# Biochemical Model of C3 Photosynthesis

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# Chapter 9

# Biochemical Model of $C_3$ Photosynthesis

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*A. Laisk, L. Nedbal and Govindjee (eds.), Photosynthesis in silico: Understanding Complexity from Molecules to Ecosystems, pp. 209–230.*

## Summary

A brief overview of the $C_3$ photosynthesis model described by Graham Farquhar, Susanne von Caemmerer and Joseph Berry is provided. The model was designed to help interpret gas exchange measurements of $CO_2$ assimilation of leaves and to represent $C_3$ photosynthesis in other systems such as stomatal control and the $CO_2$ concentrating function of $C_4$ photosynthesis. It can predict steady state $CO_2$ assimilation rates under different environmental conditions of light intensity, temperature, $CO_2$ and $O_2$ concentrations. The model is based on Rubisco's kinetic properties and the rate of $CO_2$ assimilation is given as the minimum of either a Rubisco limited rate, where the substrate ribulose bisphosphate (RuBP) is saturating, or a chloroplast electron transport (or RuBP regeneration) limited rate. The model can be used to estimate in vivo Rubisco activity and chloroplast electron transport capacity. This however requires information on the partial pressure of $CO_2$ in the chloroplast which has been shown to be less than that in the intercellular airspaces. The temperature dependence of Rubisco kinetic constants is based on both in vitro and in vivo measurements of these parameters. The temperature dependence of the maximum chloroplast electron transport has also been parameterized from both in vivo and in vitro measurements; however the fact that thermal acclimation changes thylakoid properties and the temperature dependence of chloroplast electron transport prevents a unique parameterization. Further studies are required to investigate whether $CO_2$ assimilation rate at temperature extremes is limited by Rubisco and its activation state or by electron transport capacity in order to improve the model's accuracy under these conditions.


## I. Introduction

In this chapter we discuss key attributes of the $C_3$ photosynthesis model first described by G. Farquhar, S. Von Caemmerer and J. Berry (Berry and Farquhar, 1978; Farquhar et al., 1980; Von Caemmerer and Farquhar, 1981; Farquhar and Von Caemmerer, 1982). This model was designed to help interpret gas exchange measurements of $CO_2$ assimilation of leaves. It is used to predict steady state $CO_2$ assimilation rates under different environmental conditions of light intensity, temperature, $CO_2$ and $O_2$ partial pressures ($pCO_2$ and $pO_2$) and can be embedded in larger models of the global carbon cycle and of land surface feedbacks on climate. It is also frequently used in reverse to predict underlying biochemical properties of leaves from gas exchange measurements (Long and Bernacchi, 2003).

Simplicity is the key to making this type of model useful. This requires careful consideration of the detail that needs to be incorporated and what can safely be left out. It is important to keep the number of parameters that have to be assigned to a minimum. This has been the guiding principle of the design of the model discussed in this chapter and sets it apart from other models that seek to incorporate a larger number of biochemical steps involved in $CO_2$ assimilation with the purpose of studying regulation of metabolism (Laisk and Oja, 1998; Laisk et al., 2006; Zhu et al., 2007). The model is generally most useful in describing steady state $CO_2$ assimilation rates, although it has also been incorporated into models describing $CO_2$ uptake transients during sun flecks (Pearcy et al., 1997).

The model is based on the kinetic properties of ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco, EC 4.1.1.39) and an interesting historical perspective of Rubisco research and discoveries is given by Portis and Parry (2007). The importance of Rubisco in determining the rate of photosynthesis had been inferred early on from correlations between photosynthetic rate and the amount of Rubisco protein in leaves (Björkman, 1968; Wareing et al., 1968; Bowes et al., 1971; Bowes and Ogren, 1972). But perhaps the pivotal event was the discovery that $O_2$ was a competitive inhibitor of $CO_2$ fixation, an alternative substrate leading to the side reactions that fuel photorespiration (Bowes et al., 1971; Bowes and Ogren, 1972). This led to the development of photosynthetic models based on Rubisco kinetic properties (Laisk, 1970, 1977; Laing et al., 1974; Peisker, 1974, 1976; Hall and Björkman, 1975). For example, Laing et al.

(1974) and Peisker (1974) showed that a linear dependence of the $CO_2$ compensation point could be explained from Rubisco's kinetic properties. The impact of Rubisco kinetic properties on $C_3$ photosynthesis has been elegantly highlighted in recent studies where the $C_3$-model has been used to characterize Rubisco kinetic properties in transgenic plants expressing mutated Rubisco (Whitney et al., 1999; Whitney and Andrews, 2001; Sharwood et al., 2008).

The model continues to be used almost unchanged from when it was conceived in the late 1970s and early 1980s and it has served as a template for development of other models (Collatz et al., 1991, 1992; Sellers et al., 1996a). The key innovation of this model stemmed from the recognition that losses in coupling between the light dependent reactions and the carbon reactions are minimal. Therefore, the overall rate of photosynthesis could be approximated as the minimum of the potential rates of these processes taken separately (Eq. 9.20). The basis for this efficient coupling is still not well understood (Woodrow and Berry, 1988). Perhaps most surprisingly the equations relating chloroplast electron transport rate to light intensity are still treated empirically in whole leaf models and several different equations are in use (Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Farquhar and Wong, 1984; Collatz et al., 1990, 1991, 1992; Long and Bernacchi, 2003). Equations relating ATP production to chloroplast electron transport rate continue to change according to new understanding of the proton requirements of ATP production. Sharkey and co-workers drew attention to a third limitation that may come into play by the rate of triose phosphate export (Sharkey, 1985a; Harley and Sharkey, 1991). There are however several questions that deserve further attention. For example, it is important to know what the $CO_2$ partial pressure ($pCO_2$) is at the site of Rubisco carboxylation and what defines the conductance of $CO_2$ diffusion from intercellular airspace to the chloroplast stroma. This research area is currently receiving considerable attention (Evans and Von Caemmerer, 1996; Terashima et al., 2006; Flexas et al., 2007a, b; Warren, 2007). This question is of particular importance in biotechnological research attempting to redirect photorespiratory $CO_2$ release to the chloroplast (Kebeish et al., 2007) and to attempts at introducing a $C_4$ type $CO_2$ concentrating mechanism into $C_3$ cells where one would like to be able to manipulate $CO_2$ diffusion properties of membranes (Matsuoka et al., 2001; Von Caemmerer, 2003; Mitchell and Sheehy, 2006). Understanding what limits $CO_2$ fixation at extreme temperatures has also become an important question in the endeavor to predict $CO_2$ assimilation rates in these environments. There is at present considerable debate on whether the capacity of chloroplast electron transport to regenerate RuBP or the activation state of Rubisco provide the primary limitation and it is clear that we need a better understanding how Rubisco activation state is modulated by environmental variables (Weis and Berry, 1988; Crafts-Brandner and Salvucci, 2000; Wise et al., 2004; Cen and Sage, 2005; Yamori et al., 2005, 2006b, 2008).

The photosynthesis model described here provides a set of hypotheses brought together in a quantitative form that can be used as a research tool to design and interpret both field and laboratory based experiments. Both the current availability of transgenic plants with biochemical impairments and the range of Arabidopsis knockout mutants and the interest in improving $CO_2$ assimilation rates through genetic manipulation are providing interesting new tests and applications for modeling photosynthesis (Von Caemmerer, 2000, 2003; Raines, 2003, 2006). Newer portable gas exchange systems have opened up opportunities for ecophysiological studies (Björkman et al., 1972; Ellsworth et al., 2004; Wright et al., 2004).

## II. The Rate Equations of $CO_2$ Assimilation

Farquhar et al. (1980) showed that $CO_2$ assimilation rate $A$ was given by

$$A = V_c - 0.5V_o - R_d, \tag{9.1}$$

where $A$ denotes net $CO_2$ assimilation rate, $V_c$ and $V_o$ are the carboxylase and oxygenase rates of Rubisco and $R_d$ denotes day respiration, which comprises mitochondrial $CO_2$ release occurring in the light other than that of photorespiration. Equation (9.1) can be rewritten in a simpler

form as:

$$A = V_c\,(1 - 0.5\phi) - R_d, \tag{9.2}$$

where $\phi$ is the ratio of oxygenation to carboxylation rates, $V_o/V_c$. Rubisco, located in the chloroplast stroma, catalyses the competing reactions of the carboxylation and the oxygenation of ribulose bisphosphate (Andrews and Lorimer, 1987). The carboxylation of RuBP is the first step of the photosynthetic carbon reduction (PCR) cycle and the carboxylation of 1 mol of RuBP leads to the formation of 2 mols of phosphoglycerate (PGA). The oxygenation of 1 mol of RuBP on the other hand leads to the formation of 1 mol of PGA and 1 mol of phosphoglycolate (PGly). We assume that the recycling of 1 mol of PGly in the photorespiratory carbon oxidation (PCO) cycle results in the release of 0.5 mol of $CO_2$ in the mitochondria (Fig. 9.1). It has been suggested that the release may be less than 0.5 and there continue to be reports of complete oxidation of glycolate as proposed by Israel Zelitch (Hanson and Peterson, 1986; Zelitch, 1989; Harley and Sharkey, 1991).

