oryza sativa Kcair c, dimensionless
dHa_Kcair = mean(rmmissing(table2array(Rubisco_kinetics(:, 25)))); % Hermida-
Carrera et al (2016); Oryza sativa Kcair dHa, kJ mol -1
c_Gstar = 13.7 % msuRACiFit gsPresets file
```

```
c_Gstar = 13.7000
```

```
dHa_Gstar = 24.6 % msuRACiFit gsPresets file
```

```
dHa_Gstar = 24.6000
```

```
%c_Gstar = mean(rmmissing(table2array(Rubisco_kinetics(:, 39)))); % Hermida-
Carrera et al (2016); Oryza sativa Gstar c, dimensionless
%dHa_Gstar = mean(rmmissing(table2array(Rubisco_kinetics(:, 40)))); % Hermida-
Carrera et al (2016); Oryza sativa Gstar dHa, kJ mol -1
```

Calculate Rubisco Michaelis-Menten parameters K_c , K_{cair} and K_o

$$K_o \text{ in gasphase} (\mu\text{molmol}^{-1}) = \frac{O_2 \text{ in } \mu\text{molmol}^{-1}}{\left(\frac{K_{cair} \text{ in } \mu\text{molmol}^{-1}}{K_c \text{ in } \mu\text{molmol}^{-1}}\right) - 1}$$

```
Kc_Tp = exp(c_Kc-dHa_Kc*1000/(R*(Tp+273.15))); %Kc at Tp in umol mol-1
Kcair_Tp = exp(c_Kcair-dHa_Kcair*1000/(R*(Tp+273.15))); %Kcair at Tp in umol mol -1
```

```

Ko_Tp = (O2_gas/((Kcair_Tp/Kc_Tp)-1));           %Ko at Tp in ubar or umol
mol -1

Kc_25 = exp(c_Kc-dHa_Kc*1000/(R*(25+273.15)));   %Kc at 25 in umol mol-1
Kcair_25 = exp(c_Kcair-dHa_Kcair*1000/(R*(25+273.15))); %Kcair at 25 in umol mol -1
Ko_25 = (O2_gas/((Kcair_25/Kc_25)-1));           %Ko at 25 in ubar or umol
mol -1

Kc_35 = exp(c_Kc-dHa_Kc*1000/(R*(35+273.15)));   %Kc at 35 in umol mol-1
Kcair_35 = exp(c_Kcair-dHa_Kcair*1000/(R*(35+273.15))); %Kcair at 35 in umol mol -1
Ko_35 = (O2_gas/((Kcair_35/Kc_35)-1));           %Ko at 35 in ubar or umol
mol -1

```

To find $[O_2]$ and $[CO_2]$ in μM , multiply their partial pressures in mbar/mmol mol by the solubilities at 25°C/35°C, then rescale the units:

```
CO2_25_uM = 0.4*CO2_25_sol*1e3 %mmol to uM (x 1e3)
```

```
CO2_25_uM = 13.6000
```

```
O2_25_uM = 210*O2_25_sol*1e3 %mmol to uM (x 1e3)
```

```
O2_25_uM = 273.0000
```

```
CO2_35_uM = 0.4*CO2_35_sol*1e3 %mmol to uM (x 1e3)
```

```
CO2_35_uM = 10.4800
```

```
O2_35_uM = 210*O2_35_sol*1e3 %mmol to uM (x 1e3)
```

```
O2_35_uM = 231
```

Take the means of the columns containing K_c and K_{cair} concentrations at 25°C and 35°C in Rubisco_kinetics:

```

Kc_25_uM = mean(rmmissing(table2array(Rubisco_kinetics(:, 7)))); % Hermida-
Carrera et al (2016); Oryza sativa uM at 25°C
Kcair_25_uM = mean(rmmissing(table2array(Rubisco_kinetics(:, 17)))); % Hermida-
Carrera et al (2016); Oryza sativa uM at 25°C
Kc_35_uM = mean(rmmissing(table2array(Rubisco_kinetics(:, 8)))); % Hermida-
Carrera et al (2016); Oryza sativa uM at 35°C
Kcair_35_uM = mean(rmmissing(table2array(Rubisco_kinetics(:, 18)))); % Hermida-
Carrera et al (2016); Oryza sativa uM at 35°C

```

Calculate $K_o \text{ in liquid phase } (\mu M) = \frac{O_2 \text{ in } \mu M}{\left(\frac{K_{cair} \text{ in } \mu M}{K_c \text{ in } \mu M}\right) - 1}$ using known K_c and K_{cair} :

