# 16 Modelling of Photosynthetic Response to Environmental Conditions

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CONTENTS

## 16.1 Introduction

Photosynthesis is the incorporation of carbon, nitrogen, sulphur and other substances into plant tissue using light energy from the sun. Most of this energy is used for the reduction of carbon dioxide and, consequently, there is a large body of biochemical and biophysical information about photosynthetic carbon assimilation. In an ecophysiological context, we believe that most of today's biochemical knowledge can be summarized in a few simple equations. These equations represent the rate of ribulose bisphosphate ($RuP_2$)-saturated carboxylation, the ratio of photorespiration to carboxylation, and the rates of electron transport/photophosphorylation and of "dark" respiration in the light. There are many other processes that could potentially limit $CO_2$ assimilation, but probably do so rarely in practice. Fundamentally this may be due to the expense, in terms of invested nitrogen, of the carboxylase and of thylakoid functioning. To reach our final simple equations we must first discuss the biochemical and biophysical structures – as they are understood at present – that finally reduce the vast number of potentially rate-limiting processes to the four or five listed above. A diagrammatic representation of these processes is given in Fig. 16.1.

We then discuss integrated functioning in individual leaves of $C_3$ species, and later briefly discuss canopy photosynthesis. Models of $C_4$ photosynthesis are less well developed than those of $C_3$ photosynthesis; we discuss how they may be extended. (For description of these pathways of photosynthesis see also Chap. 15, this Vol.)

Models of leaf photosynthesis have been reviewed by THORNLEY (1976), JASSBY and PLATT (1976), and TENHUNEN et al. (1980a). In this article we emphasize recent progress made in mechanistic models, but recognize the validity of other types (see Chap. 8, this Vol.) and give brief references to successful empirical models. Stomatal and boundary layer conductances affect the intercellular partial pressure of $CO_2$, C, and the leaf temperature, T. We examine responses of the rate of assimilation to C and T but do not consider submodels



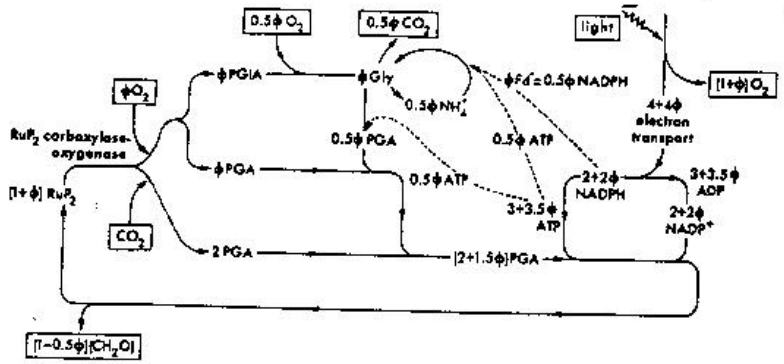


Fig. 16.1. Simplified photosynthetic carbon reduction (PCR) and photorespiratory carbon oxidation (PCO) cycles, with the cycle for regeneration of NADPH and ATP linked to light-driven electron transport. For each carboxylation, $\phi$ oxygenations occur. *Gly* glycine; $Fd^-$ reduced ferredoxin (assumed equivalent to $^1/_2$ NADPH); *PGA* 3-phosphoglycerate; *PGlA* phosphoglycolate. At the compensation point $\phi = 2$

of the response of stomatal conductance to environmental perturbations. These are dealt with in Chapter 8, this Volume (see also Chaps. 7 and 17, this Vol.).

## 16.2 Stromal and Extrachloroplastic Reactions

### 16.2.1 Kinetics of Ribulose Bisphosphate Carboxylase-Oxygenase

#### 16.2.1.1 $RuP_2$ Saturated Rates

The currently accepted equation to describe the rate, $V_c$, of carboxylation of ribulose bisphosphate ($RuP_2$), in the presence of competitive inhibition by oxygen, and of saturating concentrations of $RuP_2$ is

$$V_c = W_c = \frac{V_{c\max} C}{C + K_c(1 + O/K_o)} \tag{16.1}$$

We denote $RuP_2$ carboxylase rates in general as $V_c$, and $RuP_2$ saturated rates as $W_c$. $V_{c\,max}$ is the maximum velocity, C and O are partial pressures of $CO_2$ and $O_2$, $p(CO_2)$ and $p(O_2)$ respectively, in equilibrium with their dissolved concentrations in the chloroplast stroma, $K_c$ is the Michaelis-Menten constant for $CO_2$, and $K_o$ is the Michaelis-Menten constant for $O_2$. This equation is used in the models of LAING et al. (1974), KU and EDWARDS (1977b), TENHUNEN et al. (1977), BERRY and FARQUHAR (1978), FARQUHAR et al. (1980), COOKE and RAND (1980), BAUWE et al. (1980) and RAVEN and GLIDEWELL (1981). Earlier attempts to include competitive inhibition by oxygen in models of leaf

thesis were made by LAISK (1970), HALL (1971), PEISKER (1974), HALL and BJÖRKMAN (1975), and CHARTIER and PRIOUL (1976).

The analogous equation for the oxygenation of $RuP_2$ is

$$V_o = W_o = \frac{V_{o\,max}\,O}{O + K_o(1 + C/K_c)}, \tag{16.2}$$

where $V_{o\,max}$ is the maximum rate. Equation (16.2) is used in the models of LAING et al. (1974), TENHUNEN et al. (1977), BERRY and FARQUHAR (1978), SINCLAIR and RAND (1979), FARQUHAR et al. (1980), COOKE and RAND (1980), BAUWE et al. (1980), and RAVEN and GLIDEWELL (1981). The ratio of the activities of oxygenase and carboxylase, denoted $\phi$ by FARQUHAR et al. (1980), is (LAING et al. 1974)

$$\phi = \frac{V_o}{V_c} = \frac{V_{o\,max}}{V_{c\,max}} \cdot \frac{O K_c}{K_o C}. \tag{16.3}$$

### 16.2.1.2 $RuP_2$ Limited Rates

Equations (16.1) and (16.2) apply when the $RuP_2$ is present in saturating amounts. Equation (16.3) applies regardless, provided the mechanisms of the reactions are ordered with $RuP_2$ binding first (FARQUHAR 1979). When $RuP_2$ is not saturating, (16.1) becomes, in the absence of oxygen (BADGER and COLLATZ 1977),

$$\frac{V_{c\,max}}{V_c} = 1 + \frac{K_{rc}}{R} + \frac{K_c}{C} + \frac{K_{ir}}{R} \cdot \frac{K_c}{C} \tag{16.4}$$

and (16.2) becomes, in the absence of $CO_2$,

$$\frac{V_{o\,max}}{V_o} = 1 + \frac{K_{ro}}{R} + \frac{K_o}{O} + \frac{K_{ir}}{R} \cdot \frac{K_o}{O}, \tag{16.5}$$

where R is the concentration of free $RuP_2$, $K_{rc}$ and $K_{ro}$ are Michaelis-Menten constants for $RuP_2$ in the presence of saturating $CO_2$ and $O_2$ respectively, and $K_{ir}$ is the dissociation constant for the enzyme-$RuP_2$ complex.

The mechanism of the reactions is uncertain, being either random, or ordered with $RuP_2$ binding to the enzyme first (BADGER and COLLATZ 1977). FARQUHAR (1979) showed that the latter case modified (16.1) and (16.2)

$$V_c = W_c \cdot \frac{R}{R + K_r'} \tag{16.6}$$

$$V_o = W_o \cdot \frac{R}{R + K_r'}, \tag{16.7}$$

where $W_c$ and $W_o$ are the $RuP_2$ saturated rates given by Eqs. (16.1) and (16.2),



and $K_r'$ is the effective Michaelis-Menten constant for $RuP_2$ given by

$$K_r' = \frac{K_{rc} O/K_o + K_{ro} C/K_c + K_{ir}}{O/K_o + C/K_c + 1}. \tag{16.8}$$

An implicit form of these equations was used by HALL (1979).

### 16.2.1.3 On the High Concentration of Enzyme Sites

PEISKER (1974), aware of the high concentration of enzyme sites in the chloroplast, $E_t$, presented the equations which would apply if this concentration exceeded that of total $RuP_2$, $R_t$. These equations, written in terms of the rate constants of the individual processes, were complex, and FARQUHAR (1979) showed that they could be written more simply as

$$V_c = W_c \cdot \frac{R_t}{E_t + K_r'} \tag{16.9}$$

$$V_o = W_o \cdot \frac{R_t}{E_t + K_r'}. \tag{16.10}$$

The analysis suggested that although the $K_m$ of $RuP_2$ in vitro (where the concentration of enzyme sites is extremely small, typically 1 μM) is only about 20 μM, half maximal rates in vivo, when the enzyme site concentration is about 4 mM (JENSEN and BAHR 1977), would only be seen when the $RuP_2$ concentration exceeded 2 mM. FARQUHAR (1979) predicted a non-rectangular hyperbolic response of carboxylase activity to total $RuP_2$ concentration (as distinct from the rectangular hyperbolic response to free $CO_2$ concentration)

$$\left(\frac{V_c}{W_c}\right)^2 - \frac{V_c}{W_c}\left(1 + \frac{R_t + K_r'}{E_t}\right) + \frac{R_t}{E_t} = 0 \tag{16.11}$$

$$\left(\frac{V_o}{W_o}\right)^2 - \frac{V_o}{W_o}\left(1 + \frac{R_t + K_r'}{E_t}\right) + \frac{R_t}{E_t} = 0. \tag{16.12}$$

He showed that with the high concentration of enzyme sites in vivo this could be closely approximated by

$$V_c = W_c \cdot \min\{1, R_t/E_t\}, \tag{16.13}$$

where min{ } denotes "minimum of" and $E_t$ is the total concentration of enzyme sites, and $R_t$ is the total concentration (free plus bound) of $RuP_2$. Equation (16.3) remains valid. Equations (16.4)–(16.7) also remain valid provided R refers to the concentrations of free (unbound) $RuP_2$. However, the usual assays for $RuP_2$ measure the total concentration, $R_t$.

Data supporting the use of Eq. (16.13) have been obtained by COLLATZ (1978) in *Chlamydomonas* and spinach cells. COLLATZ measured $CO_2$ assimilation rate, A, and $RuP_2$ concentrations, $R_t$, at various irradiances. When A is plotted

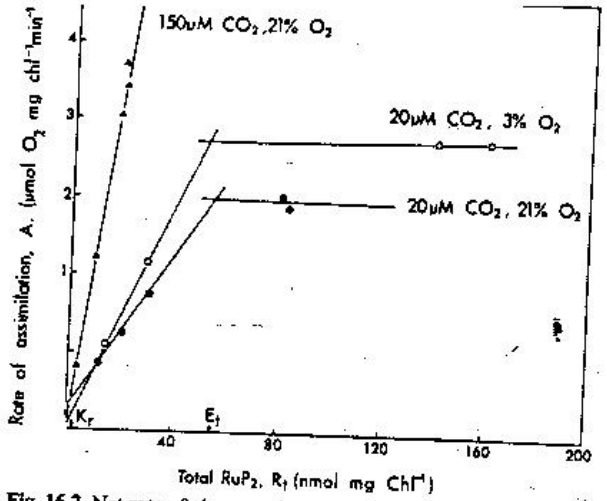


**Fig. 16.2.** Net rate of photosynthesis, $A$, vs. total $RuP_2$ concentration, $R_t$, in *Chlamydomonas reinhardtii* cells as irradiance varies at various concentrations of $CO_2$ and $O_2$. (Replotted from the data of COLLATZ 1978). Total concentration of enzyme sites, $E_t$, is approximately 55 nmol mg $Chl^{-1}$ in this species. A $K_m$ for free $RuP_2$, $K_r$, of approximately 20 μM would correspond to 0.6 nmol $RuP_2$ mg $Chl^{-1}$, since 1 mg Chl is approximately 30 μl stroma

against $R_t$ (Fig. 16.2), it is apparent that saturation does not occur until concentrations vastly in excess of the in vitro $K_m$ for (free) $RuP_2$ are reached.

### 16.2.1.4 Activation of $RuP_2$ Carboxylase-Oxygenase

The degree of activation of the carboxylase-oxygenase enzyme depends on the concentrations of $CO_2$ and of $Mg^{2+}$; this has been modelled by LORIMER et al. (1976) and LAING and CHRISTELLER (1976). In a steady, partially activated state, $V_{c\,max}$ and $V_{o\,max}$ are modified so that $W_c$ is given by (FARQUHAR 1979)

$$W_c = \frac{C \cdot [Mg^{2+}]}{C[Mg^{2+}] + K_1 \cdot K_2} \cdot \frac{V_{o\,max} C}{C + K_c(1 + O/K_o)} \qquad (16.14)$$

$W_o$ is modified in an analogous manner. $K_1$ and $K_2$ are kinetic parameters. $[Mg^{2+}]$ refers to the concentration of free (unbound) $Mg^{2+}$ and for complete activation, with a $Mg^{2+}$ ion bound to each site, the total concentration must exceed $E_t$, which is typically 4 mM. The effective $K_m$ for $RuP_2$ should also be modified when the enzyme is not fully activated (FARQUHAR 1979). Data of MEIDNER (1970) and VON CAEMMERER and FARQUHAR (1981) may be interpreted in the present context as suggesting that the effective $CO_2$ Michaelis constant of activation for intact leaves (given by $K_1 K_2/[Mg^{2+}]$) is typically about 10 μbar.

Thus under normal conditions ($C \approx 170$–$270$ μbar) the enzyme is likely to be fully activated with $W_c$ given by Eq. (16.1). Thus while the effects of enzyme inactivation on the properties of the integrated photosynthetic system are of physiological and biochemical interest, they appear at present to be unimportant in an ecophysiological context. This view could change if it were shown that stomatal closure causes low intercellular $p(CO_2)$ in natural conditions.

### 16.2.1.5 "Enzyme Associated" Rate of $CO_2$ Assimilation

In an attempt to gradually develop full equations for $CO_2$ assimilation rate, we anticipate later discussion and note that oxygenation of 1 mol of $RuP_2$ causes the release of 0.5 mol of $CO_2$ in the photorespiratory carbon oxidation (PCO) cycle. The rate of $CO_2$ assimilation, A, associated with $RuP_2$ carboxylase-oxygenase is then

$$A = V_c - 0.5\, V_o. \qquad (16.15)$$

[LAING et al. (1974), SINCLAIR et al. (1977) and COOKE and RAND (1980) have incorrectly assumed 0.25 mol of $CO_2$ per mol of oxygenation, confusing this with the fraction of glycolate carbon released.] At a whole leaf level, the above rate of assimilation needs to be offset by $CO_2$ evolution due to other processes.

