Convective Gas Flow in Plant Aeration and Graham's Law of Diffusion

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Dedicated to Professor Ludwig Bergmann (Köln) on the occasion of his 70th birthday

Experiments with porous ceramic membranes and leaves of *Nymphaea alba L.* are described which demonstrate that the counter diffusion of gaseous components of different molar mass governed by Graham's law of diffusion (not to be confused with Graham's law of effusion) has to be taken into account to understand the exchange processes of gases between leaves of aquatic and amphibic plants and the outer atmosphere. The experiments are carried out under conditions under which the ratio of the maximum pore size r of the ceramic material to the mean free path length λ of the molecules in air has a value of the order of $\lambda/r \approx 1$.

Introduction

The exchange of gases between leaves of aquatic and amphibic plants and the outer atmosphere does not occur only by diffusion regulated by stomata. It is now well established that a convective through-flow of air is part of aeration processes in these systems (Dacey, 1980, 1981; Armstrong and Armstrong, 1990; Armstrong *et al.*, 1991; Brix, 1988). In most instances the driving force of this gas flow is a pressure difference ΔP ("ventilation pressure") between the gaseous phase within the interior of leaves and the outer atmosphere ($\Delta P = (P_{\text{in.}} - P_{\text{ex.}}) > 0$). Three processes are discussed in the literature to generate such a pressure difference. They are: thermoosmosis (thermal osmosis) (e.g. Dacey, 1980, 1981, 1987; Dacey and Klug, 1987; Schröder *et al.* 1986; Grosse and Mevi-Schütz, 1987; Mevi-Schutz and Grosse, 1988; Dedes and Woermann, 1996), humidity-induced convection (Dacey 1980, 1981, 1987; Mevi-Schutz and Grosse, 1988; Grosse and Bauch, 1991; Armstrong and Armstrong, 1994), and processes governed by Graham's law of diffusion.

It is the aim of this study to show that Graham's law of diffusion (not to be confused with Graham's law of effusion) plays a role in generating convective gas flows in plant aeration. For this purpose gas flow experiments are carried out with a porous ceramic membrane as a model system and with excised leaves of *Nymphaea alba L.* The experiments are designed to demonstrate that the phenomena observed in both systems are identical and are governed by Graham's law of diffusion. Attention is drawn to the fact that this law may also play a role in other gas exchange processes between plant organs and their surroundings (e.g., accelerated O_2/CO_2 exchange in leaves; O_2/CH_4 exchange in roots and rhizomes in soil and anoxic lake sediments).

Graham's law of diffusion

Graham's law of diffusion is discussed by considering a system in which a porous membrane separates two gaseous bulk phases (index ('), left bulk phase; index (''), right bulk phase; see Fig. 1). The bulk phase (') is formed by a gaseous species 1 with a molar mass M_1 and the bulk phase ('') by gaseous species 2 with a molar mass M_2. It is assumed that the molar mass of component 1 is smaller than that of component 2. The porous membrane separating the two bulk phases is permeable to both species. The temperature of the system has a constant value throughout the experiment and the pressure of the two phases has the

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$$P' = P'' = P*$$
$$M_1 < M_2$$
$$J_v' + J_v'' = 0$$

Fig. 1. Isothermal membrane system in which a porous ceramic membrane separates two gaseous phases at atmospheric pressure ($P = P*$). The letter m represents the membrane. Its voids have a characteristic length of the order of 0.2 µm. The letters p mark the position of two plugs which are impermeable to the gases used. They can move within the horizontally positioned calibrated tubes under the influence of a infinitesimal small difference without friction. M_i is the molar mass of the gaseous component i. The volume changes of the bulk phases are reflected by displacements of the plugs p (J_v, volume flow; $J_v' + J_v'' = 0$; $J_v^{(\alpha)} = dV^{(\alpha)}/dt$; $\alpha = (')$, $('')$).

same value. The process taking place after the start of the experiment is characterized by the words "isobaric counter diffusion of two gaseous components of different molar mass across a porous membrane".

