

*Original Article***Plant growth – A thermodynamicist's view****Anja Klippel, Ingo Müller**

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Received February 14, 1997

The synthesis of glucose requires an increase of enthalpy and a decrease of entropy such that the Gibbs free energy increases. This is impossible by the laws of thermodynamics unless there is an accompanying, compensating process that decreases the Gibbs free energy. Schrödinger [1] has suggested that the accompanying process should be the absorption and reemission of radiation. This process supplies the heat of reaction and the entropy increase of radiation is more than enough to offset the chemical decrease of entropy. And yet we are not satisfied with Schrödingers proposition, because we see no connection between the entropy increase of radiation and the physiology of the plant. Therefore we propose an alternative: The accompanying process consists of the transpiration of water and the mixing of water vapour with air; in this view radiation only furnishes the heat of reaction.

**1 Introduction***1.1 A thermodynamicist's view*

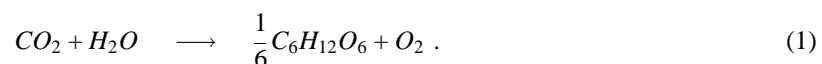
Sometimes the equations of balance of thermodynamics – in particular the first and second law – enable the thermodynamicist to reach conclusions about the performance of an engine without knowing its internal structure. Thus from the heating of the boiler and the temperature of the condenser he will know how much power to expect from a steam engine – or at least there will be an upper bound for the power. This knowledge will be irrespective of the number of pistons, or turbines, or the arrangement of the steam valves and the like.

It is the same with a plant: If we know how much air, water, heat and entropy enters and leaves the plant we can tell how fast it grows, – at least the thermodynamicist can. For his conclusions it is not necessary to know the details of the photosynthetic process, or the physiology of the leaves.

In this paper we propose to prove that the global view of the thermodynamicist may be a useful tool for an improvement of our knowledge of plant growth.

*1.2 A dilemma with glucose synthesis*

The synthesis of glucose  $C_6H_{12}O_6$  may be viewed as a prototype of the formation of organic material which the plants produce by photosynthesis. It is described by the stoichiometric formulae



The plant uses  $CO_2$  from the air and  $H_2O$  in liquid form from the soil.  $O_2$  is set free through the leaves.

The enthalpy change in the reaction and the entropies of the constituents may be read off from chemical handbooks (e.g. see [2]). We obtain

$$\Delta h^R = 466,3 \cdot 10^3 \frac{J}{mol} \quad (2)$$

$$\begin{aligned} s_{CO_2}^R &= 214 \frac{J}{molK} & s_{H_2O}^R &= 66,6 \frac{J}{molK} \\ s_{C_6H_{12}O_6}^R &= 213 \frac{J}{molK} & s_{O_2}^R &= 205 \frac{J}{molK} \end{aligned} \quad (3)$$

hence

$$\Delta s^R = -40,1 \frac{J}{molK} . \quad (4)$$

The heat of reaction may be calculated by the first and second laws and we obtain by (2) and (4)

$$1^{st} \text{ law: } q = \Delta h^R = 466,3 \cdot 10^3 \frac{J}{mol} \quad (5)$$

$$2^{st} \text{ law: } q \leq T_R \Delta s^R = 298 K \left(-40,1 \frac{J}{molK}\right) = -11,9 \cdot 10^3 \frac{J}{mol} .$$

Thus according to the first law the reaction is endothermic while the second law requires that it is exothermic. These conflicting results constitute the dilemma of photosynthesis; they cannot both be true. The values with the index  $R$  refer to the reference state which – by common consent – is  $p_R = 1 \text{ atm}$  and  $T_R = 298 \text{ K}$ .

Another aspect of the dilemma results from the elimination of  $q$  between the two laws (5) which leads to an inequality for the Gibbs free energy  $g$ , viz.

$$\Delta g^R = \Delta h^R - T_R \Delta s^R \leq 0 , \quad (6)$$

while the numbers give

$$\Delta g^R = +478,2 \cdot 10^3 \frac{J}{mol} \quad (!) . \quad (7)$$

We have to conclude that the reaction cannot proceed with heating only. Indeed, there must be an accompanying process which increases the entropy far enough that the decrease in enthalpy may be compensated for.

### 1.3 Three propositions

Two propositions have been made to resolve the dilemma and a third one is offered in this paper.

The first proposal is due to Schrödinger who remarked in passing – in his booklet "What is life?" [1] – that "the plants clearly possess their strongest store of "negative entropy" in the sunlight". It is not easy to understand what exactly Schrödinger meant with this remark<sup>1</sup>. However, it is true that between the absorption of solar radiation in the plant – or in any other absorbing material – and the reemission of radiation there is a large entropy production of radiation due to the matter. This entropy production is more than enough, by far, to compensate for the decrease of entropy in the chemical reaction. We shall discuss this in Chapter 2.

Another remedy for the dilemma was proposed by Tsuchida & Murota [4]. These authors realized that a plant transpires a lot of water and, – since the entropy grows between the liquid and the vapour phase – they concluded that the necessary entropy increase was to be found in the evaporation. This proposition can be discounted. It is true that the plant transpires water, but during the transpiration the enthalpy grows along with the entropy and the two increases are such that the Gibbs free energy stays constant. In fact, the constant

<sup>1</sup> Schrödingers remark was not specific, let alone quantitative. But it was noted and is known to plant physiologists to this day, see [3].

Actually Schrödinger adds a note in which he says that the remark was criticized by his peers; this note, however, does not help much. In retrospect one must say that the choice of words "negative entropy" was most unfortunate. It was grabbed by pseudo-scientists who made it into a new quantity, the "Negentropy", which is an unhelpful and confusing concept.

value of  $g$  is the thermodynamic condition for a phase equilibrium. Therefore, evaporation alone does not help; the dilemma in the form of (7) remains.

And yet our own proposition for an escape from the dilemma is closely related to the one by Tsuchida & Murota. We accept that indeed the plant consumes much more water than it needs for the reaction (1) - several hundred times more in fact, e.g. see [5]<sup>2</sup> – and we maintain that this water is evaporated in order to serve as a coolant, i.e. in order to keep the temperature of the plant down. The necessary increase of entropy comes from mixing the transpired water with the surrounding air. We shall demonstrate that the entropy of mixing of vapour and air provides enough entropy to pull the Gibbs free energy down below zero, so that the 1<sup>st</sup> and 2<sup>nd</sup> laws are satisfied. It is true though that for this purpose we need to supply the plant with a surplus of air. In other words, the plants must not only be *watered*, they must also be *ventilated*.

## 2 Entropy production by radiation. The Schrödinger proposition

### 2.1 Radiation fluxes of energy and entropy

As we have remarked already, Schrödingers proposition is not specific. In order to make it quantitative we have to consider the in- and effluxes of radiation; and this is what we do in this section. We think that this is the treatment which Schrödinger must have had in mind.

The flux densities of energy and entropy that reach the earth from the sun are given by

$$F_E^{(S)} = \frac{c}{4} \sigma T_S^4 \frac{r^2}{R^2} = 1330 \frac{W}{m^2} \quad \text{and} \quad F_S^{(S)} = \frac{c}{4} \frac{4}{3} \sigma T_S^3 \frac{r^2}{R^2} = 0,31 \frac{W}{m^2 K} . \quad (8)$$

$c$  is the speed of light and  $\sigma = 7,63 \cdot 10^{-16} \frac{J}{m^2 K^4}$  is the Stefan-Boltzmann constant.  $r$  and  $R$  are the radii of the sun and of the earth's orbit respectively.  $T_S = 5700 K$  is the temperature of the sun.

