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Thermochimica Acta 400 (2003) 79–85

thermochimica acta

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Determination of the enthalpy change for anabolism by four methods

Derek Ellingson [a], Aaron Olson [a], Sannali Matheson [a], Richard S. Criddle [a], Bruce N. Smith [b], Lee D. Hansen [a,*]

[a] *Department of Chemistry and Biochemistry, Brigham Young University, C100 BNSN, BYU, 84602 Provo, UT, USA*
[b] *Department of Plant and Animal Science, Brigham Young University, Provo, UT, USA*

Received 21 May 2002; received in revised form 4 September 2002; accepted 11 September 2002

Abstract

The enthalpy change for anabolism is needed to model the growth/respiration relation in plants. If all CO_2 production is assigned to catabolism, the anabolic reaction becomes $C_{substrate} \rightarrow C_{products} + xO_2$ with an enthalpy change, ΔH_b. Four methods are proposed for determining ΔH_b: (a) From the difference in the heats of combustion of substrate and anabolic products (i.e. newly grown tissue). (b) From the composition of newly grown tissue and application of Thornton's rule. (c) From independently measured values of the specific growth rate, R_{SG}, and of the product ($R_{SG}\ \Delta H_b$). The product ($R_{SG}\ \Delta H_b$) equals ($-\Delta H_{CO_2} R_{CO_2} - R_q$) where R_{CO_2} is the specific rate of CO_2 production by respiration, ΔH_{CO_2} is the heat of combustion of respiratory substrate per mole of CO_2 and R_q is the specific metabolic heat rate. ΔH_b is then calculated as the ratio $(R_{SG}\ \Delta H_b)/R_{SG}$. (d) From $(\Delta H_b = -(R_q/R_{CO_2} + \Delta H_{CO_2})\ [(1-\varepsilon)/\varepsilon]$ where ε is the substrate carbon conversion efficiency obtained from a total carbon balance. The first three methods have been tested and compared on oat seedlings and the last on corn seedlings. ΔH_b values from all four methods are in reasonable agreement despite the different assumptions involved.

Keywords: Anabolism; Enthalpy; Metabolism; Methods; Plants; Respiration

1. Introduction

Growth of organized biological systems occurs with a negative free energy change because of an increase in entropy of the surroundings. However, little is known about the magnitudes of the thermodynamic quantities. The values of the Gibb's free energy change (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS) for growth of an organism can provide much insight into the relation between metabolism and growth [1]. Determining these thermodynamic values is difficult because of the complexity of biological systems. However, the problem is simplified by dividing metabolism into anabolism and catabolism.

The purpose of this paper is to discuss methods for determining the enthalpy changes for anabolism and catabolism during aerobic respiration in tissue from green plants. Most previous work has been done on bacteria and mammalian cell cultures where many of the variables are known or can be measured or controlled (i.e. the composition of the substrate and the products). Application of enthalpy balance models to plants [2] is relatively new compared to studies done on microorganisms [1] and animal cells [3].

* Corresponding author. Tel.: +1-801-422-2040; fax: +1-801-422-0153.
E-mail address: lee_hansen@byu.edu (L.D. Hansen).

0040-6031/03/$ – see front matter
PII: S0040-6031(02)00481-1

This study focuses on respiration in plants because photosynthesis is usually capable of producing an over-abundance of carbon substrate for plant growth. The commonly cited relation between photosynthesis and plant growth is a tautology [4], i.e. integrated photosynthesis and growth are two measures of the same quantity. Many studies have shown that plant growth is a function of respiratory properties [5]. Thus, photosynthesis supplies the fuel and most of the building material, but redox reactions of catabolism supply the driving force, and anabolism is the growth process.

Most models of the relationship between plant respiration and growth are empirical and therefore provide little or no insight into the growth/metabolism relation [6]. The model used in this study is mechanistic, developed from fundamental relations between reaction rates and readily measured variables [2]. Like other models, we assume no difference between growth respiration in the dark and in the light in photosynthetic tissues. Respiration is readily measured in the dark, but difficult to determine in lighted conditions, where photosynthesis interferes with gas exchange measurements. If respiratory processes in the dark were not similar to those in the light, previous tests of the ability of models to accurately predict growth rates from measurements on dark respiration [7] would have failed.