To maintain isobaric condition during the counter diffusion process, both bulk phases are equipped with two horizontally oriented tubes which are open to the atmosphere at one end. In each tube a drop of a liquid impermeable to the gaseous components closes the volume of the two bulk phases (') and ("). It is assumed that the liquid can move back and forth within the tube without friction to equilibrate instantaneously any pressure difference between the bulk phases and the outer atmosphere which might develop during the interdiffusion experiment. The concentration gradients of the two components across the porous membrane are the driving forces of the diffusive molar flow densities j_1 and j_2.

This process has been studied first by Graham (1833). His studies led him to formulate what is now called Graham's law of diffusion: "The ratio of the molar flow densities of two gaseous components across a porous membrane in an isobaric counter transport experiment is equal to the in-

verse of the square root of the ratio of the molar masses of the components" i.e.:

$$- (j_1/j_2) \approx (M_2/M_1)^{1/2} \tag{1}$$

j_1 and j_2 are the molar flow density of the species 1 and 2 across the membrane expressed in units of [mol cm^{-2} s^{-1}]. The negative sign indicates that j_1 and j_2 have opposite directions (counter transport). Since the bulk phases are maintained at constant pressure a change of volume of the bulk phases takes place. According to Equ. (1), the volume of the right bulk phase increases and that of the left bulk phase decreases during the experiment (molar masses: $M_1 < M_2$; molar volumes: $V_1^o = V_2^o$ if the gas mixture has the properties of an ideal gas; $|j_1| > |j_2|$). The volume flow density j_v ($= - j_v' = j_v''$) is given by Equ. (2a).

$$j_v = V_1^o j_1 + V_2^o j_2 \tag{2a}$$

with

$$j_v = (1/a) \cdot (dV/dt). \tag{2b}$$

V is the volume and a the effective area of the membrane; t is the time.

Graham's law of diffusion has been rediscovered experimentally by Kramers and Kistemaker (1943) and Hoogschlagen (1953) and has since been the subject of considerable activity (Mason and Malinauskas, 1983).

If the volume of phase (') and ('') is kept constant (i.e. blocking the outlets to the attached ducts) a transient pressure difference ΔP develops between the two phases caused by the interdiffusion of the two species at different rates. The transient pressure difference ΔP is positive ($\Delta P = (P'' - P') > 0$). It can act as an effective driving force of a volume flow through a wide duct d (glass tube with a radius r_d and a length l_d, not shown in Fig. 1) connected to the bulk phase ("). But this volume flow occurs only if the mechanical permeability $d_{h,m}$ of the porous membrane is much smaller than that of the attached duct $d_{h,d}$ ($d_{h,m} \ll d_{h,d}$). The mechanical permeability is a measure of the resistance of a porous structure (membrane, glass tube) to a gas flow (more general, to a flow of a fluid). For laminar flow the volume flow density along the duct $j_{v,d}$ measured in units of [cm s^{-1}] is given by $j_{v,d} = d_{h,d}\Delta P_d/l_d$ (with $d_{h,d} = r_d^2/(8\eta)$): ΔP_d, pressure difference between the inlet and the outlet of the duct d; r_d, radius of the duct; η, vis-

cosity coefficient of the gas). Under the same conditions the volume flow density across the porous membrane is given by $j_{v,m} = d_{h,m} \Delta P/\delta$ (with $d_{h,m} = r_m^2 \varphi_m/(8\eta)$; r_m, mean value of the radius of the pores of the membrane; φ_m, porosity of the membrane; δ, thickness of the membrane).

The validity of Equ. (1) does not depend on a special structure of the porous membrane nor on the density of the gaseous phases separated by the membrane (Mason and Kronstadt, 1967; Kirk, 1967; Mason and Evans III, 1969; Evans III *et al.,* 1969; Mason and Malinauskas, 1983). In this respect Graham's law of diffusion differs from Graham's law of effusion. Graham's law of effusion is only valid if the ratio of the mean free path length λ of the molecules in the gas and of the characteristic dimension r of the pores of the membrane has a value small compared to 1 (i.e. $\lambda/r \ll 1$. A simple argument leading to Equ. (1) is given by Mason and Malinauskas (1983).