The ratio of oxygenation to carboxylation rate, $\phi$, is determined solely by the kinetic constants of Rubisco:

$$\phi = \frac{V_o}{V_c} = \left(\frac{1}{S_{c/o}}\right)\frac{O}{C} = \left(\frac{V_{o\,max}}{K_o}\,\frac{K_c}{V_{c\,max}}\right)\frac{O}{C}, \tag{9.3}$$

where $S_{c/o}$ is the relative specificity of Rubisco and $C$ and $O$ are the chloroplastic $pCO_2$ and $pO_2$; $V_{cmax}$, $V_{omax}$, $K_c$ and $K_o$ are the maximal rates and the Michaelis–Menten constants of carboxylation and oxygenation, respectively.

Inspection of Eq. (9.2) shows that when $R_d = 0$, $A = 0$ when $\phi = 2$. The chloroplast $pCO_2$ at which this occurs has been named $\Gamma^*$ (Laisk, 1977; Laisk and Oja, 1998) and from the above equation it follows that

$$\Gamma^* = \frac{0.5O}{S_{c/o}} = \gamma^* O \tag{9.4}$$

and

$$\phi = \frac{2\Gamma^*}{C}. \tag{9.5}$$

Substituting this into Eq. (9.2) one can show that

$$A = \left(1 - \Gamma^*/C\right) V_c - R_d. \tag{9.6}$$

It is assumed that some mitochondrial respiration ($R_d$) continues in the light although not necessarily at the rate that occurs in the dark (Brooks and Farquhar, 1985; Atkin et al., 1998; Hoefnagel et al., 1998). It has also been suggested that the rate of day respiration may depend on the rate of photorespiration (Bykova et al., 2005; Tcherkez et al., 2008). If this were indeed the case and the two were related in a predictable way then Eqs. (9.1), (9.2), (9.6) would need to be modified to reflect this.

The rate of photorespiration ($V_{phr}$) is half the rate of oxygenation and is given by $(\Gamma^*/C)V_c$ and can be calculated from gas exchange measurements by the following equation:

$$V_{phr} = \frac{\Gamma^*}{C - \Gamma^*}\,(A + R_d)\,. \tag{9.7}$$

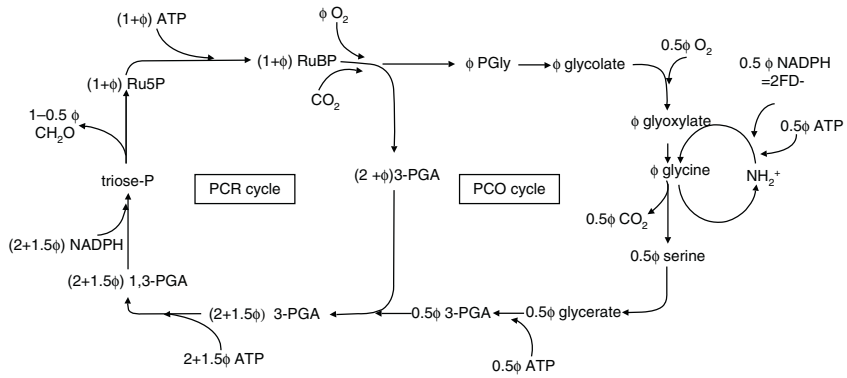


*Fig. 9.1.* Stoichiometry of the photosynthetic carbon reduction (PCR) cycle and photorespiratory carbon oxidation (PCO) cycle ($\phi$ denotes the ratio of Rubisco oxygenation to carboxylation)

The basis of the Rubisco limited part of the model is given by Eqs. (9.1)–(9.3). To complete this part of the model the dependencies of Rubisco velocity on $pCO_2$, $pO_2$, irradiance and temperature need to be added. Rubisco occurs at high concentration in the chloroplast stroma relative to the Michaelis–Menten constant for its substrate RuBP and it was the special kinetics that apply under these conditions that allowed the simple binary formulation of $CO_2$ assimilation rate as being either RuBP saturated, or limited by the rate of RuBP regeneration (Berry and Farquhar, 1978; Collatz, 1978; Farquhar, 1979; Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Collatz et al., 1990).

### *A. RuBP Saturated (or Rubisco Limited) $CO_2$ Assimilation Rate*

Since $O_2$ inhibits RuBP carboxylation competitively with respect to $CO_2$, the RuBP saturated carboxylation rate is given by

$$W_c = \frac{C V_{c\max}}{C + K_c\left(1 + O/K_o\right)}, \qquad (9.8)$$

(Bowes and Ogren, 1972; Badger and Andrews, 1974). Using Eq. (9.8) to substitute for $V_c$ in Eq. (9.6) yields an expression for the RuBP saturated rate of $CO_2$ assimilation,

$$A_c = \frac{(C - \Gamma^*)\, V_{c\max}}{C + K_c\left(1 + O/K_o\right)} - R_d. \qquad (9.9)$$

Because of its dependence on the maximum Rubisco activity ($V_{cmax}$), $A_c$ is also often called the Rubisco limited rate of $CO_2$ assimilation.

The Rubisco limited rate of $CO_2$ assimilation suggests that the dependence of $CO_2$ assimilation on $pCO_2$ should have a Michaelis–Menten form. However as noted by several researchers (Laisk and Oja, 1974; Lilley and Walker, 1975; Ku and Edwards, 1977) $CO_2$ assimilation rate saturates more quickly than can be predicted from the RuBP saturated $CO_2$ assimilation rate alone. This can be seen in the example of a $CO_2$ response curve for $CO_2$ assimilation rate of a tobacco leaf (Fig. 9.2). In the leaf of a transgenic tobacco with an antisense construct to the small subunit of Rubisco the amount of Rubisco per leaf area has been reduced with little alteration to other chloroplast components. In this case the rate of

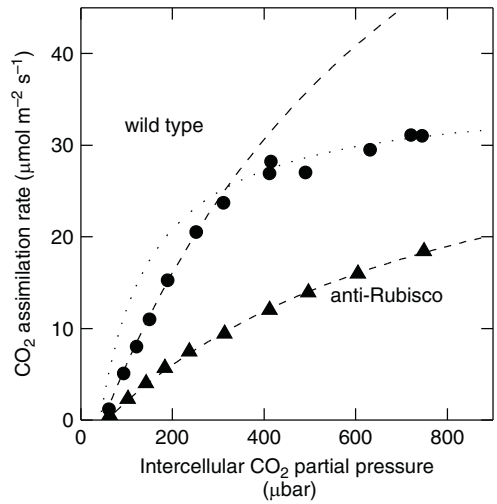


*Fig. 9.2.* $CO_2$ assimilation rate, $A$, as a function of intercellular $pCO_2$ for a leaf of a wild type (●) and transgenic tobacco with reduced amount of Rubisco (▲). Measurements were made at an irradiance of 1,000 μmol quanta $m^{-2}\,s^{-1}$ and a leaf temperature of 25 °C. The dashed lines are $A$ predicted from the Rubisco limited rate (Eq. 9.9). The dotted line is $A$ predicted from the RuBP regeneration (electron transport) limited rate (adapted from Von Caemmerer et al., 1994)

$CO_2$ assimilation can be modeled solely by the Rubisco limited rate.

### *B. RuBP Regeneration Limited (or Electron Transport Limited) $CO_2$ Assimilation Rate*

The synthesis of RuBP requires energy in the form of NADPH and ATP and the rate of the Rubisco reaction may become limited by the supply of RuBP. Farquhar (1979) showed that the partitioning of RuBP to carboxylation and oxygenation follows the same kinetics (Eq. 9.3) under limiting RuBP supply. The consumption rates of ATP and NADPH required to regenerate RuBP at the rate of $(1 + \phi)V_c$ were derived from the stoichiometries given in Fig. 9.1. Summing the requirements,

$$\text{the rate of NADPH consumption} = (2 + 2\phi)V_c \qquad (9.10)$$

and

$$\text{the rate of ATP consumption} = (3 + 3.5\phi)V_c \qquad (9.11)$$

(Berry and Farquhar, 1978; Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Von Caemmerer, 2000).