The following simplified equation describes aerobic respiratory metabolism:

$$C_s + xO_2 + (N, P, K, S, \text{etc.}) \rightarrow \varepsilon C_{AP} + (1 - \varepsilon)\, CO_2 \quad (1)$$

In the catabolic part of this reaction, substrate carbon (C_s) in sugars, lipids, or other compounds combines with oxygen to form water (not shown) and carbon dioxide. In the anabolic part of the reaction, the same substrates are used to form the anabolic product (C_{AP}). The coefficient x depends on the oxidation states of the anabolic product, carbon and nitrogen substrates, and the fraction of substrate carbon converted to anabolic products (i.e. the substrate carbon conversion efficiency, ε). The larger ε, the less catabolic energy a plant expends for a given amount of growth.

Catabolism, the energy liberating reaction, is represented by

$$C_s + \left[\frac{1 - \gamma_s}{4}\right] O_2 \rightarrow CO_2 \quad (2)$$

where the quantity γ_s represents the oxidation state of carbon in the substrate. Because catabolism is an oxidation reaction, the enthalpy change for catabolism can be estimated from the heat of combustion or from Thornton's rule [1].

The anabolic process is usually represented by

$$C_s + (N, P, K, S, \text{etc.}) \rightarrow yC_{AP} + (1 - y)\, CO_2 \quad (3)$$

The enthalpy change for reaction (3) is approximately zero, but can provide an estimate of the difference in energy between the anabolic product (C_{AP}) and the substrate carbon if the coefficient y (the yield of the reaction) is known. However, if all CO_2 is assigned as a product of catabolism, the equation for anabolism can be cast differently, so long as it agrees with the other two equations, i.e. catabolism plus anabolism must equal the overall reaction (Eq. (1)). Rewriting Eq. (3) as Eq. (4) defines anabolism such that the products of anabolism and catabolism are completely separated.

$$C_s + (N, P, K, S, \text{etc.}) \rightarrow C_{AP} + \left[\frac{(\gamma_s - \gamma_{AP})}{4}\right] O_2 \quad (4)$$

Notice the change in enthalpy for reactions (3) and (4) differ only because the stoichiometry differs; the ratio of C_s/C_{AP} differs between the reactions. Reaction (4) is used in this paper because the 1:1 C_s/C_{AP} stoichiometry eliminates the need to know y and makes it possible to determine the rate of catabolism from measurements of the CO_2 production rate. The enthalpy change for reaction (4) is a direct measure of the enthalpy difference between the substrate and the anabolic products.

We have tested four methods for determining the enthalpy change for reaction (4): combustion analysis, composition analysis, growth and metabolism analysis, and growth efficiency analysis. Three assumptions, common to all four methods were made to simplify these determinations. First we assume the enthalpy change from redox reactions of sulfur is negligible. Second, we assume that the oxidation state of all nitrogen in the system is the same as in NH_3, both in anabolic products and as a reactant. Third, we assume that CO_2 is the only carbon-containing product of catabolism and thus, ΔH_{CO_2} is an accurate estimate of the actual enthalpy change of catabolism.

Combustion analysis is based on the following thermodynamic cycle, assuming that C_s is a sugar:

$$C_{(sugar,\,solid)} + O_2 \rightarrow CO_{2(g)} + H_2O_{(l)}, \quad \Delta H_5 \quad (5)$$

$$C_{(sugar,\,aq)} \rightarrow C_{(sugar,\,solid)}, \quad \Delta H_6 \quad (6)$$

$$C_{(sugar,\,cell)}\{C_s\} \rightarrow C_{(sugar,\,aq)}, \quad \Delta H_7 \quad (7)$$

$$C_{(AP,\,cell)} \rightarrow C_{(AP,\,dry)}, \quad \Delta H_8 \quad (8)$$

$$C_{(AP,\,dry)} + O_2 \rightarrow CO_{2(g)} + yH_2O_{(l)}, \quad \Delta H_9 \quad (9)$$

$$C_s \rightarrow C_{(AP,\,cell)} + xO_2, \quad \Delta H_b \quad (10)$$

$$\Delta H_b = \Delta H_5 + \Delta H_6 + \Delta H_7 - (\Delta H_8 + \Delta H_9)$$