Experimental Section

Experiments with a porous ceramic membrane

In this section experiments are described demonstrating Graham's law of diffusion using a model system. The experimental set up is shown in Fig. 2. A porous ceramic (clay) cylinder (W. Haldenwange, D-13597 Berlin, Pichelswerder Straße 12; internal height, 143 mm; internal diameter, 33 mm; wall thickness, 3.5 mm; internal volume, 122 cm^3; internal area, 156 cm^2) is connected to a nonporous bottom plate which has two openings. A manometer with a negligible small dead volume (MKS, D-81829 München, Schatzbogen 3, type 122 AA-01000-DD) is connected to one of them to measure transient pressure differences between the internal gaseous phase of the cylinder and the external gaseous phase during the counter diffusion experiment. In these experiments the volume of the internal gas phase is kept constant (isochoric condition). The other opening is closed by a threaded plug during the isochoric experiments. It is used to change the composition of the internal gaseous phase of the cylinder before the start of an experiment. During the isobaric counter diffusion experiments a tube in combination with gasometer is connected to the internal
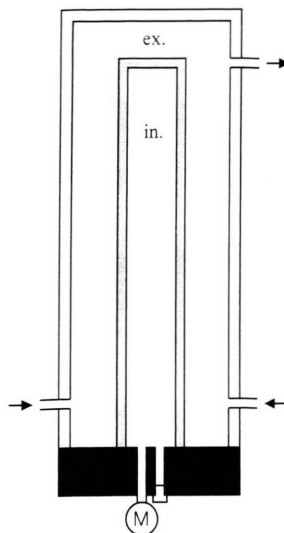
Fig. 2. Experimental set up, schematically. The external phase (index, ex.) is separated from the internal phase (index, in.) by a porous ceramic cylinder. For all practical purposes, the composition of the external phase is maintained constant in time by passing a stream of gas of known composition through the outer phase. The arrows indicate the inlet and the outlet of this stream of gas flows. *M* represents a manometer with which the transient pressure difference between the internal phase and the external phase is measured. The pressure difference is generated by a counter transport of gases across the wall of the porous cylinder. The stopper seals an opening through which the composition of the internal phase can be changed before starting a new experiment. For experiments under isobaric conditions, the stopper is replaced by a tube to measure the change of volume of the internal phase with time to keep the pressure difference between the internal and the external phase to zero.

bulk phase using one of the openings of the bottom plate of the cylinder. In this way it is possible to measure changes of volume of the internal phase.

The pore size distribution of the material forming the wall of the tube is known (see Fig. 3).

An acryl glass cylinder (internal diameter 98 mm; height 181 mm) surrounded the porous ceramic cylinder (see Fig. 2). It had three openings to allow the flow of a gas mixture of known composition through the system. This gas mixture formed the external phase of the cylinder. The effective internal volume of the acryl glass cylinder (taking into account the volume of the ceramic cylinder) had a value of 320 cm^3.
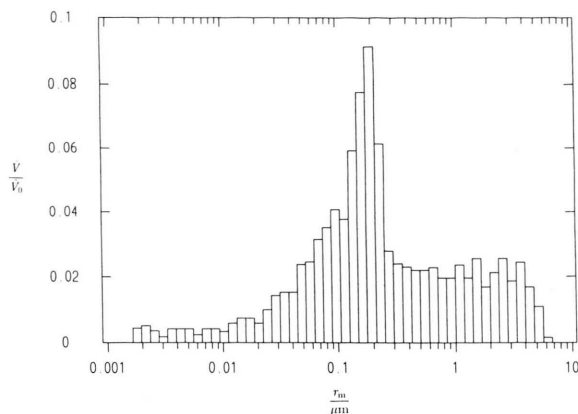
Fig. 3. Distribution of the size of voids forming the porous structure of the wall of the ceramic cylinders used in this study. The mercury intrusion method in combination with a capillary model of the porosity is used to obtain this information (Aveyard and Haydon, 1973). r is the radius of the pores. $\tilde{V}$ is the specific pore volume and $\tilde{V}_o$ the total specific pore volume. $\tilde{V}_o = 0.430$ cm^3 g^{-1}; density of the ceramic material $\varrho \approx 2.5$ g cm^{-3}; porosity of the ceramic material, $\varphi \approx 0.2$.