The reduction of $NADP^+$ to $NADPH + H^+$ requires the transfer of two electrons through the whole electron transport chain. The rate of whole chain electron transport, required to regenerate RuBP can be calculated from the rate of NADPH consumption (Eq. 9.10) as:

$$(4 + 4\phi)V_c = (4 + 8\Gamma^*/C)V_c \qquad (9.12)$$

and the electron transport limited rate of RuBP regeneration is given by

$$W_j = \frac{J}{(4 + 8\Gamma^*/C)}, \qquad (9.13)$$

where $J$ is the potential electron transport rate, which depends on irradiance.

Light driven electron transport is coupled to the transfer of protons across the thylakoid membrane into the lumen, but neither the stoichiometry of the $H^+/e^-$ ratio or the number of protons required to generate one ATP are known with certainty and may well be flexible. We therefore use the NADPH limited expressions in this chapter. For a more detailed discussion on the formulation for an ATP limited rate of electron transport see Von Caemmerer (2000) or Yin et al. (2004) and Chapter 11 by Xinyou Yin, Jeremy Harbinson and Paul Struik of this book.

Substituting $W_j$ for $V_c$ in Eq. (9.6) yields an expression for the RuBP regeneration (or electron transport) limited rate of $CO_2$ assimilation:

$$A_j = \frac{(C - \Gamma^*)J}{4C + 8\Gamma^*} - R_d. \qquad (9.14)$$

The $CO_2$ dependence of $A_j$ is shown in Fig. 9.2 by the dotted line. Here the assumption is made that chloroplast electron transport rate is limiting the rate of RuBP regeneration rather than the enzymes involved in the regeneration of RuBP such as FBPase or SBPase. Studies with transgenic tobacco plants with antisense reductions in the content of chloroplast cytochrome *bf* complex show a close linear relationship between the cytochrome $b_6f$ content and $CO_2$ assimilation rate, in support of this hypothesis (Price et al., 1995, 1998; Ruuska et al., 2000a; Baroli et al., 2008) and an example is shown in Fig. 9.3. Studies with

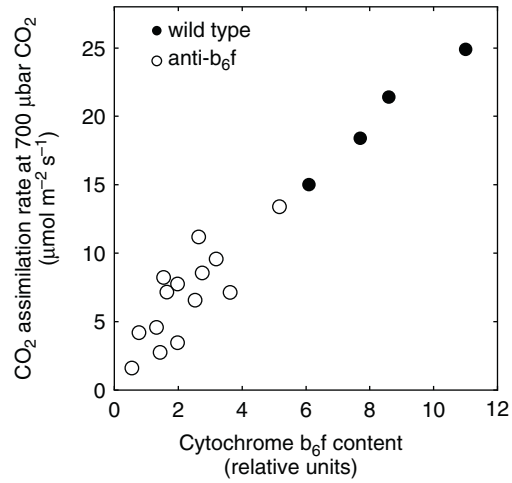


*Fig. 9.3.* $CO_2$ assimilation rate versus chloroplast cytochrome $b_6f$ content in wild type and transgenic tobacco with an antisense construct against the Rieske FeS protein of the chloroplast cytochrome $b_6f$ complex. Gas exchange measurements were made at 1,000 µmol quanta $m^{-2}\,s^{-1}$, 700 µbar $CO_2$ and a leaf temperature of 25 °C (data from Ruuska et al., 2000a)

transgenic plants with reductions in GAPDH, FBPase, SBPase, and phosphoribulokinase have also confirmed that assuming an electron transport limitation is a reasonable assumption under most circumstances (Stitt and Sonnewald, 1995; Raines, 2003). However there are also some studies that show enhanced $CO_2$ assimilation rates in transgenic plants overexpressing SBPase (Miyagawa et al., 2001; Lefebvre et al., 2005; Feng et al., 2007; Chapter 15 of this book by Ian E. Woodrow). It is possible to write expressions for limitations of $CO_2$ assimilation rate by any of the enzymes involved in RuBP regeneration following the stoichiometries given by Farquhar and Von Caemmerer (1982), Brooks and Farquhar (1985) and Von Caemmerer (2000). It is important to note that if these reactions were limiting $CO_2$ assimilation rate the $CO_2$ dependence would be different to that if electron transport limited the rate.

### *C. Light Intensity Dependence of Electron Transport Rate*

At present the following empirical equation (Farquhar and Wong, 1984) is used to link potential electron transport rate, $J$, to irradiance:

$$\theta J^2 - J(I_2 + J_{max}) + I_2 J_{max} = 0, \qquad (9.15)$$

where $I_2$ is the useful light absorbed by PS II and $J_{max}$ is the maximum electron transport rate and $\theta$ is an empirical curvature factor (0.7 is a good average value, Evans, 1989). $I_2$ is related to incident irradiance $I$ by

$$I_2 = I \cdot abs \cdot (1 - f)/2. \qquad (9.16)$$

In sunlight the absorptance ($abs$) of leaves is commonly about 0.85 and $f$ is to correct for spectral quality of the light ($f \sim 0.15$, Evans, 1987). Ögren and Evans (1993) give a detailed discussion of the parameters of Eq. (9.16). The denominator 2 is because we assume half the light absorbed needs to reach each photosystem. The equation can be solved for $J$ as follows

$$J = \frac{I_2 + J_{max} - \sqrt{(I_2 + J_{max})^2 - 4\theta I_2 J_{max}}}{2\theta}. \qquad (9.17)$$

This equation is a non-rectangular hyperbola with a smooth transition from light limitation ($J = I_2$) to light saturation ($J = J_{max}$), where $J_{max}$ is an upper limit to potential chloroplast electron transport determined by the components of the chloroplast electron transport chain. Support for this hypothesis of a limitation on the maximum capacity for RuBP regeneration is shown in Fig. 9.3 where $CO_2$ assimilation rate measured at high $pCO_2$ and high irradiance is correlated with the amount of cytochrome $b_6f$ content in tobacco plants were cytochrome $b_6f$ content has been reduced via antisense techniques (Price et al., 1998; Ruuska et al., 2000a; Baroli et al., 2008).

### *D. Export Limited $CO_2$ Assimilation Rate*

At high $CO_2$ partial pressure, particularly in combination with high irradiance, or low $O_2$ partial pressure or at low temperatures, the rate of $CO_2$ assimilation can sometimes be limited by the rate at which triose phosphates are utilized in the synthesis of starch and sucrose. Then

$$W_p = 3T_p/(1 - \Gamma^*/C) \qquad (9.18)$$

and $CO_2$ assimilation rate is given by

$$A_p = 3T_p - R_d, \qquad (9.19)$$

where $T_p$ is the rate of inorganic phosphate supply to the chloroplast, and equal to the triose phosphate export from the chloroplast (Farquhar and Von Caemmerer, 1982; Sharkey, 1985b; Harley and Sharkey, 1991). Under these conditions $A$ is insensitive to changes in $CO_2$ and $O_2$ partial pressure. For a detailed discussion see Harley and Sharkey (1991).

### *E. Summary of Rate Equations*

Equations (9.8), (9.13), (9.18) describe the basic $C_3$ model with

$$A = (1 - \Gamma^*/C) \cdot \min\{W_c, W_j, W_p\} - R_d, \qquad (9.20)$$

or using Eqs. (9.9), (9.14), (9.19)

$$A = \min\{A_c, A_j, A_p\}, \qquad (9.21)$$

when $C > \Gamma^*$. This is illustrated in Fig. 9.2 for wild type tobacco where the solid line shows the actual rate of $CO_2$ assimilation and the dashed line is the Rubisco limited rate $A_c$, and the dotted line is the electron transport limited rate $A_j$. A phosphate limitation rate for $A_p$ is not shown in this example (but see Von Caemmerer, 2000; Long and Bernacchi, 2003; Chapter 10 of this book by Carl J. Bernacchi, David Rosenthal, Carlos Pimentel, Stephen P. Long and Graham D. Farquhar).

In this form the model has discontinuities at the transitions between the different limitations. This can provide mathematical problems when the model is used as a submodel in other applications. The discontinuities can be smoothed using quadratic expressions (Kirschbaum and Farquhar, 1984; Collatz et al., 1991).