No way has been found for experimentally determining the enthalpy changes for reactions (7) and (8), so previous workers have assumed these values cancel [1]. Literature values exist for ΔH_5 [8] and ΔH_6 [9], so only ΔH_9 need be determined to calculate ΔH_b, the enthalpy change for Eq. (4) or (10). ΔH_9 is estimated as the heat of combustion of newly grown tissue.

The Composition method for finding the enthalpy change of anabolism relies on Thornton's rule. Thornton found the heat of combustion for hydrocarbons is proportional to the amount of oxygen consumed during combustion [10]. Shortly after, the rule was found to hold true for nearly all organic compounds, thus allowing estimation of the enthalpy change of oxidizing an organic compound to be based on the number of electrons transferred to oxygen [1]. The constant in Thornton's rule varies by a few percent depending on the presence and amount of O, P, N, and S in the compound [11].

In composition analysis, the percentage of carbon, hydrogen, nitrogen, sulfur, and ash in the biomass are measured and the percentage of oxygen is assumed to be the remainder. The degree of reduction, γ, is calculated from the composition

$$\gamma = 4c + h - 2x + kn + sy \quad (11)$$

where c, h, x, n, and y are the concentrations of carbon, hydrogen, oxygen, nitrogen, and sulfur respectively in units of mol g_{tissue}^{-1}. The value of k depends on the oxidation state of nitrogen; k equals –3 for N in NH_3 and proteins; s depends on the oxidation state of sulfur. Applying Thornton's rule, the enthalpy of combustion of the biomass (in kJ mol^{-1} of electrons) is found with Eq. (12) [12]:

$$\Delta H_9 = -115.4\gamma \quad (12)$$

The calculated enthalpy of combustion is then used in the thermodynamic cycle, Eqs. (5)–(10). Beyond the assumption of Thornton's rule, the same assumptions apply in this method as in the combustion method.

Growth and metabolism analysis and growth efficiency analysis are based on metabolic rate measurements and growth properties of living plant tissue. In the Growth and Metabolism method, the anabolic heat rate ($R_{10}\,\Delta H_b$, C mol $(s\,g)^{-1}$ tissue × mJ C mol^{-1}) is determined as the difference between the heat rate from respiratory metabolism (R_q, mJ $(s\,g)^{-1}$ tissue) and the heat rate of catabolism ($R_{CO_2}\,\Delta H_{CO_2}$, C mol $(s\,g)^{-1}$ tissue × mJ C mol^{-1}).

$$R_{10}\,\Delta H_b = -R_q - R_{CO_2}\,\Delta H_{CO_2} \quad (13)$$

Treating anabolism as defined in Eqs. (4) and (10); all CO_2 produced during metabolism is attributed to the catabolic reaction. Both R_q and R_{CO_2} can be measured by isothermal calorimetry [2]. ΔH_{CO_2} is the enthalpy change of catabolism mol^{-1} of CO_2 and is equal to $(\Delta H_5 + \Delta H_6 + \Delta H_7)$. ΔH_5 and ΔH_6 can be measured directly by calorimetry, but ΔH_7 must be assumed negligible. ΔH_5 may also be estimated from Thornton's rule. ΔH_b is then calculated as the ratio $\Delta H_b\,R_{10}/R_{SG}$ by assuming that R_{10} is equal to the specific growth rate, R_{SG}. (Note that only the product $\Delta H_b\,R_{10}$ is measured, ΔH_b and R_{10} are not separated.) R_{SG} (in units of reciprocal time) is evaluated from measurements of length, area, or dry mass of growing plant tissue over time.