## 16.2.2 "Day" Respiration

The extent to which "dark" respiration continues in the light has been discussed elsewhere (GRAHAM and CHAPMAN 1979). A proportion of the cells in a leaf is heterotrophic, and respiration may be expected to continue in these cells. MANGAT et al. (1974) showed that mitochondrial respiration in autotrophic cells was almost completely eliminated by high levels of ATP in the cytoplasm in experiments carried out in $CO_2$-free air. Data of PEISKER et al. (1981) suggest that at the $CO_2$ compensation point, $CO_2$ evolution by leaf respiration was inhibited by 50%. As we discuss later, there is likely to be less ATP available at the compensation point than in $CO_2$-free air, and less still at normal partial pressures of $CO_2$. Mitochondrial respiration in the light may, under normal ambient conditions, differ little from dark respiration at the same temperature; more experiments are required. Whether or not mitochondrial oxygen uptake and electron transport associated with normal dark respiration are partially inhibited by illumination, the tricarboxylic acid cycle should continue to supply α-ketoglutarate for amino acid biosynthesis. This results in $CO_2$ evolution. Some glycine decarboxylation may result from glycolate produced by reactions other than those associated with the rate of oxygenation of $RuP_2$, $V_o$, although recent evidence suggests this is minimal (SOMMERVILLE and OGREN 1979). Indeed glycine decarboxylation in photorespiration is probably the major potential source of electrons for mitochondria in the light. We denote as $R_d$ ("day respiration") all $CO_2$ evolution from the cells inside the leaf, in addition to that due (via PCO) to $V_o$. The net rate of $CO_2$ assimilation A, is then given by

$$A = V_c - 0.5\, V_o - R_d. \qquad (16.16)$$

### 16.2.3 $CO_2$ Compensation Point, $\Gamma$

#### 16.2.3.1 Introduction

If stomata were to close completely, so that $CO_2$ assimilation rate went to zero, then the intercellular $p(CO_2)$, C, should be at the $CO_2$ compensation point, $\Gamma$. There is little evidence to suggest that stomata behave this way in practice. Nevertheless, $\Gamma$ is a widely studied and modelled parameter. The fact that, in ordinary partial pressures of $CO_2$ (338 μbar in 1980), there is an irradiance, the "light compensation point", at which net $CO_2$ assimilation is zero, means that strictly the compensation point should be called the light and $CO_2$ compensation point, since it will depend on both irradiance and $CO_2$ concentration.

In our opinion, and consistent with the data of COLLATZ (1978), *most* studies of the $CO_2$ compensation point are carried out in conditions where $RuP_2$ is not limiting. In such conditions, $\Gamma$ is independent of irradiance. We discuss this situation first.

In what follows, we ignore the consequences of the sites of $CO_2$ evolution, leaf mitochondria, being seperated from those of carboxylation, the chloroplast stroma. These effects have been discussed by CHARLES-EDWARDS (1978) and PEISKER (1978a), and are most likely of secondary importance in the present context.

#### 16.2.3.2 $R_i > E_i$, $R_d = 0$

In the absence of $R_d$, we see from (16.16) that assimilation rate is zero when $\phi = V_o/V_c = 2$. Thus $\Gamma_*$, the $CO_2$ compensation point in the absence of day respiration, called the $CO_2$-photocompensation point by LAISK (1977), is given by

$$\Gamma_* = \frac{0.5 V_{o\max} K_c O}{V_{c\max} K_o}. \tag{16.17}$$

We note from this equation, together with Eq. (16.3), that the ratio of $RuP_2$ oxygenation to carboxylation is given by

$$\phi = 2\Gamma_*/C. \tag{16.18}$$

Equation (16.17) may be rewritten as

$$\Gamma_* = \gamma_* \cdot O, \tag{16.19}$$

where

$$\gamma_* = 0.5 \frac{V_{o\max} K_c}{V_{c\max} K_o}. \tag{16.20}$$

$\Gamma_*$ increases linearly with $p(O_2)$, as discussed by LAING et al. (1974).



#### 16.2.3.3 $R_i > E_i$, $R_d > O$

From earlier equations it may be shown that the $CO_2$ compensation point, $\Gamma$, in the presence of day respiration, $R_d$, is given by (TENHUNEN et al. 1980b; FARQUHAR et al. 1980)

$$\Gamma = \frac{\Gamma_* + K_c(1 + O/K_o) R_d/V_{o\max}}{1 - R_d/V_{c\max}}. \tag{16.21}$$

Again $\Gamma$ depends linearly on $p(O_2)$ and may be written as

$$\Gamma = \gamma \cdot O + \Gamma_o, \tag{16.22}$$

where

$$\gamma = \frac{K_c}{K_o} \cdot \frac{0.5 V_{o\max}/V_{c\max} + R_d/V_{c\max}}{1 - R_d/V_{c\max}}, \tag{16.23}$$

$$\gamma = \frac{\gamma_* + \dfrac{K_c R_d}{K_o V_{c\max}}}{1 - R_d/V_{c\max}}, \tag{16.23a}$$

and

$$\gamma > \gamma_*,$$

and

$$\Gamma_o = \frac{K_c R_d/V_{c\max}}{1 - R_d/V_{c\max}} \tag{16.24}$$

(TENHUNEN et al. 1980b; AZCON-BIETO et al. 1981).

It has been observed experimentally that $V_{o\max}/V_{c\max}$ is virtually constant over a range of temperatures and is approximately 0.21 (BADGER and ANDREWS 1974; BADGER and COLLATZ 1977; JORDAN and OGREN 1981). [This evidence has been ignored by TENHUNEN in his papers (TENHUNEN et al. 1976, and subsequent papers) and he has assumed a ratio of 2.0.] Consequently the temperature dependence of $\Gamma$ is due to the temperature dependencies of $K_c/K_o$ and of $R_d/V_{c\max}$. From Eqs. (16.21) to (16.24) it may be seen that whenever $R_d$ occurs it is divided by $V_{c\max}$. CHARLES-EDWARDS (1978) looked for a dependence of $\Gamma$ on the rate of respiration in the dark, $R_n$. The appropriate dependence is on $R_d/V_{c\max}$. PEISKER et al. (1981) observed a relationship between $\Gamma$ and $R_n/V_{c\max}$. They concluded that $R_d \approx 0.5 R_n$. Since $\Gamma_o$ depends on $R_d/V_{c\max}$ it is easy to see why $\Gamma_o$ has been nearly zero in some cases and larger in others, as discussed by AZCON-BIETO et al. (1981).

#### 16.2.3.4 $R_t < E_t$, $R_d = 0$

At small irradiances, the $RuP_2$ carboxylase-oxygenase is $RuP_2$ limited and $R_t < E_t$, i.e., only a proportion of the sites have $RuP_2$ available. PEISKER (1974) derived a linear dependence of $\Gamma_*$ on $p(O_2)$ for this situation with $R_d \approx 0$. From Eq. (16.6) and (16.7) it is clear that carboxylation and oxygenation are affected equally, and Eqs. (16.17)–(16.20) are valid.

#### 16.2.3.5 $R_t < E_t$, $R_d > 0$

The situation where day respiration is occurring is more complex. From Eq. (16.13) it emerges that in Eqs. (16.21)–(16.24) $V_{c\,max}$ must be multiplied by $R_t/E_t$, the proportion of enzyme sites with $RuP_2$ attached. As $R_t$ decreases, as occurs at low irradiances, $\Gamma$ increases, especially at higher temperatures where $R_d$ becomes large. Relevant recent data on compensation points have been presented by CATSKÝ and TICHÁ (1979). Unlike earlier circumstances, we do not expect a linear dependence of $\Gamma$ on $O_2$ here. Changing $p(O_2)$ at the compensation point causes changes in patterns of $RuP_2$ consumption and regeneration, and hence of $R_t/E_t$.

The estimation of these patterns is the subject of the next section, since the rate of carboxylation depends on $R_t/E_t$ [Eq. (16.13)].

### 16.2.4 Regeneration of $RuP_2$ — Stromal and Extrachloroplastic Reactions

#### 16.2.4.1 Introduction

The carboxylation of $RuP_2$ results in the production of two molecules of phosphoglyceric acid (PGA). The regeneration of the acceptor $RuP_2$ is achieved in the Calvin, or reductive pentose phosphate or photosynthetic carbon reduction (PCR) cycle, reviewed by BASSHAM (1979). The photorespiratory carbon oxidation (PCO) cycle functions to regenerate $RuP_2$ after it has been oxygenated, and was described by BERRY and FARQUHAR (1978) following studies by LORIMER et al. (1978). In Chap. 15, this Volume, it is discussed as a pathway (PCOP; Figs. 15.1 and 15.2) rather than as a cycle, although this distinction is debatable.

The integrated PCR and PCO cycles consume ATP and NADPH. We believe that, in cases where the supply of $RuP_2$ is limiting the rate of $RuP_2$ carboxylation in natural conditions, it is the supply of ATP and NADPH (discussed in Sect. 16.2.5) that is usually limiting rather than the activities of enzymes, or pool sizes of intermediates, in the PCR and PCO cycles. A possible exception is the supply of inorganic phosphate (see Sect. 16.5.1).

#### 16.2.4.2 Photorespiratory Carbon Oxidation Cycle

Oxygenation of 1 mol of $RuP_2$ produces 1 mol of PGA and 1 mol of phosphoglycolate (PGlA) (see Fig. 16.3). Following this 1 mol PGlA gives rise to 0.5 mol PGA, requiring 0.5 mol ATP in the final step, and releases 0.5 mol of $CO_2$. As well, 0.5 mol ammonia is released and refixed. The refixation of



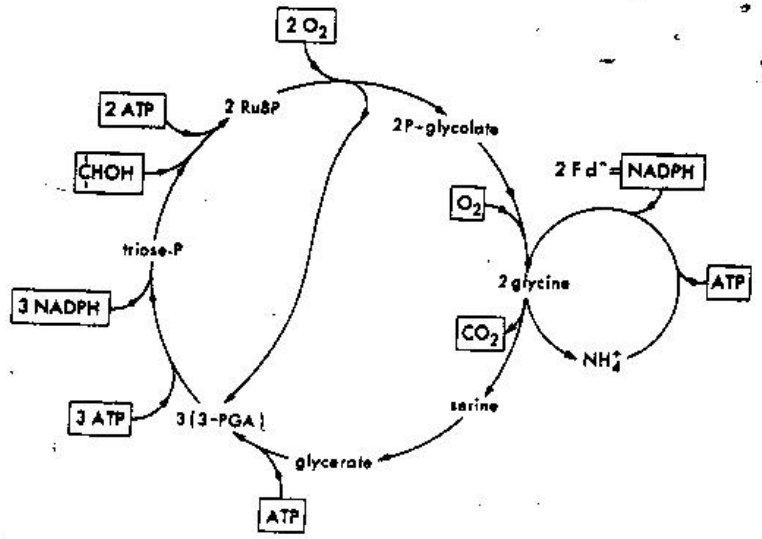


**Fig. 16.3.** The photorespiratory carbon oxidation cycle. (After BERRY and FARQUHAR 1978)

0.5 mol $NH_4^+$ requires 1 mol $F_d^-$ (reduced ferredoxin) (which, in terms of electron transport, is the equivalent to 0.5 mol NADPH) and 0.5 mol ATP. The PGA produced is then converted to $RuP_2$ as in the PCR cycle.

#### 16.2.4.3 PGA Production, ATP and NADPH Consumption in the Integrated PCR and PCO Cycles.

In the PCR cycle, 2 mol of PGA are consumed to produce 1 mol $RuP_2$ and 1 mol ($CH_2O$) (see Fig. 16.1). In the process, 2 mol NADPH and 3 mol ATP are consumed. From the considerations of BERRY and FARQUHAR (1978) and FARQUHAR et al. (1980)

$$\text{rate of PGA production} = 2\,V_c + 1.5\,V_o = (2 + 1.5\,\phi)\,V_c = (2 + 3\,\Gamma_*/C)\,V_c, \quad (16.25)$$

$$\text{rate of NADPH consumption} = 2\,V_c + 2\,V_o = (2 + 2\,\phi)\,V_c = (2 + 4\,\Gamma_*/C)\,V_c, \quad (16.26)$$

$$\text{rate of ATP consumption} = 3\,V_c + 3.5\,V_o = (3 + 3.5\,\phi)\,V_c = (3 + 7\,\Gamma_*/C)\,V_c. \quad (16.27)$$

We next examine the steps in which PGA, NADPH and ATP are consumed, and $RuP_2$ is produced.