The values (8) are called the solar energy and entropy constants. Parts of these fluxes are reflected by either the atmosphere – the blue part - , or the plant surface – the green part, and we may estimate that half of the fluxes penetrate into the plant, e.g. see [5] or [6]. Thus we assume that the incoming fluxes of energy and entropy relevant to the plant have the values

$$F_E^{in} = 650 \frac{W}{m^2} \quad \text{and} \quad F_S^{in} = 0,15 \frac{W}{m^2 K} .$$

In later parts of the paper we shall also consider the case that only the fraction  $str$  of these influxes is available to the plant. In that case we set

$$F_E^{in} = str \cdot 650 \frac{W}{m^2} \quad \text{and} \quad F_S^{in} = str \cdot 0,15 \frac{W}{m^2 K} . \quad (9)$$

The parameter  $str$  will be called the *radiation intensity*.

The plant also radiates off energy and entropy according to its temperature  $T$  and the outgoing flux densities are given by

$$F_E^{out} = \frac{c}{4} \sigma T^4 \quad \text{and} \quad F_S^{out} = \frac{c}{4} \frac{4}{3} \sigma T^3 . \quad (10)$$

### 2.2 Photosynthesis

In the briefest possible description of photosynthesis some photons from the red and orange part of the spectrum split water molecules which – upon reuniting – provide the energy for the glucose formation. Plant physiologists have long studied the details of the process, e.g. see [5] or [6]; and their studies are not finished.

While all of the energy flux of  $650 \frac{W}{m^2}$  is absorbed and active in heating the plant, only about  $\frac{1}{4}$  of this flux lies in the red and orange parts of the spectrum and can be photosynthetically active. This amounts to

<sup>2</sup> Larcher's book [5] is also available in an English translation [6].

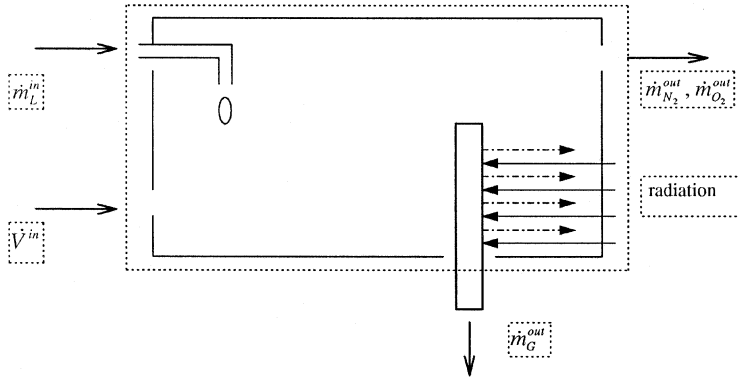


Fig. 1. Controlled stationary plant growth

$160 \frac{W}{m^2}$  approximately. By (2) this flux would be able to synthesize glucose to the extent of  $0,9 \frac{kg}{m^2 d} = 75 \frac{gr}{m^2 h}$ .<sup>3</sup> In reality, – again by [5] – the "unit leaf rate" or "net assimilation rate" is given by<sup>4</sup>

$$\dot{m}_G = 1,6 \frac{gr}{h} = 0,053 \frac{mol}{h} = 1,48 \cdot 10^{-5} \frac{mol}{s} \quad \text{for } 1 m^2 \text{ leaf surface.} \quad (11)$$

Thus only about 2 % of the low frequency radiation is involved in the reaction. The remaining 98 % heat the plant along with all the other radiation that reaches it and is not reflected.

### 2.3 Balance of masses

We consider an open system of volume  $V$  in which the plant leaf grows, while air and liquid water are entering and leaving  $V$  so as to satisfy the stoichiometric reaction, see Fig. 1. In this chapter we assume that the chemical reaction consumes *all the liquid water* and *all of the  $CO_2$*  supplied with the air. In other words, for now, there is no transpiration of water nor surplus of air. After all we are investigating the Schrödinger proposition. Also we assume – for now – that the incoming air is dry. In order to ensure stationarity the plant growth is removed from  $V$  as indicated in the figure.

The mass balance equations for the open volume indicated by the dashed line in Fig. 1 and for the constituents  $\alpha$  read in the stationary case

$$\int_{\partial V} \rho_\alpha w_i^\alpha n_i dA = \int_V \gamma_\alpha M_\alpha \mu_0 \Lambda dV . \quad (12)$$

$\Lambda$  is the reaction rate density of the reaction (1) and  $\gamma_\alpha$  and  $M_\alpha \mu_0$  are the stoichiometric coefficients and molecular masses of the constituents.  $M_\alpha$  are their relative molecular masses and  $w_i^\alpha$  their velocities. We may write these equations in terms of the mass fluxes  $\dot{m}_\alpha$  and, with  $\lambda = \int \Lambda dV$  as the reaction rate, we obtain

$$\dot{m}_\alpha^{out} - \dot{m}_\alpha^{in} = \gamma_\alpha M_\alpha \mu_0 \lambda . \quad (13)$$

We have 5 constituents going in and/or out, namely the ideal gases  $N_2$ ,  $O_2$  and  $CO_2$ , liquid water  $L$  and solid glucose  $G$ . Under the conditions considered – with no efflux of  $CO_2$  and water and no influx of glucose – we may write the equations (13) more explicitly in the form

$$\begin{aligned} \dot{m}_{N_2}^{out} - \dot{m}_{N_2}^{in} &= 0 \\ \dot{m}_{O_2}^{out} - \dot{m}_{O_2}^{in} &= M_{O_2} \mu_0 \lambda \\ &- \dot{m}_{CO_2}^{in} = - M_{CO_2} \mu_0 \lambda \\ &- \dot{m}_L^{in} = - M_{H_2O} \mu_0 \lambda \\ \dot{m}_G^{out} &= \frac{1}{6} M_G \mu_0 \lambda . \end{aligned} \quad (14)$$

<sup>3</sup> with  $1 day = 12h$  with enough sunlight to make photosynthesis possible

<sup>4</sup> mol here as in (2) etc. refers to a reaction with the stoichiometric formula (1), i.e. to the consumption of  $1 mol CO_2$  or the production of  $\frac{1}{6} mol$  glucose, which is  $30 gr$ .

For the ideal gases with  $p_\alpha \dot{V} = \dot{m}_\alpha \frac{R}{M_\alpha} T$  we may calculate the influxes  $\dot{m}_\alpha^{in}$  in terms of the natural partial pressures and the volume influx  $\dot{V}$  of air<sup>5</sup>

$$\begin{aligned} \frac{p_{N_2}^{in}}{p} &= 0,7897 & \frac{\dot{m}_{N_2}^{in}}{M_{N_2}} &= 0,7897 \cdot \frac{p\dot{V}}{RT} \\ \frac{p_{O_2}^{in}}{p} &= 0,21 & \text{hence} & \frac{\dot{m}_{O_2}^{in}}{M_{O_2}} &= 0,21 \cdot \frac{p\dot{V}}{RT} \\ \frac{p_{CO_2}^{in}}{p} &= 0,0003 & \frac{\dot{m}_{CO_2}^{in}}{M_{CO_2}} &= 0,0003 \cdot \frac{p\dot{V}}{RT} = \mu_0 \lambda . \end{aligned} \quad (15)$$