R_{SG} is calculated by fitting growth data to an equation of the form $\ln(\text{size}) = f(t)$. Taking the derivative with respect to time then provides an equation for the specific growth rate (e.g. $m^{-1}\,dm/dt$ where m is dry mass) as a function of the age of the plant or tissue [13].

The Growth and Efficiency method relies on the same idea and the same data as the Growth and Metabolism method except that growth yield is measured instead of growth rate. Eq. (1) defines the growth yield ε as the fraction of substrate carbon converted to anabolic products. In literature on plant physiology, ε is known as the substrate carbon conversion efficiency and should not be confused with a growth

yield defined to include only growth metabolism and excluding maintenance respiration [6]. From Eq. (1) we can write,

$$\varepsilon = \frac{R_{10}}{R_{CO_2} + R_{10}} \tag{14}$$

Combining Eq. (14) with Eq. (13) to eliminate R_{10} gives

$$\frac{R_q}{R_{CO_2}} = -\Delta H_{CO_2} - \Delta H_b \frac{\varepsilon}{1-\varepsilon} \tag{15}$$

The value of ε is determined from measurement of the carbon balance [14,15]. For example, by first measuring the total amount of carbon in a seed, then growing the plant in the dark so that no photosynthesis occurs, and finally measuring the total amounts of carbon remaining in the seed and in the plant [14]. The value of ε is equal to the carbon in the plant divided by the total carbon lost from the seed. Carbon balances can also be done on mature plants by measuring carbon uptake, carbon loss, and carbon retained in the plant [15].

The assumption necessary for the last two methods is different from those necessary for composition and combustion analysis. Combustion analysis must assume that the difference between ΔH_7 and ΔH_8 is negligible. Composition analysis assumes Thornton's rule, and in addition must assume that $(\Delta H_6 + \Delta H_7 - \Delta H_8)$ is negligible. On the other hand, the Growth and Metabolism and Growth and Efficiency methods must assume that growth rate is proportional to the anabolic rate or that ε accurately reflects the fraction of substrate carbon converted to anabolic products.

2. Experimental

Oats (*Avena sativa*) were grown in a growth chamber at 15, 20, or 25 °C. Seedlings were grown for several days, with more seeds being planted consecutively at the same time each day. Then, all on the same day, the average lengths of the oat shoots were measured with a ruler to determine the growth in terms of length, and 10 shoots of each planting were harvested, dried, and weighed to determine growth in terms of mass. Metabolic heat and CO_2 rates (R_q and R_{CO_2}, respectively) also were measured on the same day. R_q and R_{CO_2} were measured with CSC model 4100 MCDSC and Hart Scientific model 7707 calorimeters operated in the isothermal mode. These calorimeters have one reference cell and three sample cells. Samples are contained in sealed, 1 ml, Hastelloy ampules [2]. For heat and CO_2 rate measurements, whole shoots were cut from the seed, then cut into 1 cm lengths and placed into the ampules. Samples were allowed to equilibrate for 20–30 min for heat rate determination. Then a 40 μl vial of 0.4 M NaOH was added to each ampule and the ampules again equilibrated in the calorimeters for a second heat rate measurement. The NaOH vials were then removed, and the ampules returned to the calorimeter and equilibrated for a third heat rate measurement. Measurements were made in the calorimeter at the growth temperature. Samples were then dried overnight in a 70 °C vacuum oven to determine the dry weight. To calculate R_{CO_2}, the enthalpy change for the reaction of CO_2 with the NaOH solution was taken as –108.5 kJ mol^{-1} at all temperatures [2].