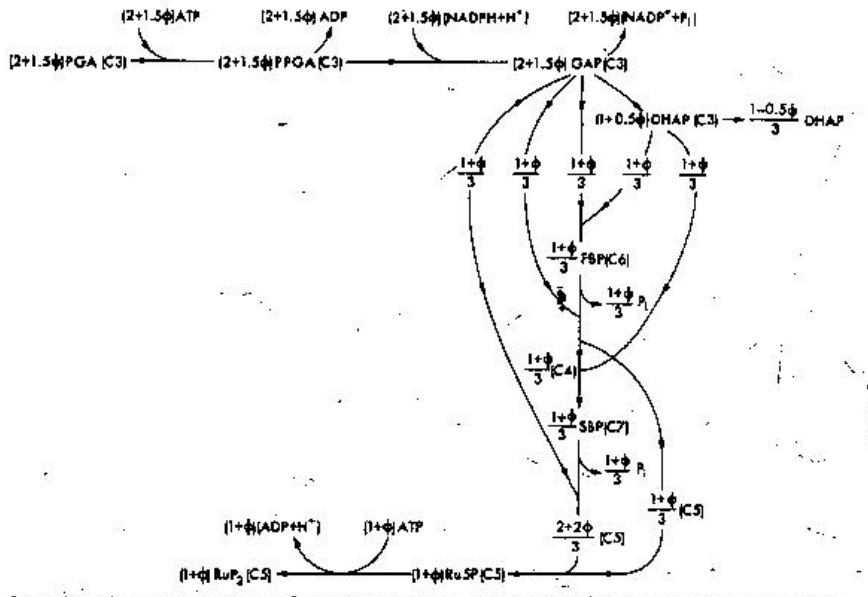


Fig. 16.4. The carbon pathway from PGA to $RuP_2$ (where $\phi$ is the number of oxygenations per carboxylation; see Fig. 16.1)

### 16.2.4.4 Enzymatic Steps from PGA to $RuP_2$

There are many enzymatic steps involved in the pathway from PGA to $RuP_2$ (BASSHAM 1979), and these are outlined in Fig. 16.4. The reactions are reversible apart from those catalyzed by fructose bisphosphatase (FBPase) and by sedoheptulose bisphosphatase (SBPase). SBPase activity also increases with SBP levels (WOODROW and WALKER 1980). The activities of both FBPase and SBPase are modulated by pH and the concentration of $Mg^{2+}$ and of reduced thioredoxin. The latter substance is reduced by ferredoxin from the electron transport chain and this ensures that futile cycles do not waste energy in the dark (BASSHAM 1979). Furthermore, since these enzymes have only a limited capacity in the light the concentration of DHAP is maintained at levels appropriate for export to the cytoplasm. However, while the maximum rates of FBPase and SBPase are regulating factors, we do not believe they are primary limiting factors in $CO_2$ assimilation by leaves. From Fig. 16.4 it may be seen that they only need to run at $^1/_3$ the rate of $RuP_2$ regeneration. LEEGOOD and WALKER (1980) measured FBPase rates of 120 μmol g $Chl^{-1}$ $h^{-1}$ in wheat chloroplasts, which were more than sufficient (by a factor of 4 in fact) to account for an assimilation rate of 100 μmol g $Chl^{-1}$ $h^{-1}$. Similarly high rates have been measured by ROBINSON and WALKER (1980) in spinach chloroplasts. Rates of SBPase sufficient to account for $CO_2$ assimilation have been measured by WOODROW and WALKER (1980) in wheat chloroplasts. Since FBPase and SBPase activities reflect the amount of reduced ferridoxin, it is possible that they may co-limit $RuP_2$ regeneration with electron transport, the latter being the more fundamental limitation.



The reactants involved in the steps between PGA and DHAP are nearly in equilibrium (LILLEY et al. 1977) and have been modelled by GIERSCH et al. (1980b). Detailed modelling of the $RuP_2$ regeneration cycle could usefully be extended. Progress might be made by assuming that other reactions, apart from those catalyzed by $RuP_2$ carboxylase-oxygenase, FBPase and SBPase, are also at equilibrium. A detailed analysis of the enzyme system involved in $RuP_2$ regeneration will probably give information about pool sizes of Calvin cycle intermediates, but not affect the estimation of $CO_2$ assimilation by leaves. To reach this conclusion we must examine the existing, crude representations of $RuP_2$ regeneration, before integrating these with the thylakoid reactions in Section 16.4.

HALL (1971) simplified the regeneration steps to a single one, first order in [PGA] and [NADPH]. Thus HALL wrote, using different symbols,

$$\text{rate of reduction of PGA} = \frac{[\text{PGA}]}{R_p} \cdot \frac{[\text{NADPH}]}{N_t} \cdot M, \tag{16.28}$$

where M is the maximum rate, a fictional composite of many reactions, $R_p$ is the potential pool size of $RuP_2$ which would occur in the absence of carboxylation and oxygenation, and $N_t$ is the total concentration of NADPH and $NADP^+$, i.e.,

$$N_t = [\text{NADPH}] + [\text{NADP}^+]. \tag{16.29}$$

This has formed the basis of models of $RuP_2$ regeneration in many subsequent models (HALL and BJÖRKMAN 1975; PEISKER 1976; HALL 1979; FARQUHAR et al. 1980). In the models of HALL (1971), HALL and BJÖRKMAN (1975) and PEISKER (1976) an increased pool of PGA requires a decreased pool of $RuP_2$ on an equimolar basis. However, LILLEY et al. (1977) have shown that total phosphate is conserved in the chloroplast; FARQUHAR et al. (1980) and FARQUHAR and VON CAEMMERER (1981) optimistically interpreted this as conservation of esterified phosphates and assumed that 1 mol extra PGA resulted in 0.5 mol less $RuP_2$, since $RuP_2$ contains twice as many phosphates.
They wrote

$$0.5[\text{PGA}] + R_t = R_p. \tag{16.30}$$

The potential PGA pool was then 2 $R_p$ and they used this to replace $R_p$ in Eq. (16.28). However, their equation is inadequate because it does not take into account changing concentrations of inorganic phosphate, $P_i$ (STITT et al. 1980). Both it, and the analogous equation used by HALL (1971)

$$[\text{RuP}_2] + [\text{PGA}] = R_p$$

ignore the autocatalytic nature of the Calvin cycle, whereby the total concentration of esterified phosphates may change.

An important distinction between Eq. (16.30) and an analogous one used by HALL (1979) is that Eq. (16.30) refers to total $RuP_2$ (free plus bound).

In HALL's model, Eqs. (16.6)–(16.8) were used in an implicit form and all $RuP_2$ was effectively assumed to be free. This is unlikely to be the case (COLLATZ 1978) and means that HALL's model has no distinct change from $RuP_2$ carboxylation limitation to regeneration limitation as $p(CO_2)$ increases, an important feature discussed in Section 16.5.

FARQUHAR and VON CAEMMERER (1981) considered that ATP may be more limiting than NADPH (see Sect. 16.4) and wrote

$$\text{rate of phosphorylation of PGA} = \frac{[\text{PGA}]}{2R_p} \cdot \frac{[\text{ATP}]}{[\text{ATP}]+[\text{ADP}]} \cdot M. \qquad (16.31)$$

This change was unimportant given that M, the maximum rate of PGA "reduction or phosphorylation to $RuP_2$", is still a fictional composite. Nevertheless, for the estimation of $CO_2$ assimilation rate in conditions where $RuP_2$ supply is limiting, we can afford to use crude representations of the enzyme steps if it is shown that their capacity is in excess of the capacity for ATP and NADPH production.

## 16.3 Thylakoid Reactions

### 16.3.1 Introduction

NADPH and (indirectly) ATP are produced by electron transport in the chloroplast thylakoids. Despite the vast amount of research that has been carried out in this field (ARNON 1977), it was only recently that models of leaf photosynthesis incorporated electron transport explicitly. FARQUHAR et al. (1980) introduced a "potential rate of whole-chain electron transport", J, depending on temperature and absorbed irradiance, I, that would occur if the acceptor $NADP^+$ were at its maximum concentration, and which they related to uncoupled rates of electron transport in vitro. The irradiance dependence was empirical and was arranged to give appropriate quantum yields, and to saturate at high irradiances.

SIGGEL (1976) modelled the function of plastoquinone as electron and proton carrier. CRAMER et al. (1981) derived a model of electron transport from plastoquinone to P-700 in photosystem I (PSI). FARQUHAR and VON CAEMMERER (1981) presented a mechanistic model of whole-chain electron transport, which included diffusion limitation on the plastoquinone shuttle, and the tendency for reverse electron flow from plastoquinone. They simplified the result to

$$J = \frac{J_{max} I}{I + 2.1 J_{max}} \qquad (16.32)$$

and presented supporting data. The form preserves the maximum rate and initial slope of the full equation, but may introduce a non-linearity of response to irradiance too early.



In this section we first examine the temperature dependence of $J_{max}$. We then derive equations for the rate of production of NADPH, including the effects of insufficient amounts of $NADP^+$. In an analogous manner we derive equations for the rate of ATP production. We examine various mechanisms by which the conflict in requirements for NADPH and ATP may be resolved.

### 16.3.2 Temperature Dependence of Potential Electron Transport Rate

The light-saturated potential rate of electron transport, $J_{max}$, depends on temperature (ARMOND et al. 1978; BJÖRKMAN et al. 1980). Several authors have suggested that the temperature dependence of whole-chain electron transport is closely linked to properties of the thylakoid membranes (see discussion in Chap. 10, Vol. 12 A). They suggest that membrane viscosity and lipid composition are important in determining temperature adaptation to high and low temperatures (NOLAN and SMILLIE 1976; RAISON and BERRY 1979; PIKE and BERRY 1979). The reactions associated with photosystem II (PS II) are the most temperature-sensitive. ARMOND et al. (1978) found that electron transport through PS I increased with temperature up to 55 °C, whereas the whole-chain transport peaked at 45 °C and then declined.

Acclimation occurs when plants are grown at different temperatures. The threshold temperature at which electron transport becomes irreversibly inhibited appears to be a function of growth temperature, high growth temperatures resulting in higher thermostability at high temperatures (ARMOND et al. 1978; BJÖRKMAN 1981). It also appears from the data of ARMOND et al. (1978) that low growth temperatures result in improved performance at temperatures below the optima. The temperature response of whole-chain electron transport may therefore be an important parameter in modelling gas exchange. FARQUHAR et al. (1980) used data of NOLAN and SMILLIE (1976) to determine the coefficient B, and parameters $E$, S, and H for use in the following expression

$$J_{max} = B \cdot \exp[-E/RT]/\{1+\exp[(ST-H)/RT]\}, \qquad (16.33)$$

where $R$ is the universal gas constant.

Equation (16.33) is a simplified version of equations developed by JOHNSON et al. (1942) and SHARPE and DE MICHELLE (1977) to describe the effects of temperature on enzyme inactivation. This equation was used by TENHUNEN et al. (1976) and HALL (1979) to model related parameters. S and H are parameters affecting the rate at high and low temperatures, respectively. The temperature optimum, $T_{opt}$, of $J_{max}$ may be different for different species and the following expression was derived by differentiation of Eq. (16.33) with respect to T

$$T_{opt} = H[S + R \ln(H/E-1)]. \qquad (16.34)$$

### 16.3.3 NADPH Production

The reduction of $NADP^+$ to NADPH requires two electrons and the rate of electron transport required to satisfy the NADPH requirement of the inte-

grated PCR and PCO cycles is, from Eq. (16.26)

$$\text{rate of whole chain electron transport} = 4\,V_o + 4\,V_o = (4+4\,\phi)\,V_c = (4+8\,\Gamma_*/C)\,V_c. \quad (16.35)$$

The enzyme which catalyzes the production of NADPH is $NADP^+$-ferredoxin reductase, which occurs after (reducing side of) PS I in the electron transport chain (Arnon 1977). There are approximately 500 chlorophyll (Chl) molecules per PS I in leaves (Melis and Brown 1980) and since 1 mol Chl is associated with 25 l stroma (Heldt and Sauer 1971), there are $1/(500 \times 25)$ mol of PS I sites per l stroma, i.e., the effective concentration of sites is approximately 80 μM (2 mmol/mol Chl). Shin and Oshino (1978) have purified the equivalent of 10.6 mg purified reductase from 2 kg fresh weight of spinach. A comparison of its diaphorase activity with that of the original crude homogenate suggests that 2 kg contains 424 mg reductase. Since the molecular weight of the dimer is 80,000 (Shin et al. 1981) and assuming a chlorophyll content of 1 mmol/kg fr. wt. (von Caemmerer unpublished), this corresponds to one mol reductase per 204 mol Chl, or approximately 196 μM (4.9 mmol/mol Chl). The $K_m$ for $NADP^+$ is only about 8 μM (Shin 1971). Thus we have a situation analogous to the high concentration of $RuP_2$ carboxylase-oxygenase relative to the $K_m$ for $RuP_2$. The rate of $NADP^+$ reduction should have a non-rectangular hyperbolic dependence on $[NADP^+]$, similar to that in Eq. (16.11) and (16.12). By analogy with Eq. (16.13) we can approximate the situation by

$$\text{rate} = 0.5\,J \cdot \min\{1, [NADP^+]/F\}, \quad (16.36)$$

where again min { } means "minimum of", and F is the concentration of $NADP^+$-ferredoxin reductase sites. Thus for maximum rates of electron transport, $[NADP^+]$ should be slightly greater than F. NADPH will be required in the stroma, and so the total pool $N_t (=[NADP^+]+[NADPH])$, should also be greater than F, which we estimated above as 5 mmol/mol Chl. Lendzian and Bassham (1976) report a value for $N_t$ of 36 mmol/mol Chl.

The above considerations help to explain the discrepancy (Lilley and Walker 1979) between the in vivo concentration of ferredoxin (19–38 mmol/mol Chl or ~1 mM in the stroma) and that required in in vitro studies (~10 μM). To the extent that ferredoxin is soluble, it will need to be at a concentration in excess of the sum of PS I and reductase sites, for maximum rates of electron transport. Measurements are needed of the levels of pyridine nucleotides, ferredoxin, and reductase sites in the same chloroplasts.

### 16.3.4 ATP Production

#### 16.3.4.1 Introduction

A situation analogous to the high concentration of reductase sites may exist for photophosphorylation, the conversion of ADP to ATP on the thylakoid membranes. Strotmann et al. (1973) have measured 0.42 g of coupling factor ($CF_1$) per g Chl. $CF_1$ is the ATP synthetase without hydrophobic subunits which anchor in the membrane. Younis et al. (1977) found 0.4 to 0.5 g $CF_1$/g Chl. Assuming $CF_1$ has a molecular weight of 325,000 (Farron 1970), this corresponds to 1.2 mmol/mol Chl, giving an effective concentration of 46 μM. Berzborn et al. (1981) have measured 1.5 mmol/mol Chl, or 62 μM. Berzborn and Müller (1977) showed that the ratio depends on the irradiance during growth. There are multiple binding sites for ADP, although usually only two show tight binding, giving half-maximal binding at about 2 μM [ADP] (McCarty 1979). The concentration of tight binding sites, approximately 0.1 mM, is again much larger than the appropriate half-saturation concentration. There is evidence that these tight binding sites are not necessarily the sites of catalysis and various models of ATP synthesis have been suggested (McCarty 1979). Some schemes and experiments (e.g., Hochman and Carmeli 1981) still favour two sites of phosphorylation, with as yet unknown affinities for ADP. In our opinion, when structural and substrate forms of bound ADP are taken into account, the dependence of the rate of photophosphorylation on the total (bound and free) ADP concentration will probably be approximated by analogy with Eq. (16.36) as

$$\text{rate} = \text{maximum rate} \cdot \min\{1, [ADP]/\mathscr{A}\}, \quad (16.37)$$

where $\mathscr{A}$ is the concentration of sites of ADP phosphorylation. Accurate measurements of $\mathscr{A}$ are needed.