From (14) we thus obtain

$$\begin{aligned} \frac{\dot{m}_{N_2}^{out}}{M_{N_2}} &= 0,7897 \cdot \frac{p\dot{V}}{RT} & \frac{p_{N_2}^{out}}{p} &= 0,7897 \\ \frac{\dot{m}_{O_2}^{out}}{M_{O_2}} &= (0,21 + 0,0003) \frac{p\dot{V}}{RT} & \text{hence} & \frac{p_{O_2}^{out}}{p} &= 0,21 + 0,0003 \\ \frac{\dot{m}_{CO_2}^{out}}{M_{CO_2}} &= 0 & \frac{p_{CO_2}^{out}}{p} &= 0 . \end{aligned} \quad (16)$$

If as stated, the unit leaf rate amounts to  $1,6 \frac{gr}{h}$  or  $1,48 \cdot 10^{-5} \frac{mol}{s}$ , the necessary volume flux  $\dot{V}$  of air is given by, eq. (14)<sub>5</sub> and (15)<sub>6</sub><sup>6</sup>

$$\frac{p\dot{V}}{RT} = 1,64 \cdot 10^{-3} \frac{mol}{s} . \quad (17)$$

#### 2.4 Balance equations of energy

We continue to consider the case shown in Fig. 1 and described sofar. If we ignore the kinetic energies of the constituents and all heat fluxes the stationary balance equations for energies of matter and radiation read

$$\begin{aligned} \int_{\partial V} \sum_{\alpha} \rho_{\alpha} h_{\alpha} w_i^{\alpha} n_i dA &= \int_V r dV \\ \int_{\partial V} F_E^i n_i dA &= - \int_V r dV . \end{aligned} \quad (18)$$

$h_{\alpha}$  is the specific enthalpy of constituent  $\alpha$  and  $F_E^i$  is the radiative energy flux density.  $r$  is the production density of energy of matter due to absorption of radiation; the total energy of matter and radiation is conserved so that the sum of the R.H.S. of the equations (18) is equal to zero.

We may write the energy flux in terms of the mass fluxes and, of course, the radiative energy flux is the balance of the in- and effluxes  $F_E$  given in (9), (10). Thus the equations (18) may be written in the form

$$\begin{aligned} \sum_{\alpha} h_{\alpha}^{out} \dot{m}_{\alpha}^{out} - \sum_{\alpha} h_{\alpha}^{in} \dot{m}_{\alpha}^{in} &= \int_V r dV \\ F_E^{out} - F_E^{in} &= - \int_V r dV . \end{aligned} \quad (19)$$

#### 2.5 Balance equations of entropy

The stationary balance equations of entropy read

$$\begin{aligned} \int_{\partial V} \sum_{\alpha} \rho_{\alpha} s_{\alpha} w_i^{\alpha} n_i dA &= \int_V (\sigma_{MS} + \sigma_{MM}) dV \\ &= \int_V \left( \frac{r}{T} + \sigma_{MM} \right) dV \\ \int_{\partial V} F_S^i n_i dA &= \int_V \sigma_{SM} dV \end{aligned} \quad (20)$$

$s_{\alpha}$  is the specific entropy of constituent  $\alpha$  and  $F_S^i$  is the radiative entropy flux density.  $\sigma_{MS}$  and  $\sigma_{SM}$  are the densities of production of entropy of matter due to radiation and of radiation due to matter respectively,

<sup>5</sup> The argon is lumped together with the nitrogen, whose 4 digit concentration is chosen so that all partial pressures add up to p.

<sup>6</sup> We remark in passing that the synthesis of 1 gr glucose requires an air influx of  $2,8 m^3$ , - if  $p = 1 atm$ ,  $T = 300 K$ , and if all  $CO_2$  from the air is consumed.

while  $\sigma_{MM}$  is the ordinary entropy production density of matter due to heat conduction, viscosity, diffusion and chemical reactions. We know from ordinary thermodynamics that  $\sigma_{MS} = \frac{r}{T}$  holds.  $\sigma_{SM}$  is less clear-cut, it will depend on the way radiation and matter interact by absorption, emission and scattering (see [7] for a simple case). Whatever else happens, the total entropy production must be non-negative so that we must have

$$\int_V \left( \frac{r}{T} + \sigma_{SM} + \sigma_{MM} \right) dV \geq 0 . \quad (21)$$

In terms of the mass fluxes  $\dot{m}_\alpha$  and in- and effluxes (9) and (10) of radiative entropy we may thus write

$$\begin{aligned} \sum_\alpha s_\alpha^{out} \dot{m}_\alpha^{out} - \sum_\alpha s_\alpha^{in} \dot{m}_\alpha^{in} &= \int_V \left( \frac{r}{T} + \sigma_{MM} \right) dV \\ F_S^{out} - F_S^{in} &= \int_V \sigma_{SM} dV . \end{aligned} \quad (22)$$

## 2.6 Equations of state

The specific enthalpies and entropies of the constituents are given by

$$\begin{aligned} h_{N_2} &= h_{N_2}^R + \frac{7}{2} \frac{R}{M_{N_2}} (T - T_R) \\ h_{O_2} &= h_{O_2}^R + \frac{7}{2} \frac{R}{M_{O_2}} (T - T_R) \\ h_{CO_2} &= h_{CO_2}^R + 4 \frac{R}{M_{CO_2}} (T - T_R) \\ h_L &= h_L^R + c_L (T - T_R) \quad \text{with } c_L = 4, 18 \frac{kJ}{kgK} \\ h_G &= h_G^R + c_G (T - T_R) \quad \text{with } c_G = 1, 22 \frac{kJ}{kgK} \end{aligned} \quad (23)$$

$$\Delta h^R \equiv M_{O_2} h_{O_2}^R + \frac{1}{6} M_G h_G^R - M_{CO_2} h_{CO_2}^R - M_{H_2O} h_L^R = 466, 3 \cdot 10^3 \frac{J}{mol} . \quad (24)$$

and

$$\begin{aligned} s_{N_2} &= s_{N_2}^R + \frac{7}{2} \frac{R}{M_{N_2}} \ln \frac{T}{T_R} - \frac{R}{M_{N_2}} \ln \frac{p_{N_2}}{p_R} \\ s_{O_2} &= s_{O_2}^R + \frac{7}{2} \frac{R}{M_{O_2}} \ln \frac{T}{T_R} - \frac{R}{M_{O_2}} \ln \frac{p_{O_2}}{p_R} \\ s_{CO_2} &= s_{CO_2}^R + 4 \frac{R}{M_{CO_2}} \ln \frac{T}{T_R} - \frac{R}{M_{CO_2}} \ln \frac{p_{CO_2}}{p_R} \\ s_L &= s_L^R + c_L \ln \frac{T}{T_R} \\ s_G &= s_G^R + c_G \ln \frac{T}{T_R} . \end{aligned} \quad (25)$$

$$\Delta s^R \equiv M_{O_2} s_{O_2}^R + \frac{1}{6} M_G s_G^R - M_{CO_2} s_{CO_2}^R - M_{H_2O} s_L^R = -40, 1 \frac{J}{mol K} . \quad (26)$$

These equations are the caloric equations of state of the ideal gases  $N_2$ ,  $O_2$  and  $CO_2$ , of the incompressible liquid  $H_2O$ , and of the solid glucose respectively. They are known to all students of thermodynamics.