## III. Parameters and their Temperature Dependencies

Depending on the application of the model most of the parameter values can be assigned a priori leaving only $V_{cmax}$ and $J_{max}$ and $g_i$ (the conductance to $CO_2$ diffusion from intercellular airspace to the chloroplast, discussed in the next section) to be assigned anew.

### A. Rubisco Kinetic Constants

Kinetic constants of Rubisco are similar amongst $C_3$ species and it is common to use the same $K_c$, $K_o$, and $S_{c/o}$ for all higher plant $C_3$ species. There are however reports of variation of Rubisco kinetic parameters which may need to be considered in some applications of the model, although very few complete data sets exist at present (Sage, 2002; Galmes et al., 2005; Tcherkez et al., 2006; Kubien et al., 2008). Farquhar et al. (1980) used constants derived from in vitro measurements by Badger and co-workers. Von Caemmerer et al. (1994) used transgenic tobacco with reduced amounts of Rubisco to determine Rubisco kinetic constants in vivo at 25°C (Table 9.1). These values were in good agreement with in vitro measurements made in tobacco (Whitney et al., 1999). Brooks and Farquhar (1985) measured $\Gamma^*$ as a function of temperature and found that spinach had a slightly higher value than wheat, a result borne out by subsequent specificity measurements in vitro (Kane et al., 1994). It is important to note that $S_{c/o}$, $K_c$ and $K_o$ are linked (Eq. 9.3) to assure consistency when assigning values.

The maximum rate $V_{cmax}$ is dependent on the amount and the activation state of Rubisco protein present in the leaf and will vary from leaf to leaf. Rubisco has a molecular weight of 550 kDa and eight catalytic sites per molecule. To be catalytically competent Rubisco's sites must be activated. This requires the carbamylation of a lysine residue within the catalytic site to allow the binding of a $Mg^{2+}$ (rev. Andrews and Lorimer, 1987). In $C_3$ species Rubiso has a catalytic turnover rate of approximately 3.5 $s^{-1}$ per site and thus 1 g $m^{-2}$ of Rubisco has a $V_{cmax}$ of 51 µmol $m^{-2}$ $s^{-1}$ when all sites are carbamylated.

*Table 9.1.* Photosynthetic parameters at 25 °C and their activation energies *E*

| Parameter | Value | E (kJ $mol^{-1}$) |
|---|---|---|
| $K_c$ (µbar) | 260[a](267)[b] | 59.36[c](80.99)[b] |
| $K_o$ (mbar) | 179[a](164) | 35.94 (23.72) |
| $S_{c/o}$ (mol/mol) | 97.5[a] | |
| $S_{c/o}$ (bar/bar) | 2,585 | |
| $\gamma^*$ (bar/bar) ($0.5/S_{c/o}$) | 0.0001935 | 23.4 |
| $\Gamma^*$ (µbar $CO_2$, 200 mbar $O_2$) | 38.6[a](36.9) | 23.4 (24.6) |
| $V_{cmax}$ (µmol $m^{-2}$ $s^{-1}$) | 80[d] | 58.52 |
| $R_d$ (µmol $m^{-2}$ $s^{-1}$) | 1[d] | 66.4 |
| $J_{max}$ (µmol $m^{-2}$ $s^{-1}$) | 160[d] | 37 |
| $H$ (kJ $mol^{-1}$) | 220 | |
| $S$ (J $K^{-1}$ $mol^{-1}$) | 710 | |

[a] (Von Caemmerer et al., 1994)
[b] Numbers in brackets are taken from Bernacchi et al. (2002) assuming an average atmospheric pressure of 987 mbar in Urbana Illinois
[c] Activation energies used by Farquhar et al. (1980)
[d] Varies dependent on photosynthetic capacity of the leaf

It was shown early on with the first gas exchange measurements that the temperature dependencies of Rubisco's carboxylation and oxygenation rates are reflected in the temperature dependency of the $CO_2$ assimilation rates of leaves (Björkman and Pearcy, 1971; Björkman et al., 1980). The need for accurate estimates of the temperature dependencies of Rubisco kinetic parameters has become more urgent as mathematical modelers try to predict the impact of increasing global $CO_2$ concentrations and temperatures (Bowes, 1991; Long, 1991; McMurtrie and Wang, 1993; Whitehead et al., 2001; Medlyn et al., 2002; Lloyd and Farquhar, 2008). The temperature dependence of the kinetic constants can be described by an Arrhenius function of the form

$$Parameter(T) = Parameter(25^oC) \times \exp\left[(t-25)\,E \big/ (298R\,(273+t))\right], \quad (9.22)$$

where $R$ (8.31 J $K^{-1}$ $mol^{-1}$) is the universal gas constant and $t$ is temperature in °C (Badger and Collatz, 1977). Using the Arrhenius function to describe temperature dependencies of the photosynthetic processes is a semi empirical approach, but allows for easy comparison between studies. The $Q_{10}$ function has also been used to approximate the temperature dependence of these kinetic constants (Woodrow and Berry, 1988). Table 2.2 in Von Caemmerer (2000) provides a comparison of experimental measurements of the in vitro temperature dependencies of Rubisco kinetic constants. Temperature dependencies were also reviewed by (Medlyn et al., 2002). Bernacchi and co workers using a similar approach to Von Caemmerer et al. (1994) determined the temperature dependence of $\Gamma^*$, $K_c$ and $K_o$ in vivo in transgenic tobacco with reduced amounts of Rubisco (Bernacchi et al., 2001, 2002; Chapter 10) and these are shown in Table 9.1. They are surprisingly similar to the initial temperature dependencies used by Farquhar et al. (1980), except that $K_c$ has a greater apparent activation energy.

Throughout this chapter, the values of chloroplastic $CO_2$ and $O_2$, $K_c$ and $K_o$ are given in units of partial pressure. The chemical activity of a dissolved gas is proportional to its gas phase (vapor) pressure and thus the partial pressure of a gas existing in equilibrium with that in solution is a better measure of its chemical activity than dissolved concentrations (Badger and Collatz, 1977). The main difference between the use of gas phase units of partial pressure and that of dissolved concentrations (μM) arises when temperature dependencies are considered. If dissolved concentrations are used the temperature dependencies of the solubility of the dissolved gas need to be considered.

### *B. Parameterization of Chloroplast Electron Transport Rate*

To parameterize the RuBP regeneration limited rate of $CO_2$ assimilation, $\Gamma^*$ and the light dependence of potential electron transport rate need to be considered (Eq. 9.15). Values of absorptance and the curvature factor $\theta$ have only a very small temperature dependence and can be assigned a priori with the values given in Eqs. (9.15), (9.16) (Bernacchi et al., 2003). The only parameter that needs to be newly assigned is the maximum electron transport rate $J_{max}$. We assume that $J_{max}$ depends on the amount of thylakoid components such as the cytochrome $b_6f$ complex for example and is dependent on the amount of thylakoid protein present (Fig. 9.3). $J_{max}$ is given in μmol $e^-$ $m^{-2}$ $s^{-1}$ and the ratio of $J_{max}$ to $V_{cmax}$ is usually between at 1.5–2 at 25 °C (Wullschleger, 1993; de Pury and Farquhar, 1997).

The dependence of $J_{max}$ on temperature has been estimated in vitro with isolated thylakoids (Armond et al., 1978; Björkman et al., 1980; Sage et al., 1995; Cen and Sage, 2005; Yamori et al., 2008). Farquhar et al. (1980) used the data of Nolan and Smillie (1976) to determine the parameters *E, S, H* in the following empirical expression:

$$J_{max} = J_{max}\left(25^oC\right)\exp\left(\frac{(T-298)\,E}{298RT}\right) * \frac{\left[1+\exp\left(\frac{298S-H}{298R}\right)\right]}{\left[1+\exp\left(\frac{ST-H}{RT}\right)\right]}, \qquad (9.23)$$

