**Appendix 1.1:**

To provide a rough determination of the atomic composition of *Synechococcus* sp. biomass based on the percentage of protein, lipid, and carbohydrate content (Nagarkar et al., 2004), we have made certain assumptions (see below). Typically, proteins, lipids, and carbohydrates have characteristic atomic compositions that we can use as a basis for this estimation:

**Proteins:** On average, proteins are composed of about 50% carbon, 7% hydrogen, 16% nitrogen, 19% oxygen, 1.5% sulphur, and minor amounts of other elements. However, the sulphur content can vary significantly, and not all proteins contain sulphur.

**Lipids:** Lipids are more varied in structure than proteins or carbohydrates, but a typical lipid might be composed of about 77% carbon, 12% hydrogen, and 11% oxygen by mass.

**Carbohydrates:** Carbohydrates generally have a formula that can be represented as

 are usually the same or very close. This gives them an approximate composition of 40% carbon, 6.7% hydrogen, and 53.3% oxygen by mass.

Given these average compositions, we can calculate the atomic composition of the cyanobacteria by applying the percentages of protein, lipid, and carbohydrate content provided (Nagarkar et al., 2004).

To calculate the rough atomic composition of cyanobacteria based on the given percentages of protein (64% dry weight, dw), lipids (28% dw), and carbohydrates (9% dw), we'll use the average atomic compositions for each component. Note that these percentages add up to 101% due to rounding.

 **Step 1: Calculate the mass contribution of each element from each component.**

**Proteins:**

Carbon (C): 64% × 50% = 32%

Hydrogen (H): 64% × 7% = 4.48%

Nitrogen (N): 64% × 16% = 10.24%

Oxygen (O): 64% × 19% = 12.16%

Sulphur (S): 64% × 1.5% = 0.96%

**Lipids:**

Carbon (C): 28% × 77% = 21.56%

Hydrogen (H): 28% × 12% = 3.36%

Oxygen (O): 28% × 11% = 3.08%

**Carbohydrates:**

Carbon (C): 9% × 40% = 3.6%

Hydrogen (H): 9% × 6.7% = 0.603%

Oxygen (O): 9% × 53.3% = 4.797%

**Step 2: Sum the contributions for each element**

Total Carbon (C): 32% + 21.56% + 3.6% = 57.16%

Total Hydrogen (H): 4.48% + 3.36% + 0.603% = 8.443%

Total Nitrogen (N): 10.24%

Total Oxygen (O): 12.16% + 3.08% + 4.797% = 20.037%

Total Sulphur (S): 0.96%

The rough atomic composition of the *Synechococcus* sp. biomass, based on the given dry weight percentages can be estimated as follows:

Carbon (C): 57.16%

Hydrogen (H): 8.443%

Nitrogen (N): 10.24%

Oxygen (O): 20.037%

Sulphur (S): 0.96%

This is a simplified estimation, and actual compositions can vary based on the specific types of proteins, lipids, and carbohydrates present in the cyanobacteria, as well as the presence of other minor components not accounted for in this calculation.

**Determine the simplified formula for *Synechococcus* sp. biomass**

Based on the rough atomic composition calculated above, we can create a simplified empirical formula for the *Synechococcus* sp. biomass. We'll use the percentages to estimate the molar ratios of the elements.

For simplicity, let's assume 100 g of biomass to use the percentages directly as grams. This allows us to calculate moles of each element:

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To simplify, we'll round these to whole numbers for an empirical formula, understanding this is a significant approximation:

**Appendix 1.2**

Since we do not have a value for we cannot complete this calculation without additional data or assumptions. The calorific value of *Chlorella* sp. biomass was assumed to be between 2.8 kJ/g DCW (Nagarkar et al., 2004) and 21 kJ/g DCW (Scragg et al., 2002). For cyanobacterial biomass, we can refine the calculation for the enthalpy of combustion. The calorific value essentially represents the energy released during the complete combustion of a substance, which is equivalent to the enthalpy change of the combustion reaction.

The given calorific value is 2.8 kJ for each gram of dry biomass can be converted in a per mol value using the atomic formula of biomass derived before.

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Total molar mass ≈ 60.05 + 8.064 + 14.01 + 16.00 ≈ 98.12 g/mol

The calorific value per mole of biomass is then:

The enthalpy of combustion for the biomass is -274.74 kJ/mol (negative because it's exothermic, releasing energy).

The estimated combustion reaction for *Synechococcus* sp. is then:

Giving us a value for the enthalpy of combustion per mol of CO2 of -54.95 kJ/mol of CO2

**Appendix 1.3**

**Determine the simplified formula for *Chlorella* sp. biomass**

To calculate the enthalpy of combustion for the *Chlorella* sp. biomass with the given empirical formula and the provided thermodynamic data, we need to consider the complete combustion reaction of the cyanobacteria, which typically involves the conversion of the organic material into , and possibly other products like (for the phosphorus content), assuming complete combustion in excess oxygen.