## 2.7 Evaluation

We combine the two energy equations by summation to get

$$\sum_\alpha h_\alpha^{out} \dot{m}_\alpha^{out} - \sum_\alpha h_\alpha^{in} \dot{m}_\alpha^{in} = F_E^{in} - F_E^{out} . \quad (27)$$

All quantities occurring in (27) have been explicitly given in previous sections, see (9) through (11) and (14) through (17) as well as (23), (24). Only the values of  $h_\alpha$  and  $F_E^{out}$  depend on the temperature  $T$  so that (27)

represents an equation for the temperature of the system if the radiative influx  $F_E^{in}$  and the growth rate  $\dot{m}_G$  are given. We obtain with the radiation intensity  $str = 1$

$$\left(466,3 \cdot 10^3 - 42,9 \frac{T - T_R}{K}\right) \frac{\dot{m}_G}{mol/s} = 650 - 5,79 \cdot 10^{-8} \frac{T^4}{K^4} \quad (28)$$

and hence, by (11)

$$T = 325 K . \quad (29)$$

Next we combine the two entropy equations by summation and obtain the entropy inequality

$$\sum_{\alpha} s_{\alpha}^{out} \dot{m}_{\alpha}^{out} - \sum_{\alpha} s_{\alpha}^{in} \dot{m}_{\alpha}^{in} = F_S^{in} - F_S^{out} + \int_V \left( \left[ \frac{r}{T} + \sigma_{SM} \right] + \sigma_{MM} \right) dV \geq 0 . \quad (30)$$

All quantities on the L.H.S. and  $F_S^{in}$ ,  $F_S^{out}$  have been given before and we obtain, always with  $str = 1$

$$\left( -40,1 - 42,9 \ln \frac{T}{T_R} - \underline{62,7} \right) \frac{\dot{m}_G}{mol/s} = 0,15 - \frac{4}{3} 5,79 \cdot 10^{-8} \frac{T^3}{K^3} + \int_V \left( \left[ \frac{r}{T} + \sigma_{SM} \right] + \sigma_{MM} \right) dV . \quad (31)$$

The attentive reader recognizes the individual contributions in (28) and (31): The underlined term in (31) represents the pressure ratios that contribute to the specific entropies, and the first two terms on the right hand sides of (28) and (31) represent the balance of in- and efflux of energy and entropy. For the temperature  $T = 325 K$  we obtain from (31), by use of (11)

$$\int_V \left( \left[ \frac{r}{T} + \sigma_{SM} \right] + \sigma_{MM} \right) dV = 2,5 \frac{W}{K} \frac{A}{m^2} . \quad (32)$$

$A$  is the area which the plant offers to the radiation.

Thus the entropy production of matter and radiation is positive and *the second law is satisfied*.

## 2.8 Discussion

Note that the radiation plays the overwhelming role in (28) and (31). Even without any left hand sides in those equations, i.e. without plant growth, the two equations would give nearly the same results for temperature and entropy production. Therefore the entropy production (32) is due to an overwhelming degree to the rearrangement of radiation by absorption, reemission and scattering.

Infact, the tiny material part  $\sigma_{MM}$  of the entropy production is *negative*. We obtain from (22)<sub>1</sub> and (19) by elimination of  $r$

$$\int_V \sigma_{MM} dV = -\frac{1}{T} \left( \sum_{\alpha} (h_{\alpha}^{out} - T s_{\alpha}^{out}) \dot{m}_{\alpha}^{out} - \sum_{\alpha} (h_{\alpha}^{in} - T s_{\alpha}^{in}) \dot{m}_{\alpha}^{in} \right) . \quad (33)$$

With the values given before the entropy production of matter comes out as

$$\int_V \sigma_{MM} dV = -\frac{1}{T} \left( 466,3 \cdot 10^3 - 42,9 \frac{T - T_R}{K} + T \left[ 40,1 + 42,9 \ln \frac{T}{T_R} + \underline{62,7} \right] \right) \frac{\dot{m}_G}{mol/s} \frac{W}{K} \frac{A}{m^2} \quad (34)$$

or with  $T = 325 K$  (cf. the energy balance (28), and (11))

$$\int_V \sigma_{MM} dV = -10,23 \cdot 10^{-3} \frac{W}{K} \frac{A}{m^2} . \quad (35)$$

We are unsatisfied with this result and we reject it, because we believe that the material entropy production should be positive. That forces us to investigate an alternative to the proposition of Schrödinger.

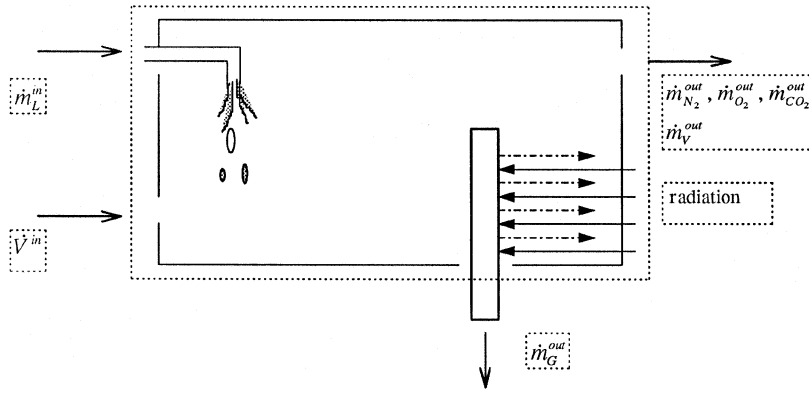


Fig. 2. Control volume with additional mass fluxes

### 3 Watering and ventilation

#### 3.1 Proposition

While in the Schrödinger proposition the plant may survive and thrive on just enough  $CO_2$  and  $H_2O$  as is needed for the stoichiometric reaction, in reality plants consume additional water, – a lot of it – and more air than is required for the  $CO_2$  supply. The thesis to be investigated in this chapter is that the excess amounts of water and air are thermodynamically relevant in the following manner:

- the excess water is transpired and thereby acts as a coolant for the plant.
- the excess air permits the transpired water to mix with a larger air volume and the corresponding entropy of mixing provides an increase of entropy large enough to resolve the dilemma described in the Introduction.

#### 3.2 Balance of masses

Since excess water and air are required in the new proposition, there is now also an efflux of water vapour and of  $CO_2$  which we did not consider before. For the purpose of formulating the balance equations we therefore replace Fig. 1 by Fig. 2 which includes the additional mass fluxes.

For good measure we permit the incoming air to be moist with  $z$  being its humidity<sup>7</sup>.

Thus, since more gases are entering and leaving the system, the evaluation of the mass balance equations is more cumbersome than before, but not basically different. We have, – in analogy to (14)

$$\begin{aligned}
 \dot{m}_{N_2}^{out} - \dot{m}_{N_2}^{in} &= 0, \\
 \dot{m}_{O_2}^{out} - \dot{m}_{O_2}^{in} &= M_{O_2} \mu_0 \lambda, \\
 \dot{m}_{CO_2}^{out} - \dot{m}_{CO_2}^{in} &= -M_{CO_2} \mu_0 \lambda, \\
 \dot{m}_V^{out} - \dot{m}_V^{in} &= x M_{H_2O} \mu_0 \lambda, \\
 -\dot{m}_L^{in} &= -(1+x) M_{H_2O} \mu_0 \lambda, \\
 \dot{m}_G^{out} &= \frac{1}{6} M_G \mu_0 \lambda.
 \end{aligned} \tag{36}$$

The indices L and V refer to liquid water and water vapour. There is no liquid water leaving the system.  $x$  is the excess amount of liquid water that we supply to the plant in addition to what the chemical reaction requires.