All the experiments were carried out at room temperature. In most of them air of atmospheric pressure formed the internal phase (index in.) of the ceramic cylinder. The external phase (index ex.) was formed by two different two-component gas mixtures: [air/CO_2] and [air/CH_4]. The use of gas mixtures makes it possible to change systematically the mean molar mass of the external gaseous phase. Air is considered a one-component gas with a (mean) molar mass of $\langle M_{air} \rangle = 28.96$ g mol^{-1}. The mean molar mass of a gaseous mixture is given by $\langle M \rangle = \Sigma x_i M_i$ (x_i, mole fraction of component i; M_i, molar mass of component i). Carbon dioxide has a molar mass of $M_{CO_2} = 44.01$ g mol^{-1} and methane a molar mass of $M_{CH_4} = 16.04$ g mol^{-1}. Carbon dioxide and methan were chosen as components of the mixture with air to be able to generate gaseous mixtures with a mean molar mass larger and smaller than that of air.

To simplify the discussion of the experimental results not only air but also the [air/CO_2] and [air/CH_4] gas mixtures are considered one-component gases characterized by their mean molar mass. The index 1 will refer to air and the index 2 to [air/CO_2] and [air/CH_4] mixtures, respectively. With the [air/CO_2]/air system the mean molar mass of the exter-

nal gaseous phase has a higher value than that of the internal phase formed by air (i.e. $\langle M \rangle_{ex.} > \langle M_{air} \rangle_{in.}$). The opposite is true for the system [air/CH_4]/air (i.e. $\langle M \rangle_{ex.} \langle M_{air} \rangle_{in.}$). The chemical nature of the gases is of no importance to the experiments except the value of their molar masses. The ratio $\langle M_{air} \rangle / M_{CO_2}$ has a value comparable to that of $M_{CH_4}/\langle M_{air} \rangle$.

The pressure difference between the inlet and the outlet (atmospheric press) of the acryl glass cylinder was adjusted to keep its value as small as possible, but at the same time to insure that the difference between composition of the gas mixture at the inlet and the outlet was negligibly small. This pressure difference had typically a value of $\delta P \approx 10$ Pa.

The apparatus to generate the binary gas mixtures of known composition is shown schematically in Fig. 4. The pure gaseous components 1 and 2 were stored in pressurized tanks. Two manostats (Wallace & Tiernan, D-89312 Günzburg, Type FA-149) were used to generate flows of the two gases which were constant in time. Care was taken that the temperature of the gases had attained room temperature before entering the gas mixing device (cooling by adiabatic expansion). To produce a flow of a mixture of the two gases with a preset composition and preset flow rate the flow of air and CO_2 (or CH_4) before mixing the gases was determined by measuring the pressure drop along a capillary tube (poly-vinylchloride; internal diameter, 2 mm; length, 2.6 m) as function of the flow rate. For calibration purposes each volume flow was measured separately with a simple gasometer. Finally, both
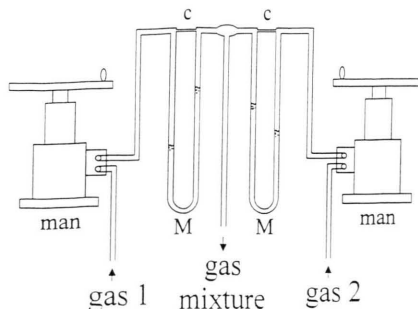

Fig. 4. Construction of the apparatus used for generating gaseous mixtures of known composition, schematically. *man*, manostate to maintain a pressure value constant. Two manometers M are used to measure the pressure difference between the two ends of two capillaries *c*.

volume flows were combined and fed into the acryl glass cylinder surrounding the porous ceramic cylinder.

Two types of experiments were carried out:
○ Measurements of the (transient) pressure difference caused by the counter transport of the gases across the wall of the porous cylinder as function of time with the volume of the internal phase kept constant;
○ measurements of the change of the volume of the internal phase necessary to maintain isobaric conditions during the counter transport experiment.

Before starting a typical experiment the following protocol was followed:

(1) The internal phase of the porous tube is filled with air at atmospheric pressure. It is checked that the reading of the manometer measuring the pressure difference be tween the internal phase and the atmosphere is zero.