```

Ko_25_uM = O2_25_uM/((Kcair_25_uM/Kc_25_uM)-1); % Hermida-Carrera et al
(2016); Oryza sativa uM at 25°C

```

```
Ko_35_uM = O2_35_uM/((Kc_35_uM/Kc_35_uM)-1); % Hermida-Carrera et al
(2016); Oryza sativa uM at 35°C
```

Bernacchi et al., 2001 has values of K_c , K_o , and Γ^* at 25°C of 404.9 μmolmol^{-1} , 278.4 mmolmol^{-1} , and 42.75 μmolmol^{-1} , respectively.

Use this as a reference to compare results/ try converting to these units.

The Rubisco specificity is often measured from an aqueous solution where the concentrations of [O₂] and [CO₂] are specified as molarities (moles of dissolved CO₂ or O₂ per mole of H₂O).

To calculate $S_{c/o}$ using $\frac{V_{cmax}}{K_c} \frac{K_o}{V_{omax}}$ we use different units depending on whether we are in liquid or gas phase

```
% Relative specificity Sc/o - ratio of Rubisco carboxylation to oxygenation when
CO2 and O2 are at equal concentrations/partial pressures
% Original Units
% PsV1 - umol m-2 s-1 or mmol L-1 s-1
% PrV111 - umol m-2 s-1 or mmol L-1 s-1
% Kc - uM or umol mol-1
% Ko - uM or umol mol-1
```

To work with liquid phase V_{cmax} and K_c , $S_{c/o}$ also needs to be calculated in liquid phase on a molarity basis:

```
Sco_25_old = (120/Kc_25_uM)*(Ko_25_uM/(0.24*120))
```

```
Sco_25_old = 123.3530
```

```
Sco_35_old = (120/Kc_35_uM)*(Ko_35_uM/(0.24*120))
```

```
Sco_35_old = 118.3838
```

```
Sco_25 = (PsV1_25/Kc_25_uM)*(Ko_25_uM/PrV111_25)
```

```
Sco_25 = 123.3530
```

```
Sco_35 = (PsV1_35/Kc_35_uM)*(Ko_35_uM/PrV111_35)
```

```
Sco_35 = 118.3838
```

Working out gas phase $S_{c/o}$ is not recommended, but would follow the same calculation with different units:

```
%Sco_gas = (PsV1_Tp/Kc_Tp)*(Ko_Tp/PrV111_Tp)
%Sco_gas_25 = (PsV1_25/Kc_25)*(Ko_25/PrV111_25)
%Sco_gas_35 = (PsV1_35/Kc_35)*(Ko_35/PrV111_35)
```

Calculate Γ^* in liquid phase using $\frac{tO}{S_{c/o}}$

The photosynthetic model by [Farquhar et al. \(1980\)](#) used $t = 0.5$. This assumes that for Rubisco catalysis of one mol of O_2 with one mol of RuBP, 0.5 mol of CO_2 are released in the photorespiratory carbon oxidation (PCO) cycle.

This stoichiometry is embedded in most photosynthetic models, but it has been suggested that the release may be less than 0.5 or more in some instances ([Busch, 2020](#); [Hanson and Peterson, 1986](#); [Harley and Sharkey, 1991](#); [Zelitch, 1989](#)).

If the photorespiratory pathway functions as a closed cycle, $t=0.5$ - corresponding to 25% of the 2PG carbon lost as CO_2 ([Busch, 2020](#)).

```
t = 0.5; % Amount of CO2 released from photorespiration per oxygenation
GammaStar_25 = t*O2_25_uM/Sco_25 % Liquid phase at 25°C - conc of C at
Rubisco - use solubility to convert back to gas phase
```

```
GammaStar_25 = 1.1066
```

```
GammaStar_35 = t*O2_35_uM/Sco_35 % Liquid phase at 35°C
```

```
GammaStar_35 = 0.9756
```

Γ^* is calculated above in liquid phase, but is commonly quoted in gas phase and therefore needs to be converted back to gas phase.

```
%GammaStar_gas = t*O2_gas/Sco_gas % Gas phase at 28.9°C
%GammaStar_gas_25_old = t*O2_gas/Sco_gas_25 % Gas phase at 25°C
%GammaStar_gas_35_old = t*O2_gas/Sco_gas_35 % Gas phase at 35°C
```

Try converting liquid phase Γ^* to gas phase Γ^* at 25 and 35C using Henry's Law constants to adjust for the different solubilities of CO_2 and O_2 in water:

$$\Gamma^* = \frac{t[O_2]}{S_{c/o}} \times \frac{[H_{CO_2}]}{[H_{O_2}]}$$