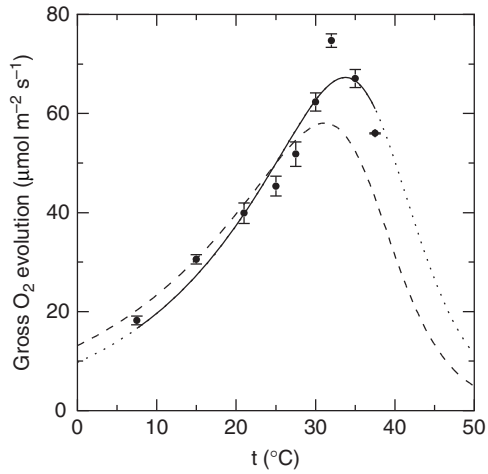


*Fig. 9.4.* Gross $O_2$ evolution as a function leaf temperature measured on leaf discs of tobacco as $^{16}O_2$ evolution at 1,700 μmol quanta $m^{-2}$ $s^{-1}$, 1.5% $CO_2$. Measurements were made as described by Ruuska et al. (2000b) and data are redrawn from Badger et al. (2000). The data were fitted with Eqs. (9.23) and (9.24) and $E = 44.72$ kJ $mol^{-1}$, $H = 210$ kJ $mol^{-1}$, $S = 673$ J $K^{-1}$ $mol^{-1}$ and gross $O_2$ evolution of 50 μmol $m^{-2}$ $s^{-1}$ at 25 °C. These measurements and the fit are compared with the temperature dependence of $J_{max}$ (Eq. 9.23) used by Farquhar et al. (1980), expressed here as gross $O_2$ evolution normalized to the value at 25 °C. Parameters are given in Table 9.1

where $T$ is in °K. This equation is shown in Fig. 9.4 with parameters listed in Table 9.1. The parameters $S$ and $H$ are the entropy and enthalpy of a hypothetical equilibrium between an active and inactive form of the limiting component of electron transport, $E$ is the apparent activation energy for low temperature limited electron transport. Discussions on the origins of Eq. (9.23) can be found in several publications (Tenhunen et al., 1976; Hall, 1979; Farquhar et al., 1980; Von Caemmerer, 2000; Medlyn et al., 2002). Acclimation of the thylakoid membrane can occur when plants are grown at different temperatures, shifting the temperature optimum (Berry and Björkman, 1980; Björkman et al., 1980; Sage et al., 1995; Yamori et al., 2008). It is therefore useful to have an equation for the temperature optimum:

$$T_{opt} = H\left[S + R\ln\left(H/E - 1\right)\right]. \qquad (9.24)$$

Equations (9.23) and (9.24) can be used together to fit temperature response curves of in vivo or in vitro measurements of electron transport rate.

An example of measurements of actual electron transport rate is shown in Fig. 9.4. In this case the actual electron transport rate was measured as $^{16}O_2$ evolution at high $pCO_2$ and high light intensity in tobacco leaf discs (Badger et al., 2000; Ruuska et al., 2000b). Other temperature dependencies have been given using empirical fitting functions (Kirschbaum and Farquhar, 1984; Bernacchi et al., 2003; June et al., 2004; Yamori et al., 2008). It needs to be borne in mind that many of the temperature dependencies derived for $J_{max}$ in vitro may not represent true temperature dependencies of maximal electron transport rate in vivo as downstream reactions in carbon metabolism can exert feedback inhibition on electron transport (Woodrow and Berry, 1988). There is concern that the steep decline in $J_{max}$ at high temperature may be an artifact of the in vitro measuring system. However, Yamori et al. (2008) compared the temperature dependence of $J_{max}$ estimated in vivo from measurements of $CO_2$ assimilation rate at high $CO_2$ with in vitro measurements and found close agreement over a wide temperature range except at the lowest and highest temperatures. Bernacchi et al. (2003) found that $J$ estimated from gas exchange could be fitted with a simple exponential function and did not saturate in high temperature grown tobacco. A simpler empirical form was introduced by June et al. (2004):

$$J(t_L) = J(t_o)e^{-\left(\frac{t_L - t_o}{\Omega}\right)^2}, \qquad (9.25)$$

where $t_L$ is the leaf temperature (°C), $J(t_o)$ is the rate of electron transport at the optimum temperature $t_o$, and $\Omega$ is the difference in temperature from $t_o$ at which $J$ falls to $e^{-1}$ (0.37) of its value at $t_o$.

## IV. The Role of Rubisco Activation State

One of the concerns in modeling Rubisco limited $CO_2$ assimilation rate is if and how to incorporate a function for the variation of Rubisco activation state. To function, Rubisco's catalytic sites must be activated through the reversible carbamylation of a lysine residue within the site, followed by the rapid binding of an essential $Mg^{2+}$ (Andrews and Lorimer, 1987). It is possible to measure both Rubisco activity and the carbamylation state of Rubisco in leaf extracts (Butz and Sharkey, 1989). In vitro studies of Rubisco activation kinetics suggest that the equilibrium carbamylation in the absence of RuBP would be less than 25% at the pH, $Mg^{2+}$, and $CO_2$ concentrations thought to occur in the chloroplast (Lorimer et al., 1976). Furthermore, when RuBP was present in vitro assays, it appeared to block carbamylation by binding tightly to non-carbamylated sites (Jordan and Chollet, 1983). These in vitro difficulties in Rubisco carbamylation are eliminated in vivo by the presence of a second protein, Rubisco activase (Portis, 2003). Activase requires ATP hydrolysis to function and removes sugar phosphates from carbamylated and uncarbamylated Rubisco sites, thereby promoting carbamylation (Andrews et al., 1995; Portis, 2003). In vivo Rubisco activation state has been shown to vary with irradiance, temperature and $pCO_2$ (Von Caemmerer and Quick, 2000; Weis and Berry, 1988; Salvucci and Crafts-Brandner, 2004a). Although Rubisco is frequently observed to be fully active at high irradiance, ambient $pCO_2$ and moderate temperatures (Von Caemmerer and Edmondson, 1986) its activation state can decline steeply at high temperature (Weis and Berry, 1988; Crafts-Brandner and Salvucci, 2000; Cen and Sage, 2005; Yamori et al., 2006b).

### *A. Variation of Rubisco Activation with Light and $pCO_2$*

Von Caemmerer (2000) reviewed the role Rubisco activation state may play in modeling $C_3$ photosynthesis with variation in irradiance and $pCO_2$. At low $pCO_2$ Rubisco can be almost fully carbamylated even at low light whereas it declines at high $pCO_2$ (Sage et al., 1990; Von Caemmerer and Quick, 2000). Sage (1990) therefore suggested that Rubisco's activation state was lowered only under conditions where RuBP regeneration rate was limiting $CO_2$ assimilation rate. If this is the case Rubisco activation state would not need to be introduced as a separate variable into the model equations. There is some support for this hypothesis in gas exchange measurements which show that the initial slope of the $CO_2$ response curve is frequently independent of irradiance down to quite low irradiance levels (Brooks and Farquhar, 1985; Evans, 1986; Sage et al., 1990). At low $pCO_2$ the capacity for RuBP

regeneration exceeds the carboxylation capacity and presumably the transthylakoid ΔpH as well as the ATP/ADP ratio are likely to be high, which in turn may translate into a greater activase activity. In the same vein, the carbamylation state was found to be high at low irradiance and ambient $pCO_2$ in transgenic tobacco plants with reduced amount of Rubisco compared to wild type plants (Quick et al., 1991), whereas transgenic tobacco with reduced cytochrome $b_6f$ content had reduced carbamylation levels compared to wild type (Price et al., 1998; Ruuska et al., 2000a). The complex dependence of activation on $pCO_2$ and irradiance illustrates that Rubisco carbamylation is no simple function of irradiance. The results with transgenic plants suggest some interaction between Rubisco activation state and the balance between potential electron transport rate and Rubisco carboxylation rate as had been suggested by Sage (1990).

### *B. Variation of Rubisco Activation with Temperature*

Experiments with a variety of species have established that Rubisco activation state declines with increasing temperature at ambient $pCO_2$ (Weis, 1981; Weis and Berry, 1988; Feller et al., 1998; Crafts-Brandner and Salvucci, 2000; Haldimann and Feller, 2004, 2005; Salvucci and Crafts-Brandner, 2004a; Yamori et al., 2006b). It is thought that Rubisco is inactivated at high temperature due to heat induced inactivation of Rubisco activase which regulates Rubisco activation state (Salvucci and Crafts-Brandner, 2004a, b). Cen and Sage (2005), who examined the interaction of $pCO_2$ and temperature on Rubisco activation in sweet potato, found Rubisco activation states to be greater at low compared to high $pCO_2$ at all temperature. There is at the moment no complete information on how temperature, $pCO_2$ and irradiance interact to modulate Rubisco activation and clearly more research is required to establish the underlying mechanisms. If both Rubisco activation and electron transport are reduced as was suggested by the study of Yamori et al. (2006b) then Rubisco activation state may need to be introduced as an extra variable in Eqs. (9.8) and (9.9). Sellers et al. (1996a) introduced the following equation for Rubisco activation as a function of leaf temperature:

$$a_R = 1/\left(1 + e^{0.3(T_l - S_2)}\right), \tag{9.26}$$

where $a_R$ is the fraction of Rubisco that is active and $S_2$ is a temperature at which half of the Rubisco is inactive. $S_2$ varies from 303 K for needle leaf conifers to 313 K for tropical evergreen trees (Table 5 in Sellers et al., 1996b). This equation has similar properties to Eq. (9.23) and can be applied equally well to $J_{max}$. There is little empirical difference between assuming that $J_{max}$ or Rubisco activation limits photosynthesis at high temperature and ambient $pCO_2$ since both activities have similar sensitivity to temperature, but there may be subtle differences in the simulated response under low or high $pCO_2$ conditions. The models of Collatz et al. (1991) and Sellers et al. (1996a) assume that Rubisco activation is most limiting.