At first sight it would appear from Eq. (16.37) that $A_t$ $(=[ADP]+[ATP])$ would only need to be slightly in excess of $\mathscr{A}$ (≈2 mmol/mol Chl). However, this is not the case. $A_t$ has variously been estimated as 70–100 (Heber and Santarius 1970), 9.2 (Lilley et al. 1977), 27 (Wirtz et al. 1980) and 44 mmol/mol Chl (Giersch et al. 1980a). This may be because a large concentration of ATP is required to keep the reversible reaction between Ru5P and $RuP_2$ favouring production of the latter. Expressed differently, it is known that ribulose-5-P kinase requires a large energy charge to support $RuP_2$ regeneration (Preiss and Kosuge 1976).

#### 16.3.4.2 Non-Cyclic Photophosphorylation via Whole-Chain Electron Transport

It is now widely accepted that three protons move across the thylakoid into the stroma every time an ATP molecule is produced (Shavit 1980). From Eq. (16.27) we see that in the steady state, the required

$$\text{rate of proton production} = 9\,V_c + 10.5\,V_o = (9+10.5\,\phi)\,V_c = (9+21\,\Gamma_*/C)\,V_c. \quad (16.38)$$

The movement of one electron through the whole electron transport chain results in the accumulation of two protons in the thylakoid spaces, one from the splitting of water in PS II and one from the shuttle of reduced plastoquinone

across the membrane (JUNGE 1977). Thus if the proton production is by whole-chain electron transport alone, the required

$$\text{rate of whole chain electron transport} = 4.5\,V_c + 5.25\,V_o = (4.5 + 5.25\,\phi)\,V_c = (4.5 + 10.5\,\Gamma_*/C)\,V_c. \quad (16.39)$$

### 16.3.4.3 Pseudo-Cyclic Electron Transport (Mehler Reaction)

Comparing Eq. (16.39) with Eq. (16.35) we see that there is a disparity of $(0.5+1.25\,\phi)\,V_c$. For this reason FARQUHAR and VON CAEMMERER (1981) developed equations to model the situation where the extra whole-chain electron transport was to an acceptor other than $NADP^+$, such as $O_2$, as occurs in the Mehler reaction (MEHLER 1951). This reaction was reported to be half saturated at a $p(O_2)$ of 80 mbar (8%) (RADMER et al. 1978). An increased requirement for $O_2$ at high rates of electron transport may explain the observation by VIII. et al. (1977) that at high $p(CO_2)$, photosynthetic rate is lowered when $p(O_2)$ is lowered from 210 to 5 mbar.

The required

$$\text{rate of electron transport to } O_2 = (0.5 + 2.5\,\Gamma_*/C)\,V_c, \quad (16.40)$$

which, with $\Gamma_* = 31$ and $C = 230$ μbar, respectively, is about 16% of the rate given by Eq. (16.35). This is comparable with the measured capacities of the Mehler reaction in higher plants (HEBER et al. 1978; MARSHO et al. 1979). Nevertheless, there are other mechanisms by which chloroplasts may meet the conflicting requirements for ATP and NADPH. The incorporation of nitrate into amino acids reduces the disparity. Other mechanisms are discussed in the following two subsections.

### 16.3.4.4 Cyclic Photophosphorylation

Whole-chain electron transport to $NADP^+$ alone leaves a deficiency in proton production of $(1+5\,\Gamma_*/C)\,V_c$. This could be met by a portion of the electron transport being cyclical around PS I. Since this cycle will probably only contribute one proton per electron involved, the required

$$\text{cyclic-electron transport} = (1 + 5\,\Gamma_*/C)\,V_c. \quad (16.41)$$

FARQUHAR and VON CAEMMERER (1981) considered this possibility and wrote an expression for whole-chain electron transport

$$J = \frac{J_{max} I}{I + K_i}, \quad (16.42)$$

where

$$K_i = \frac{9.4 + 10.9\phi}{4 + 4\phi} J_{max} \simeq 2.4\,J_{max}. \quad (16.43)$$



In this case, $J_{max}$ is the maximum rate of whole chain transport, while cyclic flow is occurring simultaneously. If the limitations to electron transport, other than irradiance, are common to both cyclic and non-cyclic flow, then $J_{max}$ is $(4.5+5.25\,\phi)/(5+6.5\,\phi)$ times the rate which would occur in the absence of cyclic flow (FARQUHAR and VON CAEMMERER 1981).

### 16.3.4.5 DHAP/PGA Shuttle

A third mechanism which may contribute to the balancing of conflicting requirements is the DHAP/PGA shuttle. In this shuttle (WALKER 1976), which does not actually involve the thylakoid, DHAP is exported from the chloroplasts, and oxidized in the cytoplasm to yield ATP, NADH and 3-PGA, the latter returning to the stroma together with a proton. If we consider that x mol PGA return in this manner per mol of carboxylations, Eqs. (16.26) and (16.27) are replaced by

$$\text{rate of NADPH consumption} = (2 + 2\,\phi + x)\,V_c \quad (16.44)$$

$$\text{rate of ATP consumption} = (3 + 3.5\,\phi + x)\,V_c \quad (16.45)$$

and the required rates of whole-chain electron transport become, respectively,

$$\text{rate} = (4 + 4\,\phi + 2x)\,V_c \quad (16.46)$$

and

$$\text{rate} = (4.5 + 5.25\,\phi + 1.5x)\,V_c. \quad (16.47)$$

If this were the *sole* mechanism for balancing requirements then (16.46) and (16.47) would have to be equated, yielding

$$x = 1 + 2.5\,\phi. \quad (16.48)$$

This, as we see later, would be energetically expensive for the chloroplast.

### 16.3.4.6 Photosynthetic Control of Whole-Chain Electron Transport

It is known that electron transport is reduced when a proton motive force (p.m.f.) occurs across the thylakoid membrane. This has been called photosynthetic control (WEST and WISKICH 1968). Thus each time a mole of ATP is produced on the stromal side, and 3 mol of protons move across the membrane, reducing the p.m.f., 1.5 mol of electrons (1.5 equivalents) should be able to move along the whole chain, or 3 mol cyclically around PS I, perhaps by removing limitations on the diffusion of reduced PQ (SIGGEL 1976). Thus

$$\text{rate of ATP production} = \tfrac{2}{3} \cdot \text{rate of whole chain electron transport} + \tfrac{1}{3} \cdot \text{rate of cyclic electron transport}. \quad (16.49)$$

An appropriate equation describing photosynthetic control in detail has not been incorporated into a model of leaf photosynthesis. Such an equation, when combined with others describing the rates of consumption and production of protons in the stroma would be useful.

Photosynthetic control by p.m.f. operates in the same direction as the ADP dependence of photophosphorylation rate [Eq. (16.37)], when $[ADP] < \mathscr{A}$. As the $RuP_2$ regeneration reactions release 1 mol ADP, which binds to the coupling factor, 3 mol protons move across the thylakoid, reducing the p.m.f. and allowing 1.5 equivalents to move along the chain. Thus we write

$$\text{rate of whole-chain electron transport} = J \cdot \min\{1, [ADP]/\mathscr{A}\}. \tag{16.50}$$

It appears from Eq. (16.36) that electron transport could be controlled by $[NADP^+]$. However, when $[NADP^+]$ is low, electrons will normally be able to move from $Fd^-$ to $O_2$ in the Mehler reaction. Equation (16.50) emerges as our link between thylakoid functioning and the stromal regeneration of $RuP_2$.

## 16.4 Integration of Factors Limiting $RuP_2$ Regeneration

In the following developments we assume that the shortfall in ATP production associated with normal whole-chain electron transport to $NADP^+$ via Fd is overcome by whole-chain electron flow to $O_2$ via Fd. When equations representing cyclic phosphorylation and the DHAP/PGA shuttle are included, the resulting models are not substantially different from the one developed here.

Equating two expressions for the rate of electron transport [Eqs. (16.39) and (16.50)], we obtain

$$V_c = J' \cdot \min\{1, [ADP]/\mathscr{A}\}, \tag{16.51}$$

where

$$J' = J/(4.5 + 10.5\,\Gamma_*/C). \tag{16.52}$$

$J'$ is the maximum carboxylation velocity allowed by the potential electron transport rate (FARQUHAR and VON CAEMMERER 1981). When $R_t > E_t$, the carboxylation rate is given by $W_c$, and the electron transport is forced to go at the rate $(4.5 + 10.5\,\Gamma_*/C)\,W_c$. The important question here is whether, when carboxylation is $RuP_2$ limited ($R_t < E_t$), $V_c$ is less than $J'$, i.e., is $[ADP] < \mathscr{A}$? Put another way, with $[ADP] \geqq \mathscr{A}$, so that $V_c = J'$, is there sufficient [ATP] ($\leqq A_t - \mathscr{A}$) to ensure that the regeneration of $RuP_2$ is sufficiently rapid? We are now forced to use the crude model of $RuP_2$ regeneration presented earlier. Combining Eqs. (16.25) and (16.31) we obtain

$$(2 + 3\Gamma_*/C)\,V_c = \frac{[PGA]}{2R_p} \cdot \frac{[ATP]\,M}{A_t}. \tag{16.53}$$



Provided M is sufficiently large, the answer is yes. More precisely, by combining Eqs. (16.51) and (16.53) for $R_t < E_t$, then $V_c = J'$, provided

$$M' > \frac{2R_p}{[PGA]} \cdot \frac{J'}{1 - A/A_t} \tag{16.54}$$

where

$$M' = M/(2 + 3\Gamma_*/C), \tag{16.55}$$

the maximum rate of carboxylation allowed by the enzymes regenerating $RuP_2$, given that $2\Gamma_*/C$ oxygenations occur per carboxylation.

We see now why the pool size of adenylates ($A_t \approx 0.45$ mM) is approximately five times larger than the concentration of ADP binding sites ($\mathscr{A} \approx 92\ \mu M$). This ensures that at low irradiance, when carboxylation is $RuP_2$ limited, there is sufficient ATP, after all the binding sites are filled by ADP, for the $RuP_2$ regeneration enzymes (e.g., Ru-5 P kinase and PGA kinase) to maintain a slight excess capacity.

We note that at the transition from carboxylation limitation to regeneration limitation, $R_t = E_t$, $V_c = W_c = J'$ and the "phosphorylation potential" should be given by

$$\text{for } R_t = E_t \quad \frac{[ATP]}{[ADP]} = \frac{A_t}{\mathscr{A}} - 1 \approx 3.9 \tag{16.56}$$

The model predicts that the potential should be lower when the irradiance is low, or even at saturating irradiance if the $p(CO_2)$ is high. In vivo estimates range between 2 and 5 (KRAUSE and HEBER 1976).

When $R_t > E_t$, electron transport rates should increase with increasing $p(CO_2)$ and, from Eq. (16.50), [ADP] should also increase, cf. Sect. 16.2.2.

It must be emphasized that our understanding of the integrated control of $RuP_2$ regeneration is meagre. One of our greatest difficulties is to explain why ATP is present in chloroplasts in the dark. More realistic models of the enzyme system will modify the expression for the required capacity for regeneration [Eq. (16.54)], but hopefully not the conclusion that when $RuP_2$ is limiting, $V_c$ can be usefully approximated by $J'$.

## 16.5 Integrated $C_3$ Metabolism

### 16.5.1 Rate of $CO_2$ Assimilation, A

We are now in a position to examine the integrated metabolism. The net rate of assimilation of $CO_2$ is given by Eq. (16.16):

$$A = V_c - 0.5\,V_o - R_d$$

which may be rewritten using Eq. (16.18) as

$$A = V_c(1 - \Gamma_*/C) - R_d. \tag{16.57}$$

We note that $\Gamma_*/C$ represents the ratio of the rates of photorespiration and of carboxylation.

In the previous sections we suggested that

$$V_c = \min\{W_c, J'\}, \tag{16.58}$$

where $W_c$ is the $RuP_2$-saturated rate of carboxylation given by

$$W_c = V_{c\max} \cdot \frac{C}{C + K_c(1 + O/K_o)} \tag{16.59}$$

(assuming the enzyme is fully activated) and $J'$ is the electron transport/photophosphorylation limited rate of $RuP_2$ regeneration given variously as

$$J' = \frac{JC}{4C + 8\Gamma_*} \tag{16.60a, b}$$

$$J' = \frac{JC}{4.5C + 10.5\Gamma_*} \tag{16.60c}$$

$$J' = \frac{JC}{6C + 18\Gamma_*} \tag{16.60d}$$

depending on whether the additional ATP to balance the NADPH production is (a) not required, or generated by (b) cyclic electron transport, (c) pseudocyclic electron transport (to $O_2$ in a Mehler reaction), or (d) via a DHAP/PGA shuttle. The form of $J'$ is not necessarily fixed, but we favour the use of Eq. (16.60c). $J$ is the potential rate of whole chain electron transport, which depends on irradiance as given approximately by Eq. (16.32)

$$J = \frac{J_{max} I}{I + 2.1 J_{max}}.$$

Eq. (16.32) probably underestimates $J$ at intermediate irradiances. For case (b) (extra ATP produced by cyclic electron transport) 2.1 in the denominator is replaced by

$$(9.4\,C + 21.8\,\Gamma_*)/(4\,C + 8\,\Gamma_*) \simeq 2.4.$$

From Eqs. (16.57) to (16.59) we obtain the $RuP_2$-saturated rate of $CO_2$ assimilation, given by (FARQUHAR et al. 1980)

$$A = V_{c\max} \cdot \frac{C - \Gamma_*}{C + K_c(1 + O/K_o)} - R_d. \tag{16.61}$$

Comparing this with Eq. (16.1), C in the numerator is offset by $\Gamma_*$ but, contrary to KU and EDWARDS (1977b), not in the denominator.

From Eqs. (16.57) and (16.60) we obtain the $RuP_2$ limited rates, e.g.,

$$A = J \cdot \frac{C - \Gamma_*}{4.5C + 10.5\Gamma_*} - R_d. \tag{16.62}$$

For brevity, we now omit analogous equations referring to cases a, b and d, wherever possible.

As an aside we note that when DHAP is exported from the chloroplast to the cytoplasm, orthophosphate moves in to maintain the supply of $P_i$ (WALKER and ROBINSON 1978). If the latter process is limiting, A becomes independent of C and O. However, in what follows, we assume that in cases where $RuP_2$ is limiting, its regeneration is limited by the potential rates of electron transport/photophosphorylation.