```
GammaStar_gas_25 = GammaStar_25*(CO2_25_sol/O2_25_sol)
```

```
GammaStar_gas_25 = 28.9413
```

```
GammaStar_gas_35 = GammaStar_35*(CO2_35_sol/O2_35_sol)
```

```
GammaStar_gas_35 = 23.2380
```

These values don't seem to be correct - below is another method to convert liquid phase Γ^* to gas phase Γ^* .

Calculating solubility at T_p :

To back calculate solubility, we can rearrange the earlier equations if we know the liquid phase concentration of the parameter at a given temperature.

Parameter concentrations in liquid phase can be converted to gaseous phase mole fractions using the following equation in Hermida Carrera et al :

$$\text{Parameter}[\mu\text{molmol}^{-1}] = \text{Parameter}[\mu\text{M}] \times K_h \times \frac{\text{air volume}[L]}{RT_p}$$

where K_h is the hydrolysis constant in $L \text{ bar}^{-1} \text{ mol}^{-1}$ ($15^\circ\text{C} = 22.2$, $25^\circ\text{C} = 29.4$, and $35^\circ\text{C} = 38.2$) and the air volume (L): $15^\circ\text{C} = 23.7$, $25^\circ\text{C} = 24.5$, and $35^\circ\text{C} = 25.4$.

To ensure the calculation returns a sensible value, we need to convert the units if appropriate:

- Liquid phase parameter from μM to μmolL^{-1}
- K_h from $L \text{ bar}^{-1} \text{ mol}^{-1}$ to $L \text{ kPa}^{-1} \text{ mol}^{-1}$ - this is the inverse of solubility ($\frac{1}{K_h}$) - multiply $\times 10^2$ to convert from 10^3 to 10^5 ($1 \text{ bar} = 10000 \text{ Pa}$ OR $1 \text{ kPa} = 100 \text{ bar}$)
- Air volume from $\frac{L}{J K^{-1} \text{ mol}^{-1}}$ to $m^3 \text{ mol}^{-1} J^{-1}$ ($1 m^3 = 1000 L$)
- $\frac{1}{\text{kPa}}$ - cancel 10^3 on each side by converting L to m^3 and kPa to Pa
- Rearranging $PV = nRT$ to $v = \frac{nRT}{P}$ where $n = 1$, $R = 8.314 J K^{-1} \text{ mol}^{-1}$, $T = 298.15 K$ (when 25°C), and $P = 101325 \text{ Pa}$.

```
Kc_at_25_umol = Kc_25_uM*29.4*24.5/(R*(25+273.15))*1e2 % Liquid uM to gas umol mol
```

```
Kc_at_25_umol = 233.3373
```

```
Kc_at_35_umol = Kc_35_uM*38.2*25.4/(R*(35+273.15))*1e2 % Liquid uM to gas umol mol
```

```
Kc_at_35_umol = 656.9251
```

```
Kc_air_at_25_umol = Kc_air_25_uM*29.4*(24.5/(R*(25+273.15)))*1e2 % Liquid uM to gas umol mol
```

```
Kc_air_at_25_umol = 501.2974
```

```
Kc_air_at_35_umol = Kc_air_35_uM*38.2*(25.4/(R*(35+273.15)))*1e2 % Liquid uM to gas umol mol
```

```
Kc_air_at_35_umol = 964.8418
```

```
GammaStar_25_umol = GammaStar_25*(29.4*1e2)*24.5/(R*(25+273.15)) % Liquid uM to gas umol mol
```

```
GammaStar_25_umol = 32.1552
```

```
GammaStar_35_umol = GammaStar_35*(38.2*1e2)*25.4/(R*(35+273.15)) % Liquid uM to gas umol mol
```

```
GammaStar_35_umol = 36.9500
```

```
GammaStar_25_Pa = GammaStar_25_umol/1000000*101325
```

```
GammaStar_25_Pa = 3.2581
```

```
GammaStar_35_Pa = GammaStar_35_umol/1000000*101325
```

```
GammaStar_35_Pa = 3.7440
```

Gamma Star from Carmen's c and dHa data:

```
Gstar_Tp_umol = exp(c_Gstar-dHa_Gstar*1000/(R*(Tp+273.15)))           %Gstar at Tp  
in umol mol-1
```

```
Gstar_Tp_umol = 49.6532
```

```
Gstar_25_umol = exp(c_Gstar-dHa_Gstar*1000/(R*(25+273.15)))           %Gstar at 25  
in umol mol-1
```

```
Gstar_25_umol = 43.6376
```

```
Gstar_35_umol = exp(c_Gstar-dHa_Gstar*1000/(R*(35+273.15)))           %Gstar at 35  
in umol mol-1
```