The partial pressures and the mass fluxes of the incoming constituents are given by

<sup>7</sup> The humidity is the mass of water divided by the mass of air that carries it.



$$\begin{aligned}
\frac{p_{N_2}^{in}}{p} &= \frac{0,7897}{1+z \frac{M_A}{M_{H_2O}}} & \frac{\dot{m}_{N_2}^{in}}{M_{N_2}} &= \frac{0,7897}{1+z \frac{M_A}{M_{H_2O}}} \cdot \frac{p\dot{V}}{RT} \\
\frac{p_{O_2}^{in}}{p} &= \frac{0,21}{1+z \frac{M_A}{M_{H_2O}}} & \frac{\dot{m}_{O_2}^{in}}{M_{O_2}} &= \frac{0,21}{1+z \frac{M_A}{M_{H_2O}}} \cdot \frac{p\dot{V}}{RT} \\
\frac{p_{CO_2}^{in}}{p} &= \frac{0,0003}{1+z \frac{M_A}{M_{H_2O}}} & \text{hence } \frac{\dot{m}_{CO_2}^{in}}{M_{CO_2}} &= \frac{0,0003}{1+z \frac{M_A}{M_{H_2O}}} \cdot \frac{p\dot{V}}{RT} = (1+y) \mu_0 \lambda & (37) \\
\frac{p_V^{in}}{p} &= \frac{z \frac{M_A}{M_{H_2O}}}{1+z \frac{M_A}{M_{H_2O}}} & \frac{\dot{m}_V^{in}}{M_{H_2O}} &= \frac{z \frac{M_A}{M_{H_2O}}}{1+z \frac{M_A}{M_{H_2O}}} \cdot \frac{p\dot{V}}{RT} \\
&& \frac{\dot{m}_L^{in}}{M_{H_2O}} &= (1+x) \mu_0 \lambda .
\end{aligned}$$

$M_A = 29$  is the mean relative molecular mass of air and  $y$  is the excess amount of air that we supply to the plant in addition to what the reaction requires.

The effluxes of all masses and the partial pressures of the outgoing gas constituents may be calculated from (36). We obtain

$$\begin{aligned}
\frac{\dot{m}_{N_2}^{out}}{M_{N_2}} &= \frac{0,7897}{0,0003} (1+y) \mu_0 \lambda & \frac{p_{N_2}^{out}}{p} &= \frac{\frac{0,7897}{0,0003} (y+1)}{\frac{(y+1)}{0,0003} \left( 0,7897 + 0,21 + z \frac{M_A}{M_{H_2O}} \right) + 1 + x + y} \\
\frac{\dot{m}_{O_2}^{out}}{M_{O_2}} &= \left( \frac{0,21}{0,0003} (1+y) + 1 \right) \mu_0 \lambda & \frac{p_{O_2}^{out}}{p} &= \frac{\frac{0,21}{0,0003} (y+1) + 1}{\frac{(y+1)}{0,0003} \left( 0,7897 + 0,21 + z \frac{M_A}{M_{H_2O}} \right) + 1 + x + y} \\
\frac{\dot{m}_{CO_2}^{out}}{M_{CO_2}} &= y \mu_0 \lambda & \text{hence } \frac{p_{CO_2}^{out}}{p} &= \frac{y}{\frac{(y+1)}{0,0003} \left( 0,7897 + 0,21 + z \frac{M_A}{M_{H_2O}} \right) + 1 + x + y} & (38) \\
\frac{\dot{m}_V^{out}}{M_{H_2O}} &= \left( \frac{z \frac{M_A}{M_{H_2O}}}{0,0003} (1+y) + x \right) \mu_0 \lambda & \frac{p_V^{out}}{p} &= \frac{z \frac{M_A}{M_{H_2O}} \frac{(y+1)}{0,0003} + x}{\frac{(y+1)}{0,0003} \left( 0,7897 + 0,21 + z \frac{M_A}{M_{H_2O}} \right) + 1 + x + y} \\
\frac{\dot{m}_L^{out}}{M_{H_2O}} &= 0 \\
\frac{\dot{m}_G^{out}}{M_G} &= \frac{1}{6} \mu_0 \lambda
\end{aligned}$$

### 3.3 Energy balance

The energy balance equations are formally the same ones as in (19) and in particular the total balance of matter and radiation reads

$$\sum_{\alpha} h_{\alpha}^{out} \dot{m}_{\alpha}^{out} - \sum_{\alpha} h_{\alpha}^{in} \dot{m}_{\alpha}^{in} = F_E^{in} - F_E^{out} . \quad (39)$$

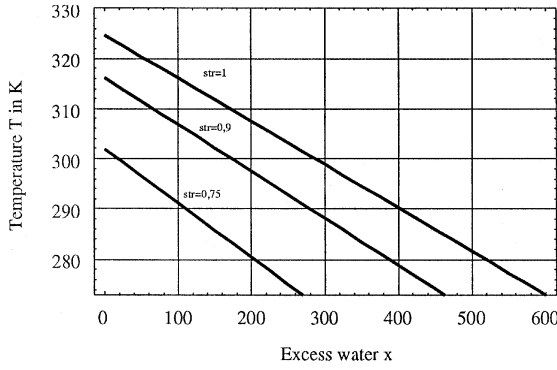
The only difference to the previous case is that the water vapour provides a new constituent and, – of course – the values of the mass fluxes are different. The only additional equation of state is the one for the water vapour and this reads

$$h_V = h_L^R + r(T_R) + 4 \frac{R}{M_{H_2O}} (T - T_R) \quad , \quad \text{where } r(T_R) = 2,44 \cdot 10^3 \frac{J}{gr} . \quad (40)$$

$r(T_R)$  is the heat of evaporation of water at the reference temperature.

If all state functions and the mass fluxes (37), (38) are inserted into (39), as well as the radiative energy fluxes (9), (10) – with  $str = 1$  – we obtain an equation for the temperature, viz.<sup>8</sup>

$$(466,3 \cdot 10^3 + x \cdot 18 \cdot 2,44 \cdot 10^3) \frac{\dot{m}_G}{mol/s} = 650 - 5,79 \cdot 10^{-8} \frac{T^4}{K^4} . \quad (41)$$



**Fig. 3.** Temperature as a function of excess water for  $F_E^{in} = 650 \frac{W}{m^2}$  ( $str = 1$ ) and two curves denoted  $str = 0,9$  and  $str = 0,75$  which correspond to the respective fractions of  $F_E^{in} = 650 \frac{W}{m^2}$

Thus  $T$  very nearly is a linearly decreasing function of the excess water  $x$ , as shown in Fig. 3. The figure is constructed for the value (11) of  $\dot{m}_G$ .

We conclude from the figure – and equation (41) – that the temperature is smaller, if more water is supplied and transpired. Thus the excess water works as coolant; its evaporation cools the system. For  $x = 0$  we obtain the old value  $T = 325 K$ , see (29) while for a temperature of  $25^\circ C$  we need an excess value  $x$  which is about 310.

Obviously the  $(T, x)$ -plot depends strongly on the influx of radiative energy. The value  $F_E^{in} = 650 \frac{W}{m^2}$  may be on the large side. Figure 3 shows two curves that correspond to influxes of  $585 \frac{W}{m^2}$  and  $490 \frac{W}{m^2}$ , i.e. radiation intensities  $str = 0,9$  and  $str = 0,75$ . It is clear that in those cases we have lower temperatures, or – for a given temperature – that we need less excess water for cooling.