## V. Estimating Chloroplast $pCO_2$

To examine the biochemistry of photosynthesis in leaves ideally one would like to measure $CO_2$ assimilation rate in relation to chloroplast $CO_2$ partial pressures, as this is the $CO_2$ pressure determining the Rubisco carboxylation. It is common practice to calculate the $CO_2$ partial pressure in the sub-stomatal cavities (referred to as intercellular $CO_2$ partial pressure) from water vapor exchange measurements. This eliminates an important variability, as stomatal conductance varies as stomata themselves respond to $CO_2$ and irradiance and this has become a standard reference $CO_2$ (Von Caemmerer and Farquhar, 1981). However measurements of carbon isotope discrimination concurrently with gas exchange measurements have shown that there is a substantial drop in $pCO_2$ from intercellular airspace to the chloroplast which needs to be considered (Evans et al., 1986; Evans and Von Caemmerer, 1996). Evans and Von Caemmerer (1991) assumed that the $CO_2$ transfer conductance from the substomatal cavities to the sites of carboxylation in the chloroplast, $g_i$, would be constant for a leaf since it is to a large degree related to the anatomy of the leaf such as the chloroplast surface area appressing intercelluar airspace. The explicit

inclusion of a constant $CO_2$ transfer conductance, $g_i$, from the sub stomatal cavities to the carboxylation sites leads to a quadratic relationship between $CO_2$ assimilation rate, $A$ and the intercellular $CO_2$ partial pressure, $C_i$. The relationship between $A$ and $g_i$ is given by

$$A = g_i (C_i - C_c), \tag{9.27}$$

and solving for $C_c$ and combining with Eq. (9.9) or Eq. (9.14) one obtains the following two quadratic equations:

$$\begin{aligned} A_c^2 - A_c \{g_i (C_i + K_c (1 + O/K_o)) + V_{c\max} + R_d\} \\ + g_i \{V_{c\max} (C_i - \Gamma^*) \\ - R_d (C_i + K_c (1 + O/K_o))\} = 0 \end{aligned} \tag{9.28}$$

and

$$\begin{aligned} A_j^2 - A_j \{g_i (C_i + 2\Gamma^*) + J/4 + R_d\} \\ + g_i \{(C_i - \Gamma^*) J/4 \\ - R_d (C_i + 2\Gamma^*)\} = 0. \end{aligned} \tag{9.29}$$

The presence of a significant internal diffusion resistance to $CO_2$ affects both the quantitative relationship between $CO_2$ assimilation rate and maximal Rubisco activity and the shape of the $CO_2$ response curve. The internal conductance to $CO_2$ has been estimated in various ways: by concurrent measurements of carbon isotope discrimination (Evans et al., 1986; Von Caemmerer and Evans, 1991; Evans and Von Caemmerer, 1996; Hanba et al., 2004; Yamori et al., 2006a), by combined measurements of chlorophyll fluorescence and gas exchange (Evans and Von Caemmerer, 1996; Bernacchi et al., 2002; Flexas et al., 2006, 2007a; Warren and Dreyer, 2006; Warren, 2007) or by fitting Eqs. (9.27) and (9.28) to $CO_2$ response curves (Ethier and Livingston, 2004; Ethier et al., 2006; Sharkey et al., 2007). There is active research in examining the temperature response of $g_i$ and it appears that $g_i$ increases with temperature but there is species to species variation in this response (Bernacchi et al., 2002; Warren and Dreyer, 2006; Yamori et al., 2006a). A review of temperature dependencies was given by Warren (2008). There has been a recent report that suggests that $g_i$ may vary with both $pCO_2$ and irradiance, which would make the approach of deriving $g_i$ from a fit of Eqs. (9.28) and (9.29) invalid (Flexas et al., 2007a).

## VI. Predicting Photosynthesis from Chloroplast Biochemistry

### A. Environmental Responses

The model provides predictions on how the $CO_2$ assimilation rate varies with $pCO_2$, $pO_2$, irradiance and temperature. Many of these predictions were discussed by Farquhar et al. (1980) and one such example is given in Fig. 9.5, which shows the predicted $CO_2$ assimilation rate at different irradiances and $pCO_2$. The model predicts that $CO_2$ assimilation rate is independent of

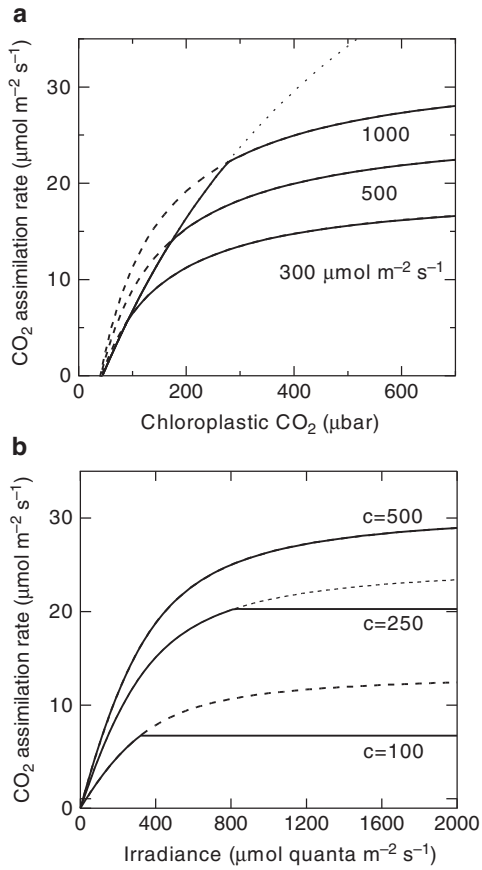


*Fig. 9.5.* (**a**) Modeled $CO_2$ assimilation rate (solid lines) as a function of chloroplast $pCO_2$ at three different irradiances. The extensions of the Rubisco limited rate $A_c$ (dotted line) and the electron transport limited rate $A_j$ (dashed lines) are also shown. Parameters used are given in Table 9.1. Leaf temperature was assumed to be 25 °C and $pO_2 = 200$ mbar. (**b**) Modeled $CO_2$ assimilation rate (solid lines) as a function of irradiance at three different chloroplast $pCO_2$. The electron transport limited rates $A_j$ (dashed lines) are also shown. Other details are as in (**a**)

irradiance (except at very low irradiance) at low $p\mathrm{CO_2}$ where $\mathrm{CO_2}$ assimilation rate is limited by (in this case) fully active Rubisco, whereas at high $p\mathrm{CO_2}$ it is determined by the electron transport limited rate. This suggested that the initial slope of the $\mathrm{CO_2}$ assimilation rate vs. $p\mathrm{CO_2}$ curve can be quantitatively related to $V_{\mathrm{cmax}}$ as was done by Von Caemmerer and Farquhar (1981). The modeled irradiance response curves predict that the light saturation of $\mathrm{CO_2}$ assimilation rate depends on $p\mathrm{CO_2}$, a fact which is often ignored. Model predictions can be tested by gas exchange measurements and are useful in planning experiments (Von Caemmerer and Farquhar, 1981). The model also predicted the measured changes in quantum yield with $p\mathrm{CO_2}$ and temperature (Ehleringer and Björkman, 1977), the linear dependence of the $\mathrm{CO_2}$ compensation point on $\mathrm{O_2}$ partial pressure (Laing et al., 1974) and its dependence on respiration rate (Farquhar and Von Caemmerer, 1982). The ability of the model to accurately predict variation of $\mathrm{CO_2}$ assimilation rate with temperature will depend on gaining a better understanding of the modulation of Rubisco activation state with temperature (see Section V.B.)