For heat of combustion measurements, plant tissue was dried in a vacuum oven at 70 °C for at least 24 h and then stored in a closed container with Drierite. The dried tissue was then ground in a coffee grinder and pressed into 1 g pellets for combustion in a Parr 1621 oxygen bomb calorimeter. Before each combustion, the crucible and pellet were weighed separately, the inside of the bomb was moistened with 2 ml of water, and the bomb was flushed with O_2 to minimize the amount of nitrogen combusted. After the combustion, the crucible was again weighed; the difference between the weight of the crucible before and after combustion is the ash weight. To determine additional heat given off by combustion of nitrogen and sulfur in the sample, the inside of the bomb was washed and the washings were collected and diluted to the equivalent of 10 l. Soluble nitrate and sulfate concentrations were determined by ion chromatography. Sample nitrate and sulfate concentrations were small and their contribution to the heat of combustion negligible. ΔH_9 is calculated by applying baseline, temperature, and fuse corrections to the value for the heat of combustion given by the calorimeter, Q_9.

$$Q_9\ (\text{kJ g}^{-1}) = \frac{\text{heat of combustion} - \text{fuse correction} - \text{baseline correction} - \text{temperature}}{\text{volume correction}} \tag{16}$$

Q_9 in kJ g^{-1} is then converted to ΔH_9 in kJ C mol^{-1} by Eq. (17).

$$\Delta H_9 = \left(\frac{m\,\Delta Q_9 - \Delta nRT}{m}\right) \times \left(\frac{g\ \text{sample}}{g\ \text{C}} 12.01\ \text{g C mol}^{-1}\right) \quad (17)$$

where m is the mass of the sample before combustion, n is the number of moles of carbon in the sample, R is the universal gas constant, and T is the temperature in Kelvin (302 K). The mass of the sample is adjusted for buoyancy. The first term in Eq. (17) converts the ΔE measured at constant volume to ΔH, and the second term converts the result from kJ g^{-1} to kJ C mol^{-1}.

The composition of ground plant tissue was determined with a LECO CHNS-932 Analyzer.

3. Results

Table 1 gives ΔH_9 values and equations for the growth of oat seedling shoots. Fig. 1 shows the plots of $\Delta H_b R_{10}$ against R_{SG} from which the ΔH_b values were derived by the Growth and Metabolism method. Table 2 gives values of ΔH_b for oat shoots by three of the methods described above. The Growth and Efficiency method was previously applied to maize (*Zea maize*) seedlings [7], but could not be used with oats because of non-uniform seed. The value of ΔH_b for maize seedling shoots is essentially the same as that for oat shoots. Comparison of the data on oat shoots from the three methods used in this study shows that all three provide similar estimates of the enthalpy change of anabolism. The value of ΔH_b is affected by the age of the shoots, but not by the growth temperature within the range studied.

4. Discussion

Although the three methods require different assumptions, they agreed with each other within 95% confidence limits. Thus, we conclude that estimations made by each method adequately represent actual values. However, the Metabolism and Growth analysis method clearly has the smallest uncertainty in the ΔH_b values. The combustion data indicate the composition of the youngest tissue is different from the composition of older plant tissue. Tissue younger than two