(2) The flow rate and the composition of the gas mixture forming the external phase of the porous cylinder was set at the desired value. With a typical flow rate of $J_{V.ex.} \approx 15$ cm^{3}s^{-1} the external phase of the acryl glass cylinder is renewed about every 20 s. An experiment is started by connecting the outlet of the gas mixing device to the inlet of the acryl glass cylinder surrounding the porous ceramic cylinder.

Experiments with leaves of Nymphaea alba L.

A young leaf of *N. alba* was cut from a plant growing in a water tub in the green house of the Experimental Garden of the Botanical Institute. Before cutting the petiole, the leaf was pulled up from the air/water interface to prevent water from plugging up the air chambers of the petiole. The leaf used for the experiment described in this section is characterized by the following data: area of gas exchange: 186 cm^2; thickness: about 0.6 mm; volume: 10.2 cm^3, internal gas volume: 5.6 cm^3; i.e. aerenchyma: $\approx 56\%$. The entire leaf was placed into a narrow acyl glass chamber (internal dimensions, hight: 8 mm, length: 220 mm, width: 210 mm, volume: 350 cm^3) which had an inlet and an outlet for a stream of gas. The openings for the gas flow were located at the diagonal of the chamber. The chamber consisted of two halfes sealed leak-tight by a silicon rubber gasket. To prevent the leaf

from dehydrating, the lower half of the chamber was filled up with water. The petiole was put through a narrow slit in the bottom of the chamber. The end of the petiole was positioned leak-tight to a flexible polyvinylchloride tube connected to an electronic volume flow meter (Mass Flowmeter, FMA 1802, Omega Engineering, INC. Stanford CT, USA; sensitivity, 0-10 cm^3 min^{-1}). The chamber containing the leaf was positioned horizontally at the air/water interface of a tub filled with water at room temperature. The chamber was immersed into the water only slightly, just enough so to keep the leaf blade floating in the chamber. Two gas tanks containing N$_2$ gas and He gas, respectively, in combination with a manostate (Wallace & Tiernan, Type Fa-149) were used to generate a stream of N$_2$ gas and He gas, respectively, at a constant rate of 100 cm^3 min^{-1} at atmospheric pressure. The gases were choosen for their low solubility in water and the ease to handle them. The volume flow was monitored by a second less sensitive electronic volume flow meter (see above; sensitivity, 0-100 cm^3 min^{-1}). A valve could be activated to let pass one or the other stream of gas through the acryl glass chamber and over the leaf's surface. The outlet of the chamber had a diameter of about 5 mm and allowed an unhindered through flow of gas to the outer atmosphere. Before starting a series of experiments, the leaf was conditioned by passing a stream of N$_2$ gas through the chamber until the gas flow meter connected to the end of the petiole showed the reading $J_v = 0$ (J_v, volume flow). Then, the N$_2$ gas flow through the chamber was switched to the He gas flow and the sign and the value of gas exchange through the upper leaf surface ($J_{He} > J_{N_2}$) was recorded as a flow of gas out of the petiole (positive value) as function of time t until a new stationary state was established. A slight shift in the location of the base line of $J_v(t)$ was observed. Thereafter, the He gas flow through the chamber was replaced by a N$_2$ gas flow. The gas flow through the leaf and the petiole was recorded as function of time again (flow of gas into the petiole, negative value). This cycle of N$_2$/He gas flows was repeated several times. Before changing from a N$_2$ flow to the He gas flow the composition of the gas in the chamber was checked several times gas- chromatographically as described by Grosse and Bauch (1991). Only traces of oxygen could be detected.

Experimental Results and Discussion

Experiments with porous ceramic membranes: transient pressure difference between the external and the internal phase at constant volume of the internal phase

Typical changes of the pressure difference ($\Delta P = (P_{in.} - P_{ex.})$) between the external and the internal phase of the porous ceramic cylinder as function of time t are shown in Fig. 5. The volume of the internal phase is kept constant. The curves refer to the system [CO_2/air] with $\langle M \rangle_{ex.} > \langle M_{air} \rangle_{in.}$. Parameters are the composition of the external phase (mole fraction of CO_2, x_{CO_2}) and the flow rate $J_{v.ex.}$ of the gaseous mixture through the external phase (two flow rates $J_{v.ex.} = 5$ cm^3 s^{-1}; 20

cm^3 s^{-1}). It turns out that the shape of the - (ΔP) versus t curves become practically independent of $J_{v.ex.}$ for values $J_{v.ex.} \geq 15$ cm^3 s^{-1}.