### 16.5.2 Quantum Yield

At low irradiances, $V_c = J'$ and Eq. (16.62) are appropriate. In cases where cyclic electron transport is not involved (a, c and d above) 2.1 mol quanta are absorbed to move 2 mol electrons (equivalents) through the whole chain and at low irradiances (I), J is replaced by I/2.1. When cyclic transport occurs (case b) approximately 2.4 mol quanta are required

$$\lim_{I \to 0} \frac{dA}{dI} = \frac{C - \Gamma_*}{4C + 8\Gamma_*} \cdot \frac{I}{2.1} \tag{16.63a}$$

$$\text{or} = \frac{C - \Gamma_*}{9.4C + 21.8\Gamma_*} \cdot I \tag{16.63b}$$

$$\text{or} = \frac{C - \Gamma_*}{4.5C + 10.5\Gamma_*} \cdot \frac{I}{2.1} \tag{16.63c}$$

$$\text{or} = \frac{C - \Gamma_*}{6C + 18\Gamma_*} \cdot \frac{I}{2.1}. \tag{16.63d}$$

The effects of $CO_2$ and oxygen concentrations, and of temperature, are summarized by Eq. (16.63) together with Eq. (16.19), see also discussion in Chapter 3, Volume 12 A.

Equations giving similar dependencies on concentrations and temperature to those of (16.63a) have been derived by PEISKER (1978b), HALL (1979), and FARQUHAR et al. (1980), although PEISKER neglected energetic costs of the reassimilation of $NH_4^+$ in the photorespiratory cycle (WOO et al. 1978; BERRY and FARQUHAR 1978; KEYS et al. 1978). Earlier predictions were made by HALL (1971). All these modelling approaches reflect competition between the PCR

and PCO cycles for limiting NADPH and ATP. FARQUHAR et al. (1980) derived an equation similar to (16.63 c) and numerical solutions of this equation were graphed by BERRY and FARQUHAR (1978). All of these models are able, with differing degrees of precision, to match the $CO_2$, $O_2$ and temperature dependencies observed by EHLERINGER and BJÖRKMAN (1977). (It is interesting to note here that KU and EDWARDS (1978) found that the quantum yield (mol $CO_2$ fixed per mol quanta absorbed) of wheat leaves was independent of temperature when the solubility ratio of $O_2/CO_2$ was kept constant. They recognized that this may, in part, be fortuitous.)

All of the published models cited above, while successful in predicting effects of environmental changes, were empirical in the sense that parameters were chosen in order to make the quantum yield close to observed values at high [$CO_2$] or low [$O_2$] (i.e., $C \gg \Gamma_*$). HALL (1979) chose a value for a fundamental parameter he called the "photochemical efficiency" and FARQUHAR et al. (1980) chose a value for the "fraction of light not effectively absorbed by chloroplasts". Eq. (16.63) suffer less from this deficiency. Under conditions where $C \gg \Gamma_*$, the quantum requirements (mol quanta absorbed per mol $CO_2$ fixed) become (a) 8.4, (b) 9.4, (c) 9.5, and (d) 12.6. Using white light, EHLERINGER and BJÖRKMAN (1977) observed requirements of 12.3 in one set of experiments and 13.7 in another, while KU and EDWARDS (1978) found requirements of 12.0. TERRY (1980), using red light, found values ranging between 8 and 11, but averaging 10.

Eq. (16.63) have other deficiencies. Firstly, there are chloroplastic requirements for ATP and NADPH outside the PCR and PCO cycles (RAVEN 1972) including additional amino acid biosynthesis, lipid metabolism and, in some cases, nitrate reduction. These will raise the apparent quantum requirement. Secondly, the quantum yields are measured at finite irradiances, often between 50 and 150 $\mu E\, m^{-2}\, s^{-1}$, where J may not necessarily increase linearly with I. From Eq. (16.32)

$$\frac{dJ}{dI} = \frac{2.1 J_{max}^2}{(I + 2.1 J_{max})^2} \tag{16.64}$$

and for case (b) (cyclic), from Eq. (16.43)

$$\frac{dJ}{dI} = \frac{K_J J_{max}}{(I + K_J)^2} \tag{16.65}$$

For $J_{max} = 200\ \mu Eq\, m^{-2}\, s^{-1}$, at $I = 100\ \mu E\, m^{-2}\, s^{-1}$, dA/dI becomes, for $C \gg \Gamma_*$, (a) 0.078, (b) 0.072, (c) 0.069, (d) 0.052, giving apparent quantum requirements of (a) 12.9, (b) 13.8, (c) 14.6, (d) 19.2. We see that case (d) would be energetically expensive. Inclusion of (b) in a strict comparison with the others may be misleading since with the same electron transport capacity $J_{max}$ should be smaller in this case (cf. Sect. 16.3.4.4) giving a greater quantum requirement than 13.8. As was mentioned before, Eq. (16.32) may lead to an underestimate of dJ/dI.

In 21% oxygen, at normal $CO_2$ concentrations, and 25 °C, the apparent quantum requirements are increased, theoretically and in practice (EHLERINGER and BJÖRKMAN 1977) by about 40%; i.e., quantum yield is inhibited by about 30%.



### 16.5.3 Carboxylation Efficiency

#### 16.5.3.1 Introduction

FARQUHAR et al. (1980) differentiated Eq. (16.61) to obtain

$$\frac{dA}{dC} = V_{c\,max} \cdot \frac{\Gamma_* + K_c(1 + O/K_o)}{[C + K_c(1 + O/K_o)]^2}, \tag{16.66}$$

i.e., the slope, sometimes called the "mesophyll conductance" and, more appropriately, the "carboxylation efficiency" (KU and EDWARDS 1977b), should have a slight dependence only on $CO_2$ concentration because $K_c$ is relatively large. Inclusion of activation effects [Eq. (16.14)] may lead to an even more linear response above the compensation point. At $C = \Gamma_*$

$$\frac{dA}{dC} = \frac{V_{c\,max}}{\Gamma_* + K_c(1 + O/K_o)}. \tag{16.67}$$

VON CAEMMERER and FARQUHAR (1981) have measured dA/dC using gas exchange techniques and $V_{c\,max}$ using biochemical techniques and found good agreement between these results and Eq. (16.67). Leaves of *Phaseolus vulgaris* were used and the sources of variation were age, nitrogen nutrition, iron nutrition, previous irradiance, and $CO_2$ concentration during growth and defoliation.

#### 16.5.3.2 Oxygen Dependence of Carboxylation Resistance

The inverse of dA/dC, the "carboxylation resistance", is

$$\frac{1}{dA/dC} = \frac{\Gamma_* + K_c(1 + O/K_o)}{V_{c\,max}} \tag{16.68}$$

$$= \frac{K_c + (\gamma_* + K_c/K_o)\,O}{V_{c\,max}} \tag{16.69}$$

which is linearly dependent on oxygen concentration, as observed by KU and EDWARDS (1977b), with a slope of $(\gamma_* + K_c/K_o)/V_{c\,max}$.

Anomalous results have been reported by PEISKER and APEL (1971), who observed that the oxygen dependence of carboxylation resistance increased with oxygen concentration. PEISKER et al. (1979) also reported anomalous changes in carboxylation resistance at high temperatures and high $O_2$ concentrations. However, KU and EDWARDS (1977b) found no such anomalies.

#### 16.5.3.3 Temperature Dependence of dA/dC

The temperature dependence of dA/dC is determined by the kinetic constants of $RuP_2$ carboxylase-oxygenase and their respective temperature dependencies.

FARQUHAR et al. (1980) used the temperature dependencies of $K_c$, $K_o$, $V_{c\,max}$ and $V_{o\,max}$, determined by BADGER and COLLATZ (1977). This model predicts that dA/dC should increase slowly with temperature (2% per degree at 25 °C) at normal $p(O_2)$, but be independent of temperature at zero $p(O_2)$. HALL (1979) used the same activation energies for $K_c$ and $K_o$ but assumed an in vivo temperature optimum for $V_{c\,max}$ and $V_{o\,max}$ of about 30 °C. Recent data of WEIS (1981) appear to support this assumption. There is, as yet, no in vitro biochemical support. KU and EDWARDS (1977b) observed increasing "carboxylation efficiency" with increasing temperature, when expressed in terms of concentration in solution. When expressed in terms of partial pressures of $CO_2$, the increase was almost zero. PEISKER et al. (1979) observed that at normal $p(O_2)$, dA/dC were similar at 23 °C and 33 °C in wheat.

### 16.5.4 Transition from Limitation Due to $RuP_2$ Carboxylation Capacity to One Due to $RuP_2$ Regeneration Capacity

The above equations [(16.66)–(16.69)] apply only when $RuP_2$ is saturating. FARQUHAR et al. (1980) suggested that this would be so at low $CO_2$ concentrations, but that at higher $p(CO_2)$ a point is reached where $RuP_2$ regeneration is limiting, and the dependence on $CO_2$ changes in nature. Their prediction of a change in the response of A to C has been confirmed by VON CAEMMERER and FARQUHAR (1981) (see Fig. 16.5). To the extent that $RuP_2$ regeneration is limited by photophosphorylation, the dependence on C is given by Eq. (16.62c). Note that A continues to increase with C in this region as limiting ATP is diverted from the PCO cycle to the PCR cycle. Analyses of $CO_2$ exchange under high $CO_2$ concentration which ignore the $RuP_2$ limitation (SINCLAIR and RAND 1979) are unreasonable.

From Eq. (16.59) and (16.60c), we can predict that the transition from $RuP_2$ carboxylation limitation to $RuP_2$ regeneration limitation occurs at

$$C=\frac{K_c(1+O/K_o)\,J/(4.5V_{c\,max})-7/3\,\Gamma_*}{1-J/(4.5V_{c\,max})}. \qquad (16.70)$$

Note that the transition depends on the ratio $J/V_{o\,max}$ and since this ratio is somewhat conservative at the growth irradiance (VON CAEMMERER and FARQUHAR 1981), the transition C also tends to be conservative.

The change in $CO_2$ dependence moving from $RuP_2$ carboxylation limitation to $RuP_2$ regeneration limitation causes faster saturation than would occur due to the kinetics of $RuP_2$ carboxylase-oxygenase alone. Failure to recognize this has led TENHUNEN et al. (1977) to fit sunflower data at 25 °C with the physiologically unreasonable values of 0.45 µbar and 1 mbar for $K_c$ and $K_o$ respectively, and wheat data at 25 °C (TENHUNEN et al. 1980a) with $K_c=12$ µbar and $K_o=82$ mbar. TENHUNEN et al. (1980a) emphasized the linear relationship between A and C as indicating support for mesophyll resistance to diffusion. However, all that is needed for such a response is to use biochemically reasonable values for the kinetic constants. FARQUHAR et al. (1980) used 460 µbar and 210 mbar,

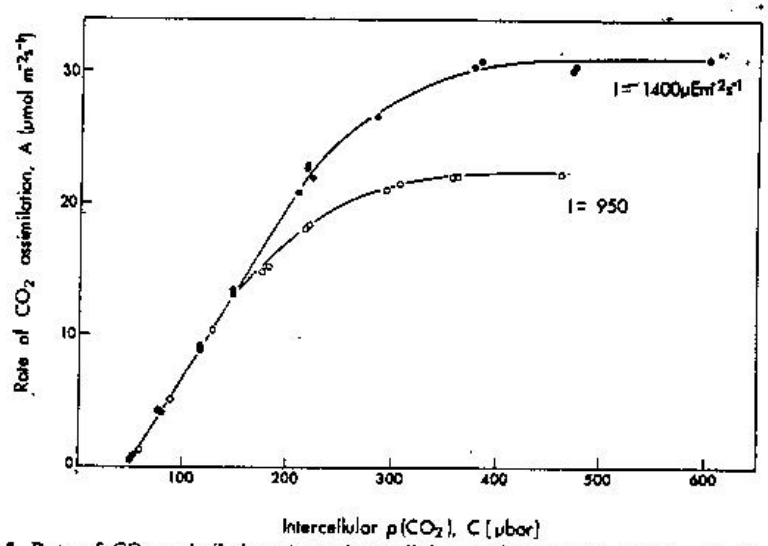


**Fig. 16.5.** Rate of $CO_2$ assimilation $A$, vs. intercellular partial pressure of $CO_2$, $C$, in *Phaseolus vulgaris* at an irradiance, $I$, of 1,400 µE m$^{-2}$ s$^{-1}$ (●), and 950 µE m$^{-2}$ s$^{-1}$ (○) at 28°C (after VON CAEMMERER and FARQUHAR 1981)

for $K_c$ and $K_o$ at 25 °C. There is still some uncertainty about exact values which, although reasonably consistent among higher $C_3$ land plants, may show a twofold variation (YEOH et al. 1981). All measurements indicate values much higher than those used by TENHUNEN.

At low $CO_2$ concentrations the response of A to C is not linear, as demonstrated by MEIDNER (1970). It is possible that this curvature may be due to carboxylase-oxygenase inactivation [cf. Eq. (16.14)].

### 16.5.5 Temperature Optimum

The dependence on temperature of the $CO_2$ assimilation rate, A, depends on that of its subprocesses, but the analysis is nevertheless complex (see also Chap. 10, Vol. 12 A). At normal $p(CO_2)$ and $p(O_2)$ the $RuP_2$ saturated rate, given by Eq. (16.61), increases with temperature. This dependence is greater at high $p(CO_2)$. At sufficiently high temperatures there is a decline due to increased day respiration, $R_d$. The latter effect is more pronounced at low $p(CO_2)$ since $R_d$ then has a greater fractional impact on A. The temperature dependence of the $RuP_2$-limited rate, given by Eq. (16.62c) is affected more by that of $J_{max}$, and the optimum is closer to that of $J_{max}$, which occurs at lower temperatures. We show in Fig. 16.6 that by increasing the ratio $J_{max}/V_{c\,max}$, which tends to release the $RuP_2$ limitation, an increase in the temperature optimum is obtained.