### 3.4 Entropy balance of matter. Growth condition I

We recall the entropy balance of matter (20)<sub>1</sub>, in which we replace  $r$  by use of the energy balance of matter (19)<sub>1</sub>. Thus we obtain the equation

$$\sum_{\alpha} (h_{\alpha}^{out} - T s_{\alpha}^{out}) \dot{m}_{\alpha}^{out} - \sum_{\alpha} (h_{\alpha}^{in} - T s_{\alpha}^{in}) \dot{m}_{\alpha}^{in} = -T \int_V \sigma_{MM} dV. \quad (42)$$

This is formally the same equation as (33) but now the sum over the constituents contains the water vapour and, of course, the values of the mass fluxes and the partial pressures are different. However, all quantities have already been given except one: the specific entropy of the water vapour. This reads

$$s_V = s_L^R + \frac{r(T_R)}{T_R} + 4 \frac{R}{M_{H_2O}} \ln \frac{T}{T_R} - \frac{R}{M_{H_2O}} \ln \frac{p_V}{p(T_R)}. \quad (43)$$

$p(T_R)$  is the pressure of saturated vapour at the temperature  $T_R = 298 K$ , i.e. we have  $p(T_R) = 3,2 \cdot 10^{-2} atm$ .

If everything is inserted into (42) we obtain a left hand side contains 4 parameters, viz.

- temperature
- excess water  $x$ , which depends on  $T$ , cf. Fig. 3
- excess air  $y$
- humidity  $z$

We introduce the dimensionless temperature  $\tau = \frac{T}{T_R}$  and we require that the material entropy production be positive, – rather than only the total entropy production (see the discussion in Sect. 2.8). Thus we obtain the inequality

<sup>8</sup> The terms proportional to  $T - T_R$  have been neglected in (41), because they are small compared to the other terms.

$$\begin{aligned}
& \frac{\Delta h^R}{RT_R} - \frac{\tau}{R} \Delta s^R + \left( \frac{7}{2} + \frac{1}{6} \frac{c_G}{R} M_G - 4 - \frac{c_L}{R} M_{H_2O} \right) (\tau - 1 - \tau \ln \tau) + \\
& 4 \quad \tau \left\{ \frac{p_{N_2}^{in}}{p_{CO_2}^{in}} (y+1) \ln \frac{p_{N_2}^{out}}{p_{N_2}^{in}} + \frac{p_{O_2}^{in}}{p_{CO_2}^{in}} (y+1) \ln \frac{p_{O_2}^{out}}{p_{O_2}^{in}} + y \ln \frac{p_{CO_2}^{out}}{p_{CO_2}^{in}} + \right. \\
& \quad \left. \ln \frac{p_{O_2}^{out}}{p_{CO_2}^{in}} + (y+1) z \frac{\frac{M_A}{M_{H_2O}}}{\frac{p_{CO_2}^{in}}{p}} \ln \frac{p_V^{out}}{p_V^{in}} \right\} + \\
& 5 \quad x \cdot \frac{r_W(T_R)}{RT_R} M_{H_2O} (1 - \tau) + \\
& 6 \quad x \cdot \left( 4 - \frac{c_W}{R} M_{H_2O} \right) (\tau - 1 - \tau \ln \tau) + \\
& 7 \quad x \cdot \tau \ln \frac{p_V^{out}}{p(T_R)} \\
& 8 \quad = -\frac{\tau}{R\mu_0\lambda} \int_V \sigma_{MM} dV \leq 0 .
\end{aligned} \tag{44}$$

We have numbered the individual terms, because we can identify their physical significance in words as follows

- 1 Heat of reaction in the reference state  $p_R = 1 \text{ atm}$ ,  $T_R = 298 \text{ K}$
- 2 Entropy of reaction in the reference state
- 3 Change of enthalpy and entropy with  $T - T_R$  due to specific heats
- 4 Entropy of mixing of gaseous constituents
- 5 Entropy of evaporation
- 6 Change of enthalpy and entropy of evaporating water with  $T - T_R$
- 7 Entropy of mixing of evaporated water
- 8 Requirement of non-negative material entropy production

We may call this inequality the growth condition. Actually we call it the *growth condition I*, because we shall have another condition which concerns the ability of the plant to transpire water.

### 3.5 Growth condition II

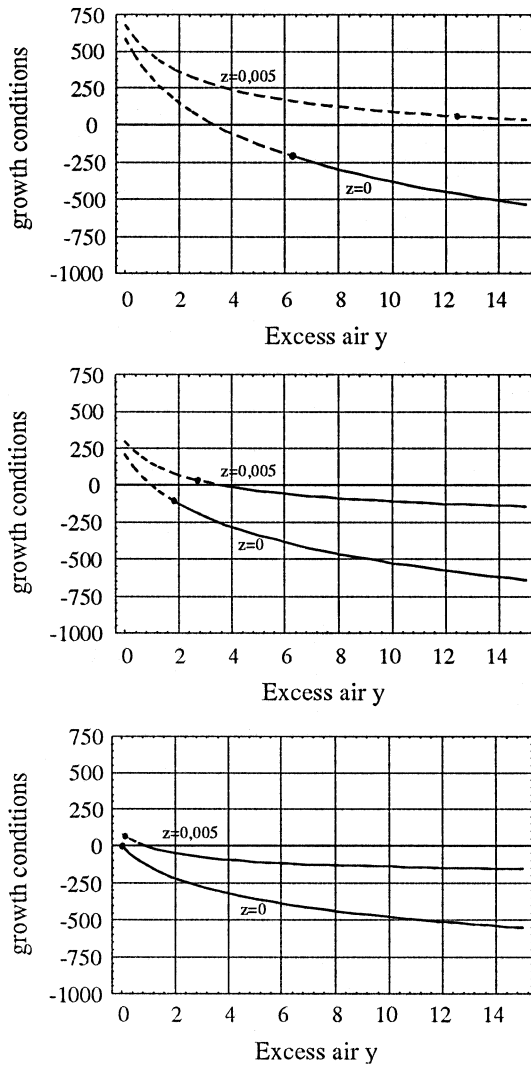
If the air has a high humidity  $z$ , it may not be able to absorb all the water that the plant wants to transpire. This effect limits the partial pressure of the outgoing water vapour: it has to be smaller than  $p(T)$ , the saturation pressure corresponding to the prevailing temperature  $T$ . Thus we come to *growth condition II* which reads

$$p_V^{out} < p(T) \quad \text{or, by (38)} \quad y+1 \geq 3 \cdot 10^{-4} \frac{1 - \frac{p(T)}{p}}{\frac{p(T)}{p} - z \frac{M_A}{M_{H_2O}} \left( 1 - \frac{p(T)}{p} \right)} \tag{45}$$

### 3.6 Evaluation

For a given temperature  $\tau = 1$  corresponding to an excess water value  $x = 310$  (see Fig. 3 for  $str = 1$ ) and two choices for the humidity  $z$  the left hand side of growth condition I – the inequality (44) – is plotted as a function of  $y$ , the excess air value. Figure 4 shows the result. The curves are thermodynamically relevant only where they fall below the abscissa, because that is where the entropy production is positive as required by growth condition I. But this is not all: The growth condition II must also be satisfied and this provides a lower bound for the excess air  $y$ . This lower bound is represented by the dot on the curves of Fig. 4 and we conclude that we must have more excess air when the air is more humid.