```
Gstar_35_umol = 60.2181
```

The hydrolysis constant K_h can be defined as the equilibrium constant for a hydrolysis reaction.

Henry's law constant dictates how gases dissolve in liquid:

$$K_h = \frac{P}{C}$$

where P is the partial pressure of the gas in the air above the liquid and C is the concentration of dissolved gas - this varies depending on which gas is dissolved and at what temperature.

Solubility data is available in the NIST Chemistry WebBook at <https://webbook.nist.gov/>

The temperature dependence of equilibrium constants such as K_h for CO₂ can be calculated using the van't Hoff equation (Carroll et al, 1991) :

$$K_{hT_p\text{CO}_2} = K_{h25\text{CO}_2} \times \exp\left(\left(-\frac{\Delta H_{\text{sol}}}{R}\right) * \left(\frac{1}{T_{p[K]}} - \frac{1}{T_{25K}}\right)\right)$$

Here ΔH_{sol} is the enthalpy of dissolution for CO₂.

Use the equation substituting gas solubility for K_h at a known temperature:

```
% % Test with known solubility to check (0.045 at 15C in HC et al 2016)  
CO2_15_sol = CO2_25_sol * exp((-CO2_Dsol / R) * (1/(25+273.15) - 1/(15+273.15)))%  
ANSWER DOES NOT MATCH HC DATA BUT RISES AS EXPECTED
```

```
CO2_15_sol = 0.0350
```

$$O2_{15_sol} = CO2_{15_sol} * \exp((-O2_{Dsol} / R) * (1/(25+273.15) - 1/(15+273.15)))$$

$$O2_{15_sol} = 0.0358$$

We know this somewhat works now so we can implement this to estimate CO2 solubility at T_p :

$$CO2_{Tp_sol} = CO2_{25_sol} * \exp(-CO2_{Dsol} / R * (1 / (Tp+273.15) - 1 / (25+273.15)))$$

$$CO2_{Tp_sol} = 0.0344$$

For O_2 solubility at T_p we can use the same equation to approximate:

$$O2_{Tp_sol} = O2_{25_sol} * \exp(-O2_{Dsol} / R * (1 / (Tp+273.15) - 1 / (25+273.15)))$$

$$O2_{Tp_sol} = 0.0013$$

Use these constants to work out new $[O_2]$ and $[CO_2]$ in μM at T_p by multiplying their partial pressures in mbar/mmole by the new solubilities and rescaling units:

$$CO2_{Tp_uM} = 0.4 * CO2_{Tp_sol} * 1e3 \text{ \%mmol to uM (x 1e3)}$$

$$CO2_{Tp_uM} = 13.7435$$

$$O2_{Tp_uM} = 210 * O2_{Tp_sol} * 1e3 \text{ \%mmol to uM (x 1e3)}$$

$$O2_{Tp_uM} = 275.4473$$

Convert K_c and K_o from gas phase to liquid phase by dividing by concentrations and multiplying to rescale units:

$$Kc_{Tp_uM} = Kc_{Tp} / CO2_{Tp_uM} * 1e6 \text{ \% Divide to get units of mol/L and multiply to get uM}$$

$$Kc_{Tp_uM} = 2.5039e+07$$

$$Ko_{Tp_uM} = Ko_{Tp} / O2_{Tp_uM} * 1e6 \text{ \% Divide to get units of mol/L and multiply to get uM}$$

$$Ko_{Tp_uM} = 9.9912e+08$$

Calculate S/co at T_p using these values:

$$Sco_{Tp} = (PsV1_{Tp}/Kc_{Tp_uM}) * (Ko_{Tp_uM}/PrV111_{Tp})$$

$$Sco_{Tp} = 166.2575$$

$$GammaStar_{liquid_Tp} = O2_{Tp_uM}/Sco_{Tp}$$

$$GammaStar_{liquid_Tp} = 1.6568$$

Convert Γ_{star} from liquid concentrations to gas phase partial pressures:

$$\Gamma^*_{\text{gas}} = \frac{\Gamma^*_{\text{liquid}}}{\text{solCO}_2}$$

Since Γ^* represents the CO₂ compensation point in the liquid phase, we need to divide by CO₂ solubility to convert it to the gas phase.

$$\text{GammaStar_gas_Tp} = \text{GammaStar_liquid_Tp} / \text{CO2_Tp_sol}$$

$$\text{GammaStar_gas_Tp} = 48.2190$$

$$\text{GammaStar_gas_Pa} = \text{GammaStar_gas_Tp} / 1000000 * 101325$$

$$\text{GammaStar_gas_Pa} = 4.8858$$