The shape of the - (ΔP) versus t curves is caused by the fact that the composition of the internal phase of the porous cylinder changes with time whereas the composition of the external phase remains constant. At the beginning of the experiment the ratio [$\langle M \rangle_{ex.}/\langle M_{air} \rangle_{in.}$] has its highest value (>1). At the end of the experiment both phases have the same composition. The same is true for ratio of the molar flow |J_1(ex. $\Leftarrow$ in.)/J_2(ex. $\Rightarrow$ in.)| (index 1: air; index 2, [air/CO_2] mixture). A pressure difference ΔP (= $P_{in.} - P_{ex.}$) develops. It has a negative value which becomes more negative with increasing times in the early phase of the experiments. The rate of change of -(ΔP) (i.e. d(-ΔP)/dt)) which is positive at the beginning of the experiment, starts to decreases as time goes on, approaches the value zero at -(ΔP)$_{max}$ and becomes negative. Finally the internal and the external phase have the same composition and the rate of pressure change (d(-ΔP)/dt) as well as the value of (-ΔP) approaches zero.

The general shape of the -(ΔP) versus time curves changes little with the composition of the external phase. The position of the maximum value of -(ΔP) on the time axis at constant flow rate of the gas mixture through the external phase remains constant indicating that the change of shape of the profiles of $\langle M \rangle_{in}$ with time is independent of the composition of the external phase for a constant value of $J_{v.ex.}$.

To a first approximation the maximum value of - (ΔP) (i.e. (-ΔP)$_{max.}$) increases linearly with increasing values of the mole fraction of CO_2 in the external phase (see Fig. 6a). This is expected on the basis of Equ. (1): At the start of each experiment the composition of the internal phase is always the same, $x_{CO_2} = 0$. The mean molar mass of the external phase is changed by changing the mole fraction of CO_2 in the mixture. $\langle M \rangle_{ex.}$ is a linear function of x_{CO_2} ($\langle M \rangle_{ex.} = \langle M_{air} \rangle + x_{CO_2}(M_{CO_2} - \langle M_{air} \rangle)$).

Results of corresponding experiments with the system [air/CH_4]/air are shown in Fig. 6b. The interpretation of the data follows the same line of reasoning described for the system [air/CO_2] provided it is taken into account that for the system [air/CH_4] the ratio [$\langle M \rangle_{ex.}/\langle M_{air} \rangle_{in.}$] has a value smaller than 1.

Fig. 5. Transient pressure difference ΔP (= $P_{in.} - P_{ex.}$) versus time t curves. The external phase is formed by [CO_2/air] mixtures of different compositions. The internal phase is formed by air. Parameters: (a) volume flow $J_{v.ex.}$ through the external phase; (b) composition of the external phase. From above to below, x_{CO_2}: 1; 0.8; 0.6; 0.4; 0.2; 0.1; 0.05; 0.02. x_{CO_2}, mole fraction of CO_2. $P_{ex.} = 1$ bar.

Therefore, the molar flow is directed into the interior phase of the cylinder causing a pressurization of the internal phase.

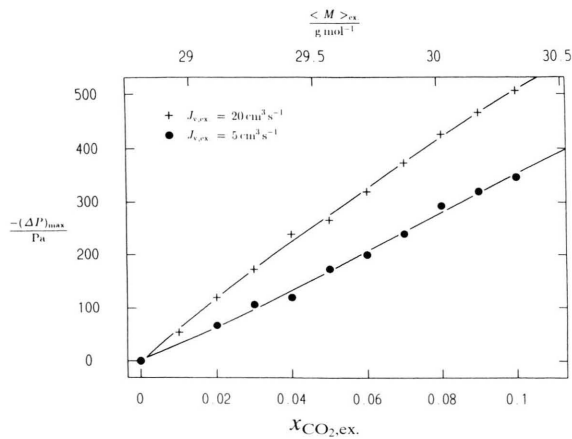Fig. 6