Inspection shows that the items (3), (5) and (6) vanish from the growth condition I (44) when  $T = T_R$  holds, i.e.  $\tau = 1$ . But even for other values of  $\tau$  these items never amount to much numerically; we must realize that  $\tau$  cannot move far out of the range  $0,9 < \tau < 1,1$  or photosynthesis will stop. Figure 5 shows



**Fig. 4.** Material entropy production (normalized) as a function of excess air  $y$  for the three temperatures  $T_1 = 15^\circ\text{C}$ ,  $T_2 = 25^\circ\text{C}$  and  $T_3 = 35^\circ\text{C}$ . For each temperature the two curves represent two values of humidity  $z$  as indicated

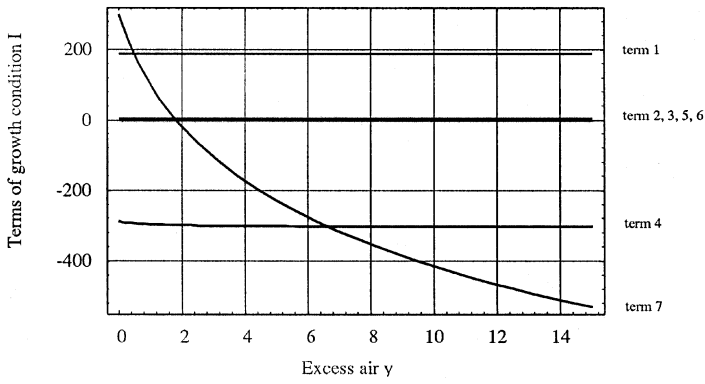
the respective values of all terms in (44) for  $T = T_R$ ,  $z = 0$  and as a function of excess air  $y$ . We see that only term (1), the heat of reaction, and the two terms (4) and (7), the entropies of mixing are relevant. And while (1) and (4) are either fully or nearly independent of  $y$ , term (7), the entropy of mixing of the evaporated water with the surrounding air, depends strongly on  $y$ : The more excess air there is, the more mixing of vapour and air will occur.

Seeing that only the terms (1), (4) and (7) contribute significantly to the inequality (44) we may simplify growth condition I and write

$$\frac{\Delta h^R}{RT_R} + \tau(1+y) \left\{ \frac{p_{N_2}^{in}}{p_{CO_2}^{in}} \ln \frac{p_{N_2}^{out}}{p_{N_2}^{in}} + \frac{p_{O_2}^{in}}{p_{CO_2}^{in}} \ln \frac{p_{O_2}^{out}}{p_{O_2}^{in}} \right\} + x \cdot \tau \cdot \ln \frac{p_V^{out}}{p(T_R)} \leq 0. \quad (46)$$

In this formula item (4) in (44) has also been truncated, because only its first two terms are numerically relevant.

In conclusion we may say that thermodynamic principles require watering to the extent of 50 to 500 times, – depending on  $\tau$  – the amount of water that is needed for the reaction. Also ventilation is required to the extent of 0 to 6 times – depending on  $\tau$  – the amount of air than is needed for the supply of  $CO_2$  to the plant.



**Fig. 5.** The individual terms in the growth condition I. Case:  $\tau = 1$ ,  $z = 0$

While the need for watering is well known to plant physiologists, e.g. see [5], -and really to everybody – , the excess air is not quantified in the literature to our knowledge, although it is generally recognized that ventilation affects the plant growth positively (e.g. see [8]).

#### 4 Growth rate for the reversible reaction

##### 4.1 Reversibility

It is unfortunate that the entropy balance (44) is an *inequality* rather than an *equation*, because that fact leaves us with only *one* equation – the energy balance – for the 6 parameters of our system. The parameters are

$$\begin{aligned}
 & \text{growth rate } \dot{m}_G \\
 & \text{temperature } T \\
 & \text{radiation intensity } str \\
 & \text{excess water } x \\
 & \text{excess air } y \\
 & \text{humidity } z .
 \end{aligned} \tag{47}$$

However, we may assume – perhaps – that the entropy production is small, because the whole process of glucose formation in plants runs quite slowly. Therefore we suggest that the process is reversible to a reasonable approximation and this means that there is no entropy production.<sup>9</sup> By this assumption we gain another equation, because the entropy inequality (44) becomes an entropy equality.

The energy equation contains four of the parameters (47), viz.  $\dot{m}_G$ ,  $T$ ,  $str$  and  $x$ , while the new entropy equation also contains four parameters, albeit different ones, viz.  $T$ ,  $x$ ,  $y$ ,  $z$ . The two equations read

$$\frac{\dot{m}_G}{mol/s} = \frac{str \cdot 650 - 5,79 \cdot 10^{-8} \frac{T^4}{K^4}}{466,3 \cdot 10^3 + x \cdot 18 \cdot 2,44 \cdot 10^3} , \tag{48}$$

$$\frac{\Delta h^R}{RT_R} + \tau (y + 1) \left\{ \frac{p_{N_2}^{in}}{p_{CO_2}^{in}} \ln \frac{p_{N_2}^{out}}{p_{N_2}^{in}} + \frac{p_{O_2}^{in}}{p_{CO_2}^{in}} \ln \frac{p_{O_2}^{out}}{p_{O_2}^{in}} \right\} + x \cdot \tau \cdot \ln \frac{p_V^{out}}{p(T_R)} = 0 . \tag{49}$$

Note that, by (37) and (38), the in-pressures depend on  $z$ , while the out-pressures depend on  $x$ ,  $y$  and  $z$ .

In one respect the excess air  $y$  is not a good variable to have, because it is difficult to control. What we *can* control easily is the volume flux  $\dot{V}$  of the incoming air. By (37) and (38) we have

$$1 + y = \frac{3 \cdot 10^{-4} \frac{1}{6} M_G p \dot{V}}{1 + z \frac{M_A}{M_{H_2O}} \frac{\dot{m}_G^{out}}{RT}} \tag{50}$$

<sup>9</sup> For the present argument – for simplicity – we ignore the constraints that growth condition II imposes upon the reaction.

and this relation may be used to replace  $y$  in (49) wherever it occurs, namely in the out-pressures.

Thus in synthetic notation the two equations (48) and (49) read

$$F(\dot{m}_G, T, str, x) = 0 \quad \text{and} \quad G(\dot{m}_G, T, x, \dot{V}, z) = 0. \quad (51)$$

#### 4.2 Growth rate as a function of temperature

So as to get an idea about what the theory predicts – apart from the need for watering and ventilation – we calculate the growth rate  $\dot{m}_G$  as a function of temperature. We proceed as follows: We fix

$$z = 0, \quad \dot{V} = 0,053 \frac{m^3}{s}, \quad str = 1, 0,9, 0,75 \quad (52)$$

and eliminate  $x$  between the equations (51)<sub>1,2</sub>, thus obtaining  $\dot{m}_G = \dot{m}_G(T, str)$ . The left hand side of Fig. 6 shows the result for the three values (52)<sub>3</sub> of the parameter values  $str$ .

We itemize three salient features of these curves

- there is an optimal temperature for growth
- the optimal temperature grows with an increasing influx of radiation
- the growth rate is promoted by a higher influx of radiation.

All three of these conclusions from the theory are confirmed by observations. Indeed, the right hand side of Fig. 6 shows a plot taken from the book by Larcher [5], valid for the plant *Atriplex patula*, vulgo spinach. The curves of this plot show the same properties qualitatively as the calculated curves.