### *B. Photosynthesis for Photosynthetic Mutants*

Recent advances in chloroplast transformation have made it possible to engineer tobacco expressing mutant Rubiscos (Whitney et al., 1999; Whitney and Andrews, 2003). Using the in vitro kinetic constants of those Rubiscos it was possible to use the model to predict the characteristics of the expected $\mathrm{CO_2}$ assimilation rate of these plants (Fig. 9.6). Whitney et al. (1999) also used the model in the reverse direction and predicted Rubisco kinetic properties from gas exchange measurements. This example highlights the predictive power of the model. An elegant application of the model to the question of how will canopy photosynthesis be affected if we could engineer plants with different Rubiscos was given by Zhu et al. (2004), exemplifying the use of the model to answer a "what if" question.

### *C. Integration of the Leaf Photosynthesis Model with Stomatal Models*

Photosynthesis and transpiration by leaves in nature is determined by the photosynthetic activity of the mesophyll cells within the leaf and by the diffusive conductance of the epidermis that separates the intercellular air space from the surrounding atmosphere. Diffusion may be thought of as the supply function and biochemical processes as the demand function for $\mathrm{CO_2}$ and the $p\mathrm{CO_2}$ within the intercellular air spaces of the leaf is determined by the interaction of supply and demand. Figure 9.7 shows a graphical solution for the intercellular $p\mathrm{CO_2}$ at which the rate of diffusion of $\mathrm{CO_2}$ into the leaf exactly matches the rate of $\mathrm{CO_2}$ uptake by the leaf cells. Given a value for conductance, the ambient $p\mathrm{CO_2}$, and the inputs required for the biochemical model, one can develop an analytical solution or use a computer program to seek the intercellular $p\mathrm{CO_2}$ that satisfies both the supply and demand functions.

The biochemical model has been widely used in this way to examine physiological responses of leaves in natural environments (e.g. Tenhunen et al., 1994). However, a major limitation of this

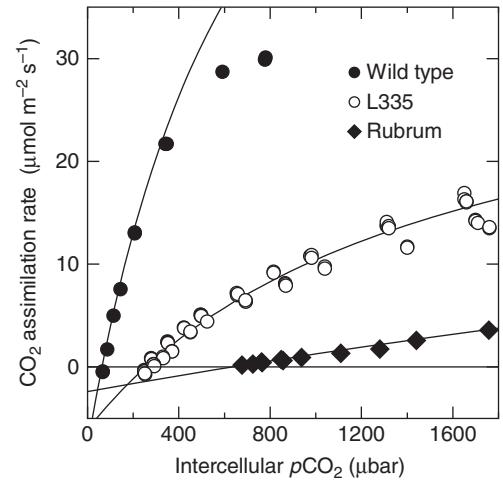


*Fig. 9.6.* $\mathrm{CO_2}$ assimilation rate, $A$, as a function of intercellular $p\mathrm{CO_2}$ for a leaf of a wild type (●), transgenic tobacco with a mutant Rubisco where the Leu335 was changed to a Val (○), transgenic tobacco where native Rubisco was replaced by Rubisco from *Rhodospirillum rubrum* (◆). Measurements were made at an irradiance of 1,000 µmol quanta $\mathrm{m^{-2}\,s^{-1}}$ and a leaf temperature of 25 °C at $p\mathrm{O_2} = 200$ mbar. The lines are $A$ predicted from the Rubisco limited rate (Eq. 9.9). For the L335 mutant tobacco $V_{\mathrm{cmax}} = 37$ µmol $\mathrm{m^{-2}\,s^{-1}}$, $K_{\mathrm{c}} = 318$ µbar, $K_{\mathrm{o}} = 55.6$ mbar, $\Gamma^* = 140$ µbar and $R_{\mathrm{d}} = 2.5$ µmol$\mathrm{m^{-2}\,s^{-1}}$. For the *R. rubrum* tobacco mutant $V_{\mathrm{cmax}} = 42$ µmol $\mathrm{m^{-2}\,s^{-1}}$, $K_{\mathrm{c}} = 4,461$ µbar, $K_{\mathrm{o}} = 126$ mbar, $\Gamma^* = 415$ µbar and $R_{\mathrm{d}} = 1$ µmol $\mathrm{m^{-2}\,s^{-1}}$ (Whitney et al., 1999; Whitney and Andrews, 2001; Mueller-Cajar et al., 2007)

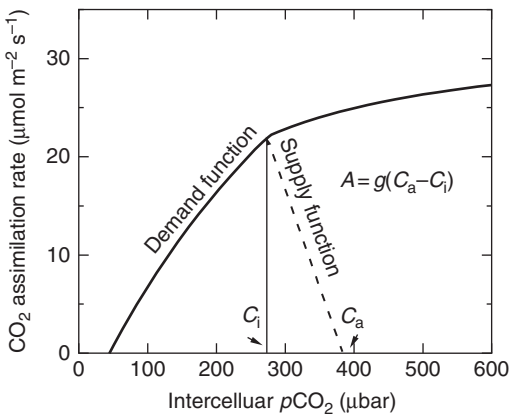


*Fig. 9.7.* $CO_2$ assimilation rate, $A$, versus intercellular $pCO_2$. The solid line indicates the "demand function" the dependence of $A$ on intercellular $pCO_2$. The dashed line indicates the "supply function", the equation describing the gaseous diffusion of $CO_2$ from the atmosphere to the intercellular spaces. In this diagram the $pCO_2$ at the site of carboxylation is assumed to be equal to the $pCO_2$ in the intercellular space

approach is that conductance itself is a dynamic and regulated property of the leaf. Variation of conductance can have very profound effects on energy and water exchange by leaves in nature, modifying not only the intercellular $pCO_2$, but also the physical environment (principally temperature and water potential) of the mesophyll cells. Therefore, an understanding of the full extent of physiological control of photosynthesis and transpiration of leaves in nature requires a second model capable of predicting stomatal conductance that could be coupled to the photosynthesis model.

Models of stomatal response to environmental variables had long been available (e.g. Jarvis, 1976; see also Collatz et al., 1991), but these considered conductance as separate from photosynthesis and proved difficult to integrate with a photosynthesis model. Systematic measurements of stomatal conductance and photosynthesis to changes in light, $pCO_2$, leaf temperature and atmospheric humidity were used by Ball et al. (1987) to develop an empirical relationship for stomatal conductance as a function of $CO_2$ assimilation rate:

$$g = m \cdot A \cdot h_s/C_s + b, \qquad (9.30)$$

where $m$ and $b$ are regression coefficients, $A$ is the rate of net $CO_2$ assimilation, and $h_s$ and $C_s$ are the partial pressure of water vapor and $CO_2$ at the surface of the leaf – inside the laminar boundary layer. It is of interest that without some independent means of predicting the rate of photosynthesis, the Ball et al. model would have no predictive value. On the other-hand, when used together with a photosynthesis model the terms for the response to temperature, light intensity and leaf to leaf variation in humidity deficit and water potential used in other models of stomatal conductance (e.g. Jarvis, 1976) are subsumed in the response of $A$ to these variables, making it easier to combine these models. This linkage of stomatal conductance to $A$ was indicated by Wong et al. (1979, 1985), who showed that stomatal conductance of leaves during steady-state photosynthesis is strongly correlated with the rate of $CO_2$ assimilation, and it is consistent with the theoretical arguments on optimal control of stomatal conductance proposed by Cowan and Farquahr (1977).

Ball (1988), Tenhunen et al. (1990), Leuning (1990), Collatz et al. (1991, 1992) and Harley et al. (1992) developed coupled models of photosynthesis, transpiration and the leaf energy budget using the Ball et al. (1987) stomatal model and the Farquhar et al. (1980) photosynthesis model. Lloyd and Farquhar (1994) and Leuning et al. (1995) have developed alternative stomatal models for use in coupled model systems. These coupled models are now widely used to simulate carbon, water and energy exchange at the scale of fields (de Pury and Farquhar, 1997) ecosystems (Colello et al., 1998) and the globe (Randall et al., 1996).