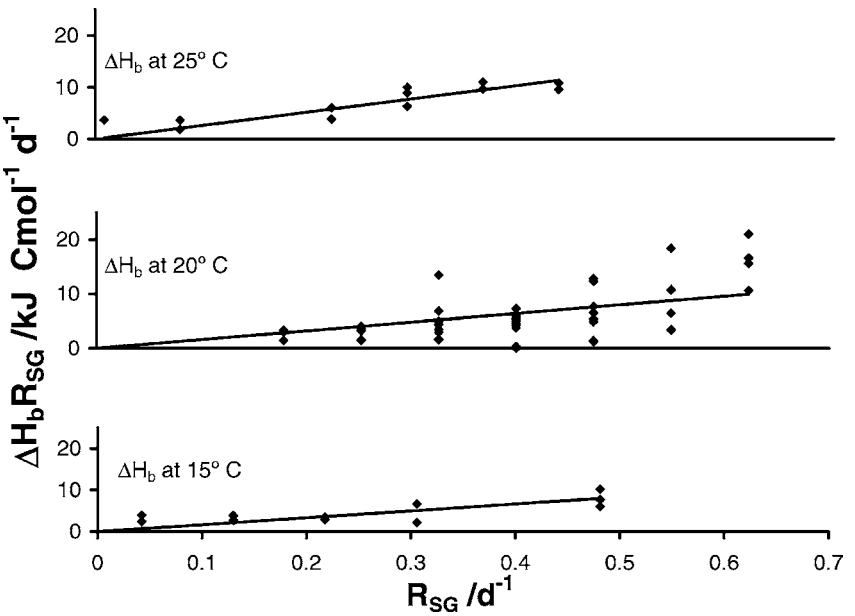

Fig. 1. Plots of the growth rate calculated from measurements of heat and CO_2 production rates ($\Delta H_b R_{10}$, see Eq. (13)) vs. the directly measured dry mass growth rate (R_{SG}). The slope of a line through the origin equals ΔH_b in kJ C mol^{-1}.

Table 1
Heat of combustion and growth of shoots of oat seedlings

		$-\Delta H_q$ (kJ C mol)$^{-1}$ [a]
Composition analysis		
15 °C	Mean[b]	490 ± 23 (4)
25 °C	Mean[c]	477 ± 14 (7)
Combustion analysis		
15 °C	Mean	493 ± 22 (13)
20 °C	Mean	489 ± 21 (26)
	Old tissue[d]	482 ± 18 (21)
	Young tissue	517 ± 6 (5)
25 °C	Mean	509 ± 21 (31)
	Old tissue	501 ± 18 (25)
	Young tissue	535 ± 22 (8)
Metabolism and growth analysis (growth equation)		
15 °C	$y_1 = -0.0439x^2 + 0.5692x + 0.1281$[e]	
	$y_2 = -0.0391x^2 + 0.5513x + 0.3795$[f]	
20 °C	$y_1 = -0.037x^2 + 0.6971x - 0.5426$	
	$y_2 = -0.0553x^2 + 0.7895x - 0.0833$	
25 °C	$y_1 = -0.0359x^2 + 0.5113x + 0.3075$	
	$y_2 = -0.0444x^2 + 0.6125x + 0.7289$	

[a] Error limits are given as standard deviations with number of determinations given in parentheses.
[b] Calculated from mean mass percentages of C = 44.8 ± 1.4, H = 6.1 ± 0.2, N = 5.3 ± 1.1, S = 0.5 ± 0.1, and ash = 11 ± 7.
[c] Calculated from mean mass percentages of C = 45.0 ± 1.8, H = 6.0 ± 0.3, N = 4.6 ± 0.9, S = 0.5 ± 0.1, and ash = 8 ± 3.
[d] Old tissue is older than 2 days post-emergence.
[e] y_1 is ln (average dry mass per shoot in mg); x is the number of days post-emergence.
[f] y_2 is the ln (average shoot length in cm).

Table 2
Enthalpy change for the anabolic reaction, $C_{substrate} \rightarrow C_{anabolic\ product} + xO_2$, as determined by four different methods

		ΔH_b [a] (kJ C mol)$^{-1}$ [b]
Composition analysis		
15 °C	Mean	20 ± 23 (4)
25 °C	Mean	7 ± 14 (7)
Combustion analysis[c]		
15 °C	Mean	24 ± 22 (13)
20 °C	Mean	19 ± 21 (26)
	Old tissue[d]	12 ± 18 (21)
	Young tissue	47 ± 6 (5)
25 °C	Mean	39 ± 21 (31)
	Old tissue	31 ± 18 (25)
	Young tissue	65 ± 22 (8)
Metabolism and growth analysis[e]		
15 °C	Mean	
	R_{SG} (mass)	17 ± 2
	R_{SG} (length)	16 ± 2
20 °C	Old tissue	
	R_{SG} (mass)	15 ± 2
	R_{SG} (length)	13 ± 1
	Young tissue	
	R_{SG} (mass)	20 ± 3
	R_{SG} (length)	19 ± 3
25 °C	Mean	
	R_{SG} (mass)	25 ± 1
	R_{SG} (length)	22 ± 1
Growth and efficiency analysis (maize)		
30 °C	Mean	26 ± 16 (3)

[a] $\Delta H_b = -470 - \Delta H_q$ from Table 1.
[b] Error limits are given as standard deviations with number of determinations given in parentheses.
[c] Average value for carbon content taken from composition analysis is 44.9 ± 1.7 mass%.
[d] Old tissue is older than 2 days post-emergence.
[e] R_{SG} is the specific growth rate calculated from the derivative of the growth equations in Table 1.

days may have a higher heat of combustion than older tissue. The plot of data taken at 20 °C in Fig. 1 also suggests ΔH_b may be larger for very young tissue.