Moreover, the amounts of the growth rates are roughly the same ones in the two diagrams. Indeed, for glucose we have the typical value<sup>10</sup>

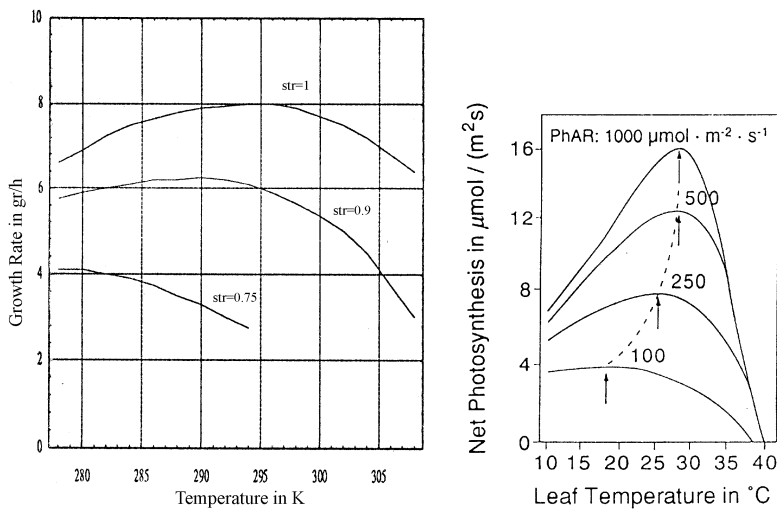
$$12 \frac{\mu mol CO_2}{s} = 1,3 \frac{gr}{h}.$$

The radiation rates in the measured plot refer to the Photosynthetically Active Radiation and it is given here in terms of mols of the photons that carry the energy. Thus

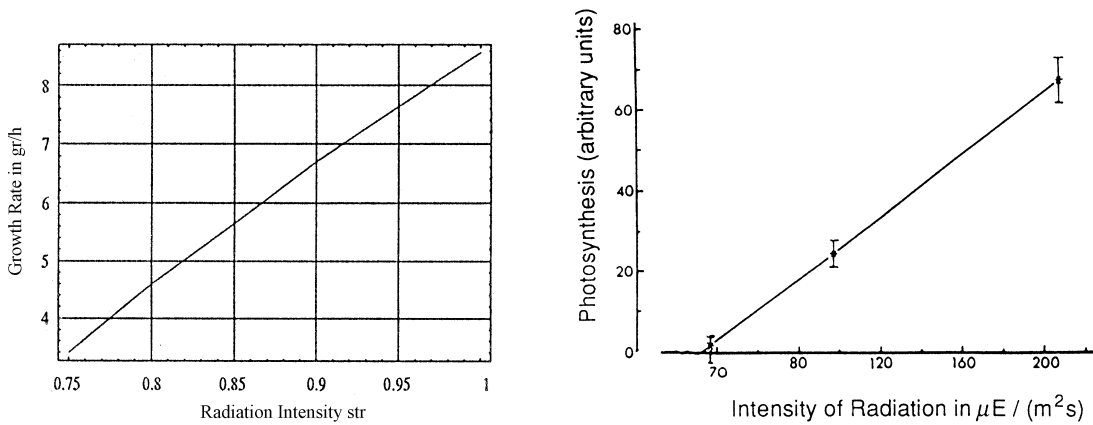
$$\frac{10^3 \mu mol Ph}{s} \hat{=} 220 W.$$

It will be recalled that the radiation intensity factor  $str = 1$  corresponds to  $650 W$ . We have argued previously, – see Sect. 2.2 – that only a quarter of the radiative influx is photosynthetically active. Therefore the parameter values of the experimental and theoretical plots of Fig. 6 are also roughly the same.

<sup>10</sup>  $mol CO_2$  is one mol of  $CO_2$ , which is used to synthesize  $\frac{1}{6} mol$  of glucose, i.e.  $30 gr$ .



**Fig. 6.** Growth rate as a function of temperature. Left: Theory. Right: Observation[5]



**Fig. 7.** Growth rate as a function of energy influx. Left: Theory. Right: Observation [8];  $\frac{\mu\text{E}}{\text{s}}$  means  $\frac{\mu\text{molPh}}{\text{s}}$

If we refer the volume flux  $(52)_2$  to the growth rate maximum of  $8 \frac{\text{gr}}{\text{h}}$  we obtain a specific volume of  $24 \frac{\text{m}^3}{\text{gr}}$  which is 8 to 9 times as much as the maximum amount needed, if the stoichiometric reaction alone would occur, see Sect. (2.3).

All in all this is satisfactory, qualitatively and quantitatively so that, perhaps, our thermodynamic theory of glucose synthesis gains some credence.

#### 4.3 Growth rate as a function of radiation intensity

We may also fix parameters as follows

$$z = 0, \quad \dot{V} = 0,071 \frac{\text{m}^3}{\text{s}}, \quad T = 18^\circ\text{C}$$

and eliminate  $x$  between the two equations (51). Thus we obtain  $\dot{m}_G = \dot{m}_G(\text{str})$ . The left hand side of Fig. 7 shows the resulting curve which is nearly a straight line: Not unexpectedly the growth rate grows linearly with the radiation density. Actually the behaviour has also been observed by botanists and the right hand side of Fig. 7 represents one such observation, made for the plant *Chrysanthemum Horim*. Quantitative conclusions cannot be drawn from Fig. 7 since the range of energy fluxes is different in the two diagrams and the "relative units" of the experimental picture are difficult to translate into  $\text{gr}/\text{h}$ .

#### 4.4 Growth rate as a function of volume flux and of humidity

We investigate other aspects of the formula (51), viz.

- Set  $z = 0$ ,  $T = 25^\circ\text{C}$ ,  $\text{str} = 1$  and calculate  $\dot{m}_G = \dot{m}_G(\dot{V})$ .
- Set  $T = 25^\circ\text{C}$ ,  $\dot{V} = 0,069 \frac{\text{m}^3}{\text{s}}$ ,  $\text{str} = 1$  and calculate  $\dot{m}_G = \dot{m}_G(z)$ .

The results are shown in the diagrams of Fig. 8. We conclude that better ventilation with dry air promotes growth, while a higher humidity of the air – at a given volume flux – is bad for growth.

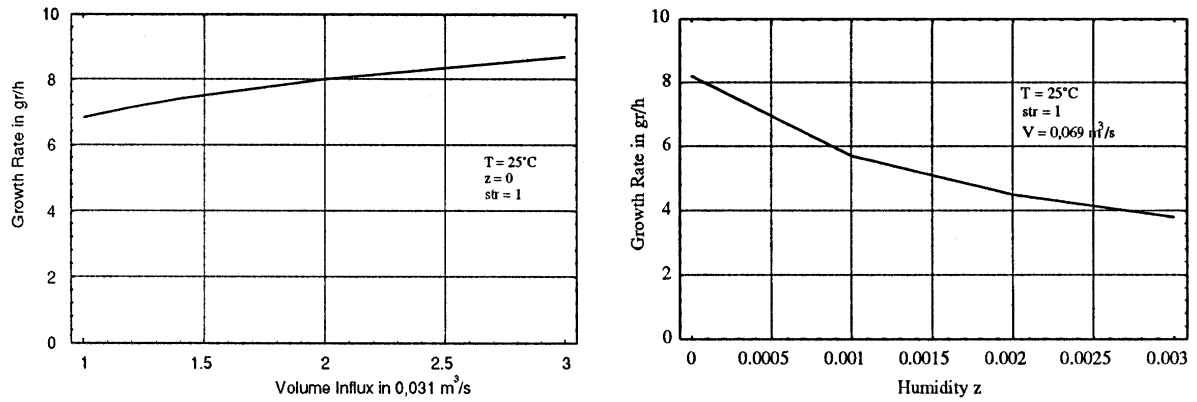


Fig. 8. Left: Growth rate as a function of volume flux. Right: Growth rate as a function of humidity

*Acknowledgement.* We are indebted to Prof. A. Stahl who called our attention to this subject and accompanied the work with constructive criticism.

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