Baldocchi (1994) proposed an analytical solution to a coupled system of models arguing that iterative solutions were unreliable. One factor contributing to this problem is that the approach of taking the minimum of the rates of the potential biochemical processes leads to discontinuities or "breaks" in the response curve at the transitions from one factor to the next (Fig. 9.1). Collatz et al. (1991) addressed this problem by using quadratic equations of the form

$$\theta J^2 - J(J_1 + J_2) + J_1 J_2 = 0, \qquad (9.31)$$

where the value of $J$ obtained from the root is the minimum of $J_1$ and $J_2$ with a smooth transition between these with a curvature in the transition

defined by the parameter, $\theta (1 < \theta > 0)$. Two quadratic equations can be used in sequence to select among three potential limitations. The $C_3$ and $C_4$ models presented by Collatz et al. (1991, 1992) are structured such that expressions for the potential limiting processes unique to each pathway are processed by identical quadratic expressions making it possible to easily switch between pathways in the same subroutine. This approach yields very similar answers to the original Farquhar et al. implementation with continuous functions of net $CO_2$ assimilation leading to robust iterative solutions.

### *D. Canopy Photosynthesis*

Leaf models are now commonly used as a basis for simulating the water, carbon and energy exchange of plant canopies consisting of millions of leaves. Calibration of these models is largely based on leaf scale measurements with only limited constraint from measurements such as eddy correlation at the scale of application. The accuracy of such models is therefore highly dependent on the assumptions used in integrating from the leaf to the canopy scale. Heterogeneity in the thermal, aerodynamic and light climates within the canopy is important as is the corresponding heterogeneity in the property of leaves that develop in different positions within the canopy. This is a complex area that is beyond the scope of this review. The reader is referred to papers by de Pury and Farquhar (1999), Wang and Leuning (1999), Baldocchi et al. (2002) and to Chapter 16 by Ülo Niinemets and Niels P. R. Anten and Chapter 18 by Manfred Küppers and Michael Pfiz. Interestingly, this has become an important approach for simulating the conductance of vegetated land surfaces to water vapor. This is a critical parameter controlling the partitioning of absorbed radiation to sensible heat or evaporation of water – an important driver of the physical climate system. The reader is referred to Sellers et al. (1997) for a review of this topic.

## VII. Predicting Chloroplast Biochemistry from Leaf Gas Exchange

The $C_3$ model is most often used to infer chloroplast biochemistry from gas exchange measurements (Ainsworth et al., 2002; Leuning, 2002; Medlyn et al., 2002; Long and Bernacchi, 2003; Ethier and Livingston, 2004; Sharkey et al., 2007). Von Caemmerer and Farquhar (1981, 1984) compared in vitro measurements of Rubisco activity and chloroplast electron transport with gas exchange measurements and showed that they could be quantitatively related to gas exchange measurements made in *Phaseolus vulgaris* grown under different environmental conditions. It is often easier to infer leaf biochemistry from gas exchange measurements than make the required in vitro measurements especially since it is difficult to extract functional enzymes from many species. Long and Bernacchi (2003) provide an excellent review and discussion of how to best make these measurements. A routine that facilitates the fitting of gas exchange data has been provided by Sharkey et al. (2007).

It is possible to determine whether RuBP regeneration capacity (including electron transport capacity) limits $CO_2$ assimilation rate from measurements of $CO_2$ responses and calculations of the RuBP regeneration rate, as well as other fluxes, such as of FBP formation and consumption and electron transport rate required to support measured $CO_2$ assimilation rates (Farquhar and Von Caemmerer, 1982; Brooks and Farquhar, 1985; Von Caemmerer and Quick, 2000). An example is solving for the actual electron transport rate $J_a$ using Eq. (9.14) as was done by Von Caemmerer and Farquhar (1981). It can be seen (Fig. 9.8) that $J_a$ calculated form $A$ increases with increasing intercellular $pCO_2$ and then becomes constant at higher $C_i$. A constant $J_a$ can be taken as an indication of an electron transport limitation (although some caution is needed, especially at high irradiance, as other components of RuBP regeneration have the same relative dependencies on $pCO_2$ and $pO_2$). Triose phosphate limitation may also occur at high $pCO_2$, but should cause $J_a$ to decrease with increasing $pCO_2$. Note that $CO_2$ assimilation rate continues to increase with increasing $C_i$ as energy consumption is diverted from photorespiration to carboxylation. The calculated electron transport rate was confirmed with concomitant measurements of the quantum yield of PS II ($\phi_{PSII}$) from chlorophyll fluorescence, which is proportional to chloroplast electron transport rate at a given irradiance (Genty et al., 1989).

Combined measurements of gas exchange and chlorophyll fluorescence have become a popular

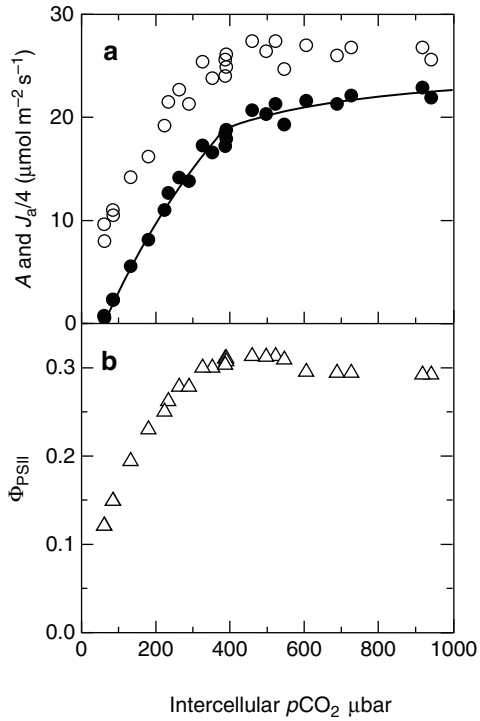


*Fig. 9.8.* (**a**) $CO_2$ assimilation rate, $A$, and calculated actual chloroplast electron transport rate, $J_a/4$, as functions of intercellular $pCO_2$ for a tobacco leaf. Measurements were made at an irradiance of 1,000 μmol quanta m$^{-2}$ s$^{-1}$, leaf temperature of 25 °C and $pO_2 = 200$ mbar. $J_a/4$ was calculated from $CO_2$ assimilation rate by estimating chloroplast $pCO_2$ from Eq. (9.26) with an internal conductance $g_i = 0.3$ mol m$^{-2}$ s$^{-1}$ bar$^{-1}$ (data from Hudson et al., 1992). (**b**) The quantum yield of PS II ($\Phi_{PSII}$) estimated from chlorophyll fluorescence measured concurrently with gas exchange. Chlorophyll fluorescence was measured on the adaxial surface and $\Phi_{PSII}$ was calculated according to Genty et al. (1989)

tool to assess chloroplast biochemistry (Long and Bernacchi, 2003). The chlorophyll fluorescence provides an excellent way to distinguish RuBP regeneration limited $CO_2$ assimilation rate from Rubisco limited rate, because chloroplast electron transport calculated from fluorescence becomes independent of $pCO_2$ when RuBP regeneration limits $CO_2$ assimilation rate (Fig. 9.8). We believe that this is a useful tool at low light or temperature extremes where it may be difficult to distinguish an RuBP regeneration limitation from a Rubisco limitation. The quantitative comparison between $CO_2$ assimilation rate measurements and chlorophyll fluorescence measurements can however be more problematic as the two measurements average different chloroplast populations of the leaf.

If estimates of $V_{cmax}$ and $J$ are to be related to other leaf measurements such as nitrogen or chlorophyll content, it is important to also estimate the conductance to internal $CO_2$ diffusion as otherwise these parameters will be underestimated (Long and Bernacchi, 2003; Ethier and Livingston, 2004; Ethier et al., 2006; Warren, 2007). Careful measurements of $CO_2$ and light response curves over a range of temperature have been valuable in providing in vivo temperature responses for both Rubisco and electron transport parameters and provide a means for species comparisons (Kirschbaum and Farquhar, 1984; Von Caemmerer et al., 1994; Walcroft et al., 1997; Bernacchi et al., 2001, 2002, 2003).

## VIII. Concluding Remarks

The photosynthesis model described here provides a quantitative framework that can be used as a research tool to design and interpret both field and laboratory based experiments. The papers cited here represent only a small fraction of studies that have used the model to interpret results. Both in vivo and in vitro studies have provided us with parameterization of the Rubisco limited $CO_2$ assimilation rate and studies with transgenic plants with mutant Rubiscos have highlighted the predictive power of the model in this regard. An elegant application of the model to the question of how will canopy photosynthesis be affected if we could engineer plants with different Rubiscos was given by Zhu et al. (2004), exemplifying the use of the model to answer "what if" questions. However there are three main areas were further research is needed. We need to learn more about what governs Rubisco activation in vivo, work towards a more mechanistic understand of what determines chloroplast electron transport rate and the conductance to $CO_2$ diffusion from intercellular airspace to the chloroplast.

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