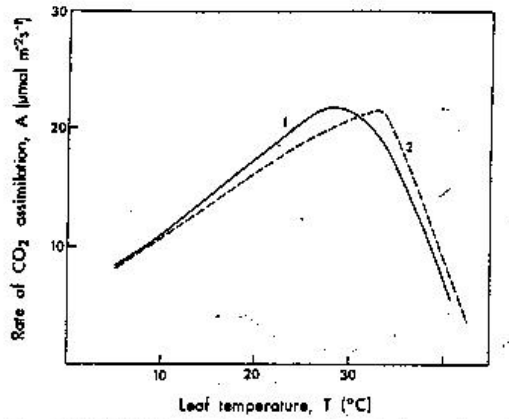


Fig. 16.6. Modelled rate of $CO_2$ assimilation, $A$, vs. leaf temperature, $T$, for two ratios of $J_{max}/V_{c\,max}$:

$$1\quad \frac{J_{max}}{V_{c\,max}}=\frac{190\,\mu Eq\,m^{-2}s^{-1}}{115\,\mu mol\,m^{-2}s^{-1}}=1.65, \qquad 2\quad \frac{J_{max}}{V_{c\,max}}=\frac{210\,\mu Eq\,m^{-2}s^{-1}}{98\,\mu mol\,m^{-2}s^{-1}}=2.14.$$

The irradiance is 2,000 μE m$^{-2}$ s$^{-1}$, intercellular $p(CO_2)$ is 230 μbar

Increasing $p(CO_2)$ from a low level causes an increase in the optimum temperature, as does increasing the irradiance from a low level. Both also cause the temperature response to become sharper, as discussed by HALL (1979). All these phenomena are observed in practice (ENOCH and SACKS 1978; BERRY and BJÖRKMAN 1980). Decreasing the $p(O_2)$ from an initially high value causes a similar response as observed by JOLLIFFE and TREGUNNA (1968).

### 16.5.6 Resistance of the Intercellular Spaces

YOCUM and LOMMEN (1975) estimated the drop in the concentration of $CO_2$ at cells some distance from the substomatal cavities. They used equations developed to describe a system where enzymes are uniformly distributed in a diffusing medium without carriers for facilitated transport. They regarded the distributed cells as being analogous to the distributed enzymes, and estimated that the $CO_2$ concentration at the farthest distance from the substomatal cavities was 0.91 of that in the cavities, $C_c$. However, their dimensionless Michaelis-Menten constant, $K_m/C_c$, was probably too low by at least an order of magnitude, as they chose a value for $K_m$ of only 25 μbar. The latter value was determined, presumably, using the erroneous method of assessing $K_m$ from A vs C response curves, without considering electron transport and photophosphorylation limitations. If a more reasonable estimate of $K_m[=K_c(1+0/K_o)]$ is used in their equations, with the parameters they determined for an ivy leaf, the estimated drawdown in $CO_2$ concentration in remote regions of the intercellular spaces is negligible.



RAND (1977) estimated the maximum drawdown to be 50% of the substomatal concentration. His sink strengths were unreasonable and he subsequently (RAND 1978) revised this estimate to 2%–14%. The substomatal concentration is typically 220 μl l$^{-1}$ in $C_3$ species (WONG et al. 1979). COOKE and RAND (1980) estimated the intercellular air space (ias) resistance to be typically 0.25 m$^2$ s mol$^{-1}$ for $CO_2$. PARKHURST (1977) has derived a three-dimensional model for $CO_2$ uptake in which he estimated an ias resistance of 6.3 m$^2$ s mol$^{-1}$. The reasons for the disparity are not obvious to us.

We now give independent estimates. The maximum drawdown, at cells most remote from the stomata, in a hypostomatous leaf assimilating uniformly throughout its volume is approximately $A_1\,r_i/2$, where $A_1$ (μmol m$^{-2}$ s$^{-1}$) is the flux of $CO_2$ into the lower surface, and $r_i$ is the resistance to diffusion of $CO_2$ across the whole leaf through the intercellular spaces. In an amphistomatous leaf the maximum drawdown $\simeq\frac{A_1 A_2}{A_1+A_2}\cdot\frac{r_i}{2}$, where $A_2$ is the $CO_2$ flux into the upper surface. FARQUHAR and RASCHKE (1978) measured the resistance to the diffusion of helium across leaves of cotton and *Xanthium strumarium*. After allowing for stomatal and boundary layer resistances on each side of the leaf, and for the ratio of the diffusivities of $CO_2$ and helium in air, the total intercellular resistances were approximately 8 and 3.2 m$^2$ s mol$^{-1}$ for cotton and *X. strumarium*, respectively. With $A_1=A_2=10$, and $A_1=8$, $A_2=5$, respectively, the maximum drawdowns are then 20 and 5 μl l$^{-1}$. The average drawdowns in the leaves are approximately half these values.

At a whole leaf level these predictions for average drawdown may be mimicked by resistances to the diffusion of $CO_2$ in the intercellular air spaces of 0.5 and 0.2 m$^2$ s mol$^{-1}$, respectively, in agreement with the estimates of COOKE and RAND (1980). These resistances are relatively unimportant, but may underestimate the effects of close packing in, for example, sclerophyllous leaves.

### 16.5.7 Liquid-Phase Resistance

YOCUM and LOMMEN (1975) pointed out that most of the liquid diffusion path is within the chloroplasts themselves. They used the equations relevant to distributed sinks with Michaelis-Menten kinetics to examine $CO_2$ diffusion across a chloroplast. They estimated that the $CO_2$ concentration at the surface away from the wall would be 0.5 of that nearest it if the diffusing species were $CO_2$ alone. Unfortunately the $K_m$ chosen for $CO_2$ was only 25 μbar and with a more appropriate value the drawdown is again very small. YOCUM and LOMMEN (1975) estimated that carbonic anhydrase activity would reduce the depletion to almost zero.

SINCLAIR et al. (1977) have developed equations to describe the net characteristics associated with both diffusion through cytoplasm and kinetics of $RuP_2$ carboxylase-oxygenase. When geometric characteristics of $C_3$ plants are used, certain simplifications are possible, but the equations still *appear* to depend on geometry. In fact the resulting equations may be further reduced to a description based on the amount of carboxylase per unit area of leaf, with no depen-

dence on liquid-phase resistance, or on cell geometry. COOKE and RAND (1980) treated the results of SINCLAIR et al. (1977) as an expression of "liquid-phase resistance", but the terminology in this case is inappropriate.

HALL (1971) estimated that the liquid-phase resistance contributed an effective resistance, in terms of gaseous diffusion of only 0.4 $m^2$ s $mol^{-1}$. With a net assimilation rate of 20 µmol $m^{-2}$ $s^{-1}$, the depletion in partial pressure would then be only 8 µbar. Considering carbonic anhydrase activity and the aqueous and lipid portions of the pathway, RAVEN and GLIDEWELL (1981) estimated the liquid-phase resistance as 25 to 38 $m^2$ s $mol^{-1}$ on a cell area basis. NOBEL et al. (1975) observed a correlation between mesophyll cell surface area per unit leaf area and assimilation rate, irradiance during growth being the independent variable. In *Plectranthus parviflora* when the surface area ratio was 50, the assimilation rate was 7.3 µmol $m^{-2}$ $s^{-1}$. On this basis the above estimate of liquid-phase resistance would correspond to a depletion of 3.6 to 5.5 µbar. However, ratios are often smaller, and assimilation rates are often higher in other species (RAVEN and GLIDEWELL 1981), and if these changes do occur simultaneously the drawdown could be greater. LONGSTRETH and NOBEL (1980) found that with varying nutrition, cotton gave varying rates, but that the area ratio remained relatively constant (≈25). At the highest assimilation rate, 30 µmol $m^{-2}$ $s^{-1}$, RAVEN and GLIDEWELL's estimate of liquid-phase resistance would correspond to a drawdown of 30 to 45 µbar.

FARQUHAR et al. (1980) and BJÖRKMAN (1981) have pointed out that an increase in mesophyll cell area is usually associated with increases in photosynthetic enzymes and electron carriers, which are the prime cause of increased assimilation rates. An excess of photosynthetic machinery per cell will cause inefficiency (RAVEN and GLIDEWELL 1981), but there is little evidence that this problem occurs. A reduced ratio of surface areas, because it is generally accompanied by decreased photosynthetic capacity, does not necessarily cause a significant $CO_2$ drawdown.

### 16.5.8 On the Appropriate Measure of $CO_2$ Concentration

Summarizing the previous two sections, it appears that, unless there is bicarbonate pumping in cells, as occurs in some algae (BADGER et al. 1980) and submerged macrophytes (see Chap. 15, this Vol.), the $CO_2$ concentration, C, at the sites of carboxylation is usually only marginally less than in the substomatal cavities. FARQUHAR et al. (1982) came to the same conclusion from considerations of observed carbon isotope fractionations. Controversy exists whether the most appropriate measure of C is the molar concentration in solution (KU and EDWARDS 1977a, b, 1978) or the equilibrium partial pressure (BADGER and COLLATZ 1977). The question will be resolved when it is known whether or not the $CO_2$ in solution is in equilibrium with that bound to the carboxylase sites. KU and EDWARDS (1977a, b) have shown that much of the temperature dependence of various processes is reduced when the solubilities of $CO_2$ and $O_2$ are taken into account. However, it is unlikely that the kinetic constants are completely independent of temperature. If the molar concentration is the appropriate measure, the temperature dependence of the kinetic constants can still be treated in terms of partial pressures by absorbing the temperature dependence of solubility (HALL 1979).

## 16.6 Long-Term Effects of Environment on Leaf Photosynthesis

Photosynthetic $CO_2$-assimilation by leaves is affected by plant nutrition, light and temperature regimes, leaf age and other physiological factors. If analytical, mechanistic models are to be used to estimate the influence of individual components on the integrated performance, an understanding of which parameters may change and which are invariant under environmental changes is important. As discussed previously, there is evidence that the ratio $V_{o\,max}/V_{c\,max}$ is constant among species and under different growth conditions. Similarly the Michaelis-Menten constants for the $RuP_2$ carboxylase-oxygenase, $K_c$ and $K_o$ are not affected by different growth conditions such as high temperature (BERRY and BJÖRKMAN 1980) and high $[CO_2]$ (YEOH et al. 1981). However, the amounts of carboxylase and of electron transport components may vary greatly. This has been shown by several authors. For example, BJÖRKMAN et al. (1972) and POWLES and CRITCHLEY (1980) found that $RuP_2$ carboxylase activity, $V_{c\,max}$, and maximum electron transport rate, $J_{max}$, were higher, on a leaf area basis,

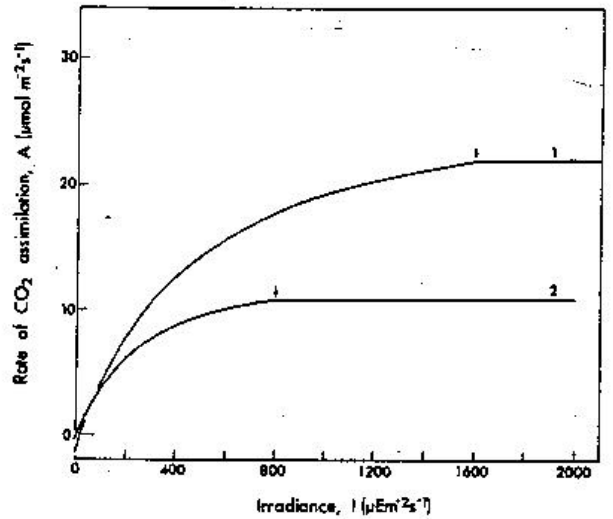


**Fig. 16.7.** Modelled rate of $CO_2$ assimilation, *A*, vs. irradiance, *I*. *1* represents high light grown plant with $V_{c\,max}$ = 115 µmol $m^{-2}$ $s^{-1}$ and $J_{max}$ = 210 µEq $m^{-2}$ $s^{-1}$; *2* represents low light grown plant with $V_{c\,max}$ = 57 µmol $m^{-2}$ $s^{-1}$ and $J_{max}$ = 105 µEq $m^{-2}$ $s^{-1}$. Values of $J_{max}$ and $V_{o\,max}$ chosen are typical of those determined experimentally by the authors. Rates of day respiration have been scaled accordingly. *Arrows* indicate transition from $RuP_2$ regeneration limitation to $RuP_2$ carboxylation limitation

in plants grown at high light than in plants grown at low light (see Chap. 3, Vol. 12 A). The modelled effects are shown in Fig. 16.7. Plants grown at differing levels of nitrogen nutrition also have differing values of $V_{c\,max}$ and $J_{max}$ (MEDINA 1969; VON CAEMMERER and FARQUHAR 1981). The decrease in $CO_2$-assimilation rate observed during leaf ageing is associated with a decline in $V_{c\,max}$ and $J_{max}$. Similarly the increase in $CO_2$-assimilation rate after defoliation of other leaves (WAREING et al. 1968) has been correlated with an increase in $V_{c\,max}$. WONG (1979) has shown that the lowered assimilation rate at normal $p(CO_2)$ of cotton plants grown at enhanced $p(CO_2)$, is associated with a lowered carboxylase activity.

Temperature adaptations may also to some extent be explained by changes in the amount and ratio of $J_{max}$ and $V_{c\,max}$. BERRY and BJÖRKMAN (1980) reported that high temperature grown plants have less carboxylase than low temperature grown plants. This will cause an increase in the temperature optimum of $CO_2$-assimilation rate as discussed earlier. The temperature optimum of electron-transport rate itself did not change significantly in the example cited, although there was greater thermal stability at temperatures greater than the optimum.

Thus it appears that many longer-term environmental effects may be modelled by suitable changes in two key parameters, $V_{c\,max}$ and $J_{max}$.

## 16.7 $C_4$-Photosynthesis

The mathematical modelling of $CO_2$ assimilation by $C_4$-species is in its infancy. Nevertheless, many of the gas exchange characteristics observed with intact leaves have been predicted using models based on the known biochemical and anatomical characteristics. PEISKER (1978a) and BERRY and FARQUHAR (1978) predicted the low compensation point, insensitive to $p(O_2)$. BERRY and FARQUHAR predicted the insensitivity of quantum yield to $p(CO_2)$, $p(O_2)$ and temperature, and the lack of $O_2$ effects on assimilation rate. They predicted that photorespiration should nevertheless continue at a low rate in the bundle-sheath cells, as observed in several studies and most recently by MOROT-GAUDRY et al. (1980). They also predicted the greater nitrogen use efficiency of $C_4$ plants, especially at higher temperatures.

Factors needing consideration in future models are the mechanism of action of phosphoenol pyruvate (PEP) carboxylase, the malate and aspartate inhibitions of PEP carboxylation, the feedback inhibition by free $CO_2$ of $C_4$ acid decarboxylation (RATHNAM and CHOLLET 1980), and the higher $K_c$ for $RuP_2$ carboxylase in $C_4$ species (YEOH et al. 1981).