The four methods vary in the ease of performing the experiments, the time required, and the assumptions that must be made. Combustion analysis is inexpensive and rapid. Each sample requires only about 20 min to run and uses inexpensive supplies. These advantages are perhaps the reasons this method is the most commonly used. The greatest disadvantages are (a) the assumption that the enthalpy change for converting aqueous sugar to carbon substrate and the enthalpy change for drying the plant tissue are negligible or cancel, and (b) the uncertainty in how age and growth temperature affect the results. Although the effects of age and growth temperature were measured in this study, their effects are usually assumed to be negligible.

Composition analysis requires these same assumptions and has further problems that increase the uncertainty. One of these problems is the necessary determination of the percentage of oxygen in the sample. Because of the difficulty of reliably measuring oxygen, only carbon, hydrogen, nitrogen, sulfur and ash are determined. Oxygen is assumed to be the

remaining component. The ash of unknown composition contributes about 10% of the mass of the sample and causes the majority of the uncertainty in the oxygen content. Composition analysis requires more expensive supplies than combustion analysis. However, at 30 samples per hour, composition analysis is faster.

The major advantage of Metabolism and Growth and Growth and Efficiency analyses is that ΔH_b is derived from heat and CO_2 rates measured on living tissue rather than from measurements on dried tissue. These methods are much better suited for studies of the effects of environmental and physiological variables on plant metabolism. The major disadvantage of these methods is their relative slowness. Each sample requires about 2 h in the calorimeter. A disadvantage peculiar to the Metabolism and Growth method is that the anabolic rate is calculated by subtracting numbers of similar magnitude (see Eq. (13)). The resulting value for $R_{10}\,\Delta H_b$ is typically an order of magnitude less than the measured quantities, thus increasing the relative uncertainty by an order of magnitude. An advantage of Growth and Efficiency analysis is that the relative uncertainty is smaller because the ratio rather than difference of measured values is used to calculate ΔH_b (see Eq. (15)). However, Growth and Efficiency analysis requires that ε values be determined instead of growth rates. Determinations of ε are more difficult, tedious, and time consuming than measurements of growth rate and are not applicable to all situations. In this method, the uncertainty in ε is the major source of uncertainty in ΔH_b.

Because the heat effect of anabolism is endothermic, measured metabolic heat rates of plant tissues are less than would be calculated by application of Thornton's rule to CO_2 rates, i.e. by indirect calorimetry based on measured CO_2 rates. Neglecting anabolism in CO_2 based energy balances thus causes an error of about 10%. The actual error of course depends on conditions because reactions 2 and 4 occur in the ratio $(1-\varepsilon)/\varepsilon$ and ε ranges from zero to a maximum of about 0.9 depending on conditions and the composition of the anabolic products. Energy balances based on O_2 consumption rates do not contain this error, i.e. anabolism contributes nothing to the enthalpy, because then anabolism is described by reaction 3 for which the enthalpy change is approximately zero. Because the total O_2 rate is assigned to catabolism, Thornton's rule or the oxycaloric ratio gives the correct indirectly calculated metabolic heat rate. Note that there is no dependence on conditions of the heat liberated per O_2 consumed, i.e. the heat per O_2 is independent of ε.

Although the enthalpy change for anabolism is useful in modeling growth and provides some insight into plant respiratory metabolism, determining the Gibb's free energy change would be even more useful. Therefore the next logical step is to find a method for determining the entropy change of anabolism, which can then be combined with the enthalpy change to calculate the change in Gibb's free energy for plant growth.

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