Given data:

- Enthalpy of formation

- Entropy of formation

- Gibbs free energy of formation

The general combustion reaction for the cyanobacteria can be written as:

To balance the reaction, we need to ensure that the number of atoms for each element is the same on both sides of the equation. This involves solving for the c andthat balance the equation. The nitrogen and phosphorus will likely end up as and respectively, due to their common oxidation states in combustion products.

**Balancing carbon, hydrogen, oxygen, nitrogen, and phosphorus:**

- For Carbon C:

- For Hydrogen H:

- For Oxygen O:

- For Nitrogen N:

- For Phosphorus P:

 **Calculate the enthalpy of combustion:**

The enthalpy of combustion can be calculated using the enthalpies of formation for the reactants and products. The general formula for the enthalpy changes of a reaction is:

Given that the enthalpy of formation for the cyanobacteria is -95.34 kJ/mol, and assuming standard enthalpies of formation for :

 Note: This calculation involves approximations, especially in balancing the reaction and assuming the state and enthalpy of formation for phosphorus combustion products. The actual enthalpy of combustion might differ based on experimental conditions and the precise composition of the cyanobacteria.

To calculate the entropy of combustion for the cyanobacteria Chlorella, we use the standard molar entropies of the reactants and products in the balanced combustion reaction. The general formula for the entropy change of a reaction is:

For the balanced combustion reaction:

We use typical values for these species at 298 K (25°C):

(liquid water, since combustion typically produces liquid water at standard conditions)

Substituting the values into the equation:

An entropy change of 4.4 J/mol·K for the combustion of a complex organic substance like *Chlorella* sp. biomass might seem low, but it's not uncommon for such processes, especially when considering the following factors:

1. Phase Changes: Combustion reactions often involve the formation of gases (e.g) from solid or liquid reactants, which typically leads to an increase in entropy due to the higher disorder in the gaseous state. However, if the water produced in the combustion is in the liquid phase, as often assumed for standard state conditions, the increase in entropy will be less pronounced because the liquid phase is more ordered than the gas phase.
2. Molecular Complexity: The combustion of complex organic molecules like those in biomass can lead to products that are simpler (e.g., ) but also include other complex molecules depending on the composition of the biomass (e.g., ). The reduction in complexity can lead to a decrease in entropy, which might offset the entropy increase due to the phase change and the increase in the number of moles of gas.
3. Balancing Effects: The overall entropy change in a reaction is the net effect of entropy increases due to the production of gases and entropy decreases due to the loss of complex structures and potential formation of more ordered phases. In some cases, these effects can nearly balance out, leading to a relatively small net change in entropy.
4. Reaction Conditions: The standard entropy changes are calculated under standard conditions (1 bar, 25°C), which might not fully capture the entropy changes at higher temperatures or pressures that are common in actual combustion processes.
5. Accuracy of Data: The accuracy of the calculated entropy change also depends on the precision of the entropy values used in the calculation. Estimated or assumed values, particularly for complex substances like biomass, can introduce uncertainty into the calculation.

**Appendix 1.4**

Code for generating the Gibbs free energy contour plot.

import numpy as np

import matplotlib.pyplot as plt

# Constants

T = 298.15  # Standard temperature in Kelvin (25°C)

# Range for Delta H and Delta S values for the plot

delta\_H = np.linspace(-600, 100, 400)  # Change in enthalpy (kJ/mol)

delta\_S = np.linspace(-10, 100, 400)   # Change in entropy (J/mol·K), adjusted for the new points

Delta\_H, Delta\_S = np.meshgrid(delta\_H, delta\_S)

# Calculate Delta G for each combination of Delta H and Delta S

Delta\_G = Delta\_H - T \* Delta\_S / 1000  # Convert Delta\_S to kJ/mol·K for consistency

# Create the contour plot

plt.figure(figsize=(10, 7))

contour = plt.contourf(Delta\_H, Delta\_S, Delta\_G, levels=50, cmap='viridis')

plt.colorbar(contour, label='Gibbs Free Energy Change ($\Delta G$, kJ/mol)')

# Specific points to plot with new entropy value for point 3

points = [(-551.7, 4.4), (-276.05, 4.4), (0, 65.03)]

colors = ['red', 'blue', 'green']

labels = ['Chlorella', 'Synechococcus', 'Atmospheric capture at thermodynamic minimum']

# Add points to the plot

for point, color, label in zip(points, colors, labels):

    plt.scatter(\*point, color=color, label=label, zorder=5)

# Labeling the plot

plt.title('Gibbs Free Energy Change Contour Plot T = 298.15 K')

plt.xlabel('Enthalpy Change ($\Delta H$, kJ/mol)')

plt.ylabel('Entropy Change ($\Delta S$, J/mol·K)')

plt.legend()

plt.show()

**References**

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Scragg, A.H., Illman, A.M., Carden, A., Shales, S.W., 2002. Growth of microalgae with increased calorific values in a tubular bioreactor. Biomass and Bioenergy 23, 67–73. https://doi.org/10.1016/S0961-9534(02)00028-4