## 16.8 Canopy Photosynthesis

Photosynthesis of canopies of $C_3$-species has been the subject of a great deal of experimentation and modelling (HESKETH 1980; see also Chaps. 4–10, Vol.



12D). It is useful to examine how the equations for leaf photosynthesis may be utilized in this context.

Earlier we suggested that for an individual leaf the rate of assimilation should be given by

$$A=(1-\Gamma_*/C)\cdot\min\{W_c, J'\}-R_d. \tag{16.71}$$

Since $W_c$ and $J'$ are usually correlated (VON CAEMMERER and FARQUHAR 1981) and since irradiance is often limiting in the canopy, we can expect that to a good approximation $W_c \leqq J'$ for most leaves. Substituting for $J'$ using Eq. (16.60c) we obtain the $RuP_2$ limited rate of assimilation for a single leaf (16.62c) and using Eq. (16.32) this yields

$$A=\frac{J_{max}I}{I+2.1J_{max}}\cdot\frac{C-\Gamma_*}{4.5C+10.5\Gamma_*}-R_d. \tag{16.72}$$

The problem of predicting canopy photosynthesis, the rate of assimilation per unit ground surface, reduces to that of determining how $J_{max}$, $R_d$, I, T and C vary through the canopy, and integrating appropriately. It is possible that treatments could be developed which exploit the correlation that can occur between $J_{max}$ and growth irradiance to predict how $J_{max}$ is reduced lower in the canopy. Further, $R_d$ may be correlated with A (ANGUS and WILSON 1976). Intercellular $p(CO_2)$ depends on stomatal conductance, but at a particular temperature is often insensitive to I (GOUDRIAAN and VAN LAAR 1978; WONG et al. 1979), except at low irradiances where contributions to photosynthesis are, in any case, minimal. The main problem, therefore, relates to the penetration, propagation and absorption of radiation (DE WIT 1965), which in turn depends on canopy structure (MONSI et al. 1973).

Regardless of the details of light absorption in the canopy, the irradiance dependence of canopy photosynthetic rate (per unit ground area) will be similar to that given by Eq. (16.72), but with $J_{max}$ much greater than that for a single leaf, and with $R_d$ summed over the whole canopy. This result may be seen in the classical papers of BOYSEN JENSEN (1932, 1949).

## 16.9 Empirical Models

At present, even in the models of short-term responses discussed earlier, the dependence of $J_{max}$ on temperature is fairly empirical. So too are the effects of water stress and salinity. Models concerned with time scales in which $V_{c\,max}$, $J_{max}$ and $R_d$ change are also, of necessity, empirical at present. Models which successfully deal with these longer times include that of LANGE et al. (1977), in which the productivity of lichens is predicted. Even over the short-time scales discussed earlier, some authors have found it easier to make statistical analyses of gas exchange characteristics such as the response of A to appropriately spaced changes in C, T and I than to assume a particular underlying

biochemical structure (ENOCH and SACKS 1978). Nevertheless it is probably easier for most ecophysiologists interested in $C_3$-photosynthesis to assume a structure such as the one described earlier, measure $CO_2$-assimilation rate under certain conditions, and fit values to $V_{c\,max}$ and to $R_d$ and $J_{max}$ and their temperature dependencies, using techniques similar to those described by HALL (1979). Hopefully further research and modelling of the mechanistic kind will continue to decrease the areas where empiricism is still required.

## References


Angus JF, Wilson JH (1976) Photosynthesis of barley and wheat leaves in relation to canopy models. Photosynthetica 10:367–377

Armond PA, Schreiber U, Björkmann O (1978) Photosynthetic acclimation to temperature in the desert shrub, *Larrea divaricata*. II. Light harvesting efficiency and electron transport. Plant Physiol 61:411–415

Arnon DI (1977) Photosynthesis 1950–75: Changing concepts and perspectives. In: Trebst A, Avron M (eds) Photosynthesis I. Photosynthetic electron transport and photophosphorylation. Encyclopedia of plant physiology New Ser Vol V. Springer, Berlin Heidelberg New York, pp 7–56

Azcon-Bieto J, Farquhar GD, Caballero A (1981) Effects of temperature, oxygen concentration, leaf age and seasonal variations on the $CO_2$ compensation point of *Lolium perenne* L: Comparison with a mathematical model including non photorespiratory $CO_2$ production in the light. Planta 152:497–504

Badger MR, Andrews TJ (1974) Effects of $CO_2$, $O_2$ and temperature on a higg-affinity form of ribulose diphosphate carboxylase-oxygenase from spinach. Biochem Biophys Res Commun 60:204–210

Badger MR, Collatz GJ (1977) Studies on the kinetic mechanism of ribulose-1,5-bisphosphate carboxylase and oxygenase reactions, with particular reference to the effect of temperature on kinetic parameters. Carnegie Inst Washington Yearb 76:355–361

Badger MR, Kaplan A, Berry JA (1980) Internal inorganic carbon pool of *Chlamydomonas reinhardtii*. Evidence for a carbon dioxide-concentrating mechanism. Plant Physiol 66:407–413

Bassham JA (1979) The reductive pentose phosphate cycle. In: Gibbs M, Latzko E (eds) Photosynthesis II. Photosynthetic carbon metabolism and related processes. Encyclopedia of plant physiology New Ser Vol VI. Springer Berlin Heidelberg New York, pp 9–30

Bauwe H, Apel P, Peisker M (1980) Ribulose 1,5-bisphosphate carboxylase/oxygenase and $CO_2$ exchange characteristics in $C_3$ and $C_3$–$C_4$ intermediate species checking mathematical models of carbon metabolism. Photosynthetica 14:550–556

Berry JA, Björkman O (1980) Photosynthetic response and adaptation to temperature in higher plants. Annu Rev Plant Physiol 31:491–543

Berry JA, Farquhar GD (1978) The $CO_2$ concentrating function of $C_4$ photosynthesis. A biochemical model. In: Hall D, Coombs J, Goodwin T (eds) Proc 4th Int Congr Photosynthes. Biochem Soc London, pp 119–131

Berzborn RJ, Müller D (1977) Correlation of grana in chloroplasts with the variability in the size of 'photophosphorylation unit'. In: Coombs J (ed) Read Abstr, pp 30–31

Berzborn RJ, Müller D, Roos P, Andersson B (1981) Significance of different quantitative determinations of photosynthetic ATP-synthase $CF_1$ for heterogeneous $CF_1$ distribution and grana formation. In: Akoyunoglou G (ed) Proc Fifth Int Congr Photosynthesis Vol. III. Balaban Philadelphia, pp 107–120

Björkman O (1981) Ecological adaptation of the photosynthetic apparatus. In: Akoyunoglou G (ed) Proc Fifth Int Congr Photosynthesis Vol. VI. Balaban Philadelphia, pp 191–202

Björkman O, Badger MR, Armond PA (1980) Response and adaptation of photosynthesis to high temperatures. In: Turner NC, Kramer PJ (eds) Adaptation of plants to water and high temperature stress. Wiley and Sons, New York, pp 233–249

Björkman O, Boardman NK, Anderson JM, Thorne SW, Goodchild DJ, Pyliotis NA (1972) Effect of light intensity during growth of *Atriplex patula* on the capacity of photosynthetic reactions, chloroplast components and structure. Carnegie Inst Washington Yearb 71:115–135

Boysen Jensen P (1932) Die Stoffproduktion der Pflanzen. Fischer, Jena 108 pp

Boysen Jensen P (1949) The production of matter in agricultural plants and its limitation. Biol Med 21:1–28

Caemmerer von S, Farquhar GD (1981) Some relationships between the biochemistry of photosynthesis and the gas exchange of leaves. Planta 153:376–387

Čatský J, Tichá I (1979) $CO_2$ compensation concentration in bean leaves: Effect of photon flux density and leaf age. Biol Plant 21:361–364

Charles-Edwards DA (1978) Leaf carbon dioxide compensation points at high light flux densities. Ann Bot (London) 42:733–739

Chartier P, Prioul JL (1976) The effects of irradiance, carbon dioxide and oxygen on the net photosynthetic rate of the leaf: A mechanistic model. Photosynthetica 10:20–24

Collatz GJ (1978) The interaction between photosynthesis and ribulose-$P_2$ concentration – effects of light, $CO_2$ and $O_2$. Carnegie Inst Washington Yearb 77:248–251

Cooke JR, Rand RH (1980) Diffusion resistance models. In: Hesketh JD, Jones JW (eds) Predicting photosynthesis for ecosystem models Vol I. CRC Press, Boca Raton, pp 93–122

Cramer WA, Whitmarsh J, Widger W (1981) On the properties and function of cytochromes *b*-559 and *f* in chloroplast electron transport. In: Akoyunoglou G (ed) Proc Fifth Int Congr Photosynthesis Vol. II. Balaban Philadelphia, pp 509–522

Ehleringer J, Björkman O (1977) Quantum yields for $CO_2$ uptake in $C_3$ and $C_4$ plants. Dependence on temperature, $CO_2$ and $O_2$ concentrations. Plant Physiol 59:86–90

Enoch HZ, Sacks JM (1978) An empirical model of $CO_2$ exchange of a $C_3$ plant in relation to light, $CO_2$ concentration and temperature. Photosynthetica 12:150–157

Farquhar GD (1979) Models describing the kinetics of ribulose bisphosphate carboxylase-oxygenase. Arch Biochem Biophys 193:456–468

Farquhar GD, Caemmerer von S (1981) Electron transport limitations on the $CO_2$ assimilation rate of leaves: a model and some observations in *Phaseolus vulgaris* L. In: Akoyunoglou G (ed) Proc Fifth Int Congr Photosynthesis Vol. IV. Balaban Philadelphia, pp 163–175

Farquhar GD, Raschke K (1978) On the resistance to transpiration of the sites of evaporation within the leaf. Plant Physiol 61:1000–1005

Farquhar GD, Caemmerer von S, Berry JA (1980) A biochemical model of photosynthetic $CO_2$ assimilation in leaves of $C_3$ species. Planta 149:78–90

Farquhar GD, O'Leary MH, Berry JA (1982) On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. Aust J Plant Physiol 9:121–137

Farron F (1970) Isolation and properties of a chloroplast coupling factor and heat-activated adenosine triphosphatase. Biochemistry 9:3823–3828

Giersch Ch, Heber U, Kobayashi Y, Inoue Y, Shibata K, Heldt HW (1980a) Energy charge, photophosphorylation potential and proton motive force in chloroplasts. Biochim Biophys Acta 590:59–73

Giersch Ch, Heber U, Krause GH (1980b) ATP transfer from chloroplasts to the cytosol of leaf cells during photosynthesis and its effect on leaf metabolism. In: Spanswick RM, Lucas WJ, Dainty J (eds) Plant membrane transport: current conceptual issues. Elsevier/North-Holland Biomedical Press, Amsterdam New York, pp 65–79

Goudriaan J, Laar van HH (1978) Relations between leaf resistance $CO_2$-concentration and $CO_2$-assimilation in maize, bean, lalang grass and sunflower. Photosynthetica 12:241–249

Graham D, Chapman EA (1979) Interactions between photosynthesis and respiration in higher plants. In: Gibbs M, Latzko E (eds) Photosynthesis II: Photosynthetic carbon metabolism and related processes. Encyclopedia of plant physiology New Ser Vol VI. Springer, Berlin Heidelberg New York, pp 150–162

Hall A (1971) A model of leaf photosynthesis and respiration. Carnegie Inst Washington Yearb 70:530–540
Hall A (1979) A model of leaf photosynthesis and respiration for predicting carbon dioxide assimilation in different environments. Oecologia 143:299–316
Hall A, Björkman O (1975) A model of leaf photosynthesis and respiration. In: Gates D, Schmeri R (eds) Perspectives of biophysical ecology. Ecol Stud Vol 12. Springer, Berlin Heidelberg New York, pp 55–72
Heber Uh, Hank EU, Jensen M, Koster S (1978) Regulation of photosynthetic electron transport in intact chloroplasts and leaves of *Spinacia oleraceae* L. Planta 143:41–49
Heber U, Santarius KA (1970) Direct and indirect transfer of ATP and ADP across the chloroplast envelope. Z Naturforsch 25b:718–728
Heldt HW, Sauer F (1971) The inner membrane of the chloroplast envelope as the site of specific metabolite transport. Biochim Biophys Acta 234:83–91
Hesketh JD (1980) Predicting canopy photosynthesis from gas exchange studies in controlled environments. In: Hesketh JD, Jones JW (eds) Predicting photosynthesis for ecosystem model Vol I. CRC Press, Boca Raton, pp 37–50
Hochman Y, Carmeli C (1981) Binding of manganese ions to $CF_1$ and their effect on the kinetics of ATPase activity. In: Akoyunoglou G (ed) Proc Fifth Int Congr Photosynthesis Vol. II. Balaban Philadelphia, pp 821–827
Jassby AD, Platt T (1976) Mathematical formulation of the relationship between photosynthesis and light for phytoplankton. Limnol Oceanogr 21:540–547
Jensen RG, Bahr JT (1977) Ribulose 1,5-bisphosphate carboxylase-oxygenase. Annu Rev Plant Physiol 28:379–400
Johnson F, Eyring H, Williams R (1942) The nature of enzyme inhibitions in bacterial luminescence: Sulfanilamide, urethane, temperature, and pressure. J Cell Comp Physiol 20:247–268
Jolliffe PA, Tregunna EB (1968) Effect of temperature, $CO_2$ concentration, and light intensity on oxygen inhibition of photosynthesis in wheat leaves. Plant Physiol 43:902–906
Jordan DB, Ogren WL (1981) A sensitive assay procedure for simultaneous determinations of ribulose-1-5, bisphosphate carboxylase and oxygenase activities. Plant Physiol 67:237–245
Junge W (1977) Physical aspects of light harvesting, electron transport and electrochemical potential generation in photosynthesis of green plants. In: Trebst A, Avron M (eds) Photosynthesis I. Photosynthetic electron transport and photophosphorylation. Encyclopedia of plant physiology new Ser Vol V. Springer, Berlin Heidelberg New York, pp 59–93
Keys AJ, Bird IF, Cornelius MJ, Lea PJ, Wallsgrove RM, Miflin BJ (1978) Photorespiratory nitrogen cycle. Nature (London) 275:741–743
Kirk JTO, Tilney-Bassett RAE (1978) The plastids, 2nd edn. Elsevier/North-Holland Biomedical Press, Amsterdam New York 960 pp
Krause GH, Heber U (1976) Energetics of intact chloroplasts. In: Barber J (ed) The intact chloroplast. Academic Press, London New York, pp 171–214
Ku S, Edwards G (1977a) Oxygen inhibition of photosynthesis. I. Temperature dependence and relation to $O_2/CO_2$ solubility ratio. Plant Physiol 59:986–990
Ku S, Edwards G (1977b) Oxygen inhibition of photosynthesis. II. Kinetic characteristics as affected by temperature. Plant Physiol 59:991–999
Ku S, Edwards G (1978) Oxygen inhibition of photosynthesis. III. Temperature dependence of quantum yield and its relation to $O_2/CO_2$ solubility ratio. Planta 140:1–6
Laing WA, Christeller JT (1976) A model for the kinetics of activation and catalysis of ribulose 1,5-bisphosphate carboxylase. Biochem J 159:563–570
Laing WA, Ogren W, Hageman R (1974) Regulation of soybean net photosynthetic $CO_2$ fixation by the interaction of $CO_2$, $O_2$ and ribulose-1,5-diphosphate carboxylase. Plant Physiol 54:678–685
Laisk A (1970) A model of leaf photosynthesis and photorespiration. In: Prediction and measurement of photosynthetic productivity. Proc IBP/PP Tech Meet Tfeboň 1969. PUDOC, Wageningen, pp 295–306



Laisk A (1977) Modelling of the closed Calvin cycle. In: Unger K (ed) Biophysikalische Analyse pflanzlicher Systeme. Fischer, Jena, pp 175–182
Lange OL, Geiger IL, Schulze E-D (1977) Ecophysiological investigations on lichens of the Negev Desert. V. A model to simulate net photosynthesis and respiration of *Ramalina maciformis*. Oecologia 28:247–259
Leegood RC, Walker DA (1980) Autocatalysis and light activation of enzymes in relation to photosynthetic induction in wheat chloroplasts. Arch Biochem Biophys 200:575–582
Lendzian K, Bassham JA (1976) NADPH/$NADP^+$ ratios in photosynthesising reconstituted chloroplasts. Biochim Biophys Acta 430:478–489
Lilley RMcC, Chon CJ, Mosbach A, Heldt HW (1977) The distribution of metabolites between spinach chloroplasts and medium during photosynthesis in vitro. Biochim Biophys Acta 460:259–272
Lilley RMcC, Walker DA (1979) Studies with the reconstituted chloroplast system. In: Gibbs M, Latzko E (eds) Photosynthesis II: Photosynthetic carbon metabolism and related processes. Encyclopedia of plant physiology New Ser vol VI. Springer, Berlin Heidelberg New York, pp 41–53
Longstreth DJ, Nobel PS (1980) Nutrient influences on leaf photosynthesis. Effects of nitrogen, phosphorus and potassium for *Gossypium hirsutum* L. Plant Physiol 65:541–543
Lorimer GH, Badger MR, Andrews TJ (1976) The activation of ribulose-1,5-bisphosphate carboxylase by carbon dioxide and magnesium ions. Equilibria, kinetics, a suggested mechanism, and physiological implications. Biochemistry 15:529–536
Lorimer GH, Woo KC, Berry JA, Osmond CB (1978) The C2 photorespiratory carbon oxidation cycle in leaves of higher plants: Paths and consequences. In: Hall DO, Coombs J, Goodwin TW (eds) Photosynthesis 77. Biochem Soc London, pp 311–322
Mangat BS, Levin WB, Bidwell RGS (1974) The extent of dark respiration in illuminated leaves and its control by ATP levels. Can J Bot 52:673–681
Marsho TV, Behrens PW, Radmer RJ (1979) Photosynthetic oxygen reduction in isolated intact chloroplasts and cells from spinach. Plant Physiol 64:656–659
McCarty RE (1979) Roles of a coupling factor for photo-phosphorylation in chloroplasts. Annu Rev Plant Physiol 30:79–104
Medina E (1971) Relationships between nitrogen level, photosynthetic capacity and carboxydismutase activity in *Atriplex patula* leaves. Carnegie Inst Washington Yearb 69:655–662
Mehler AH (1951) Studies on reactions of illuminated chloroplasts. I. Mechanism of the reduction of oxygen and other Hill reagents. Arch Biochem Biophys 33:65–77
Meidner H (1970) Precise measurements of carbon dioxide exchange by illuminated leaves near the compensation point. J Exp Bot 21:1067–1075
Melis A, Brown JS (1980) Stoichiometry of System I and System II reaction centres and of plastoquinone in different photosynthetic membranes. Proc Natl Acad Sci USA 77:4712–4716
Monsi M, Uchijima Z, Oikawa T (1973) Structure of foliage canopies and photosynthesis. Annu Rev Ecol Syst 4:301–327
Morot-Gaudry JF, Farineau J, Huet JC (1980) Oxygen effect on photosynthetic and glycolate pathways in young maize leaves. Plant Physiol 66:1079–1084
Nobel PS, Zaragoza LJ, Smith WK (1975) Relation between mesophyll surface area, photosynthetic rate and illumination level during development for leaves of *Plectranthus parviflorus* Henckel. Plant Physiol 55:1067–1070
Nolan WG, Smillie RM (1976) Multi-temperature effects on Hill reaction activity of barley chloroplasts. Biochim Biophys Acta 440:461–475
Parkhurst DF (1977) A three-dimensional model for $CO_2$ uptake by continuously distributed mesophyll in leaves. J Theor Biol 67:471–488
Peisker M (1974) A model describing the influence of oxygen on photosynthetic carboxylation. Photosynthetica 8:47–50
Peisker M (1976) Ein Modell der Sauerstoffabhängigkeit des photosynthetischen $CO_2$-Gaswechsels von $C_3$-Pflanzen. Kulturpflanze 24:221–235
Peisker M (1978a) Der Einfluß von Sauerstoff auf die $CO_2$-Kompensationskonzentration von $C_3$- und $C_4$-Pflanzen und von Intermediärformen. Kulturpflanze 26:81–98

Peisker M (1978b) A comment on the effects of carbon dioxide, oxygen and temperature on photosynthetic quantum yield in $C_3$ plants. Acta Physiol Plant 1:23–26
Peisker M, Apel P (1971) Untersuchungen zum Einfluß von Sauerstoff auf den $CO_2$-Gaswechsel assimilierender Blätter. Biochem Physiol Pflanz 162:165–176
Peisker M, Tichá I, Apel P (1979) Variations in the effect of temperature on oxygen dependence of $CO_2$ gas exchange in wheat leaves. Biochem Physiol Pflanz 174:391–397
Peisker M, Tichá I, Cätský J (1981) Ontogenetic changes in the internal limitations to bean-leaf photosynthesis. 7. Interpretations of the linear correlation between $CO_2$ compensation concentration and $CO_2$ evolution in darkness. Photosynthetica 15:161–168
Pike CS, Berry JA (1979) Phase separation temperatures of phospholipids from warm and cool climate plants. Carnegie Inst Washington Yearb 78:163–168
Powles SB, Critchley C (1980) Effect of light intensity during growth on photoinhibition of intact attached bean leaflets. Plant Physiol 65:1181–1187
Preiss J, Kosuge T (1976) Regulation of enzyme activity in metabolic pathways. In: Bonner J, Varner JE (eds) Plant biochemistry, 3rd edn. Academic Press, London New York, pp 277–336
Radmer R, Kok B, Ollinger O (1978) Kinetics and apparent $K_M$ of oxygen cycle under conditions of limiting carbon dioxide fixation. Plant Physiol 61:915–917
Raison JK, Berry JA (1979) Viscotropic denaturation of chloroplast membranes and acclimation to temperature by adjustment of lipid viscosity. Carnegie Inst Washington Yearb 78:149–152
Rand RH (1977) Gaseous diffusion in the leaf interior. Trans Am Soc Agric Eng 20:701–704
Rand RH (1978) A theoretical analysis of $CO_2$ absorption in sun versus shade leaves. J Biomech Eng 100:20–24
Rathnam CKM, Chollet R (1980) Photosynthetic carbon metabolism in C4 plants and $C_3$–$C_4$ intermediate species. Prog Phytochem 6:1–48
Raven JA (1972) Endogenous inorganic carbon sources in plant photosynthesis. I. Occurrence of the dark respiratory pathway in illuminated green cells. New Phytol 71:227–247
Raven JA, Glidewell SM (1981) Processes limiting carboxylation efficiency. In: Johnson CB (ed) Processes limiting plant productivity. Butterworth, London, pp 109–136
Robinson RP, Walker DA (1980) The significance of light activation of enzymes during the induction phase of photosynthesis in isolated chloroplasts. Arch Biochem Biophys 202:617–623
Sharpe PSH, De Michelle DW (1977) Reaction kinetics of poikilothermic development. J Theor Biol 64:649–670
Shavit N (1980) Energy transduction in chloroplasts: Structure and function of the ATPase complex. Annu Rev Biochem 49:111–138
Shin M (1971) Ferredoxin-NADP reductase from spinach. In: San Pietro A (ed) Methods in enzymology Vol 23. Academic Press, London New York, pp 440–447
Shin M, Oshino R (1978) Ferredoxin-sepharose 4B as a tool for the purification of ferredoxin-$NADP^+$ reductase. J Biochem (Tokyo) 83:357–361
Shin M, Wakita R, Yamasaki Y, Oshino R (1981) Interrelation of two forms of ferredoxin-$NADP^+$ reductase with different molecular weights. Plant Cell Physiol 22:461–464
Siggel U (1976) The function of plastoquinone as electron and proton carrier in photosynthesis. Bioelectrochem Bioenerg 3:302–318
Sinclair TR, Goudriaan J, Wit de CT (1977) Mesophyll resistance and $CO_2$ compensation concentration in leaf photosynthesis models. Photosynthetica 11:56–65
Sinclair TR, Rand RH (1979) Mathematical analysis of cell $CO_2$ exchange under high $CO_2$ concentrations. Photosynthetica 13:279–244
Sommerville CR, Ogren WL (1979) A phosphoglycolate phosphatase-deficient mutant of *Arabidopsis*. Nature (London) 280:833–835
Stitt M, Wirtz W, Heldt HW (1980) Metabolite levels during induction in the chloroplast and extra chloroplast compartments of spinach protoplasts. Biochim Biophys Acta 593:85–102
Strotmann H, Hesse H, Edelmann K (1973) Quantitative determination of coupling factor $CF_1$ of chloroplasts. Biochim Biophys Acta 314:202–210
Tenhunen JD, Weber J, Filipek L, Gates D (1977) Development of a photosynthesis model with an emphasis on ecological applications. III. Carbon dioxide and oxygen dependencies. Oecologia 30:189–207
Tenhunen JD, Hesketh JD, Gates DM (1980a) Leaf photosynthesis models. In: Hesketh JD, Jones JW (eds) Predicting photosynthesis for ecosystem models Vol I. CRC Press, Boca Raton, pp 123–182
Tenhunen JD, Hesketh JD, Harley PC (1980b) Modelling $C_3$ respiration in the light. In: Hesketh JD, Jones JW (eds) Predicting photosynthesis for ecosystem models Vol II. CRC Press, Boca Raton, pp 17–47
Tenhunen JD, Yocum CS, Gates DM (1976) Development of a photosynthesis model with an emphasis on ecological applications. I. Theory. Oecologia 26:89–100
Terry N (1980) Limiting factors in photosynthesis. I. Use of iron stress to control photochemical capacity in vivo. Plant Physiol 65:114–120
Thornley J (1976) Mathematical models in plant physiology – a quantitative approach to problems in plant and crop physiology. Academic Press, London New York 318 pp
Viil J, Laisk A, Oja V, Pärnik T (1977) Enhancement of photosynthesis caused by oxygen under saturating irradiance and high $CO_2$ concentrations. Photosynthetica 11:251–259
Walker DA (1976) $CO_2$ fixation by intact chloroplasts: Photosynthetic induction and its relation to transport phenomena and control mechanisms. In: Barber J (ed) The intact chloroplast. Elsevier/North-Holland Biomedical Press, Amsterdam New York, pp 235–278
Walker DA, Robinson SP (1978) Regulation of photosynthetic carbon carbon assimilation. In: Siegelman HW, Hind G (eds) Photosynthetic carbon assimilation. Plenum, New York London, pp 43–59
Wareing PF, Khalifa MM, Treharne KJ (1968) Rate-limiting processes in photosynthesis at saturating light intensities. Nature (London) 220:453–457
Weis E (1981) Reversible heat inactivation of the Calvin cycle: A possible mechanism of the temperature regulation of photosynthesis. Planta 151:33–39
West KR, Wiskich JT (1968) Photosynthetic control by isolated pea chloroplasts. Biochem J 109:527–532
Wirtz W, Stitt M, Heldt HW (1980) Enzymic determination of metabolites in the subcellular compartments of spinach chloroplasts. Plant Physiol 66:187–193
Wit de CT (1965) Photosynthesis of leaf canopies. Agric Res Rep 663:1–57
Wong SC (1979) Elevated atmospheric partial pressure of $CO_2$ and plant growth. I. Interactions of nitrogen and photosynthetic capacity in $C_3$ and $C_4$ plants. Oecologia 44:68–74
Wong SC, Cowan IR, Farquhar GD (1979) Stomatal conductance correlates with photosynthetic capacity. Nature (London) 282:424–426
Woo KC, Berry JA, Turner GL (1978) Release and refixation of ammonia during photorespiration. Carnegie Inst Washington Yearb 77:240–245
Woodrow IE, Walker DA (1980) Light-mediated activation of stromal sedoheptulose-1,7-bisphosphate. Biochem J 191:845–849
Yeoh H-H, Badger MR, Watson L (1981) Variations in kinetic properties of ribulose-1,5-bisphosphate carboxylases among plants. Plant Physiol 67:1151–1155
Yocum CS, Lommen PW (1975) Mesophyll resistances. In: Gates DM, Schmerl RD (eds) Perspectives of biophysical ecology. Ecol Stud Vol 12. Springer, Berlin Heidelberg New York, pp 45–54
Youmis HM, Winget GD, Racker E (1977) Requirement of the $\delta$ subunit of chloroplast coupling factor 1 for photophosphorylation. J Biol Chem 252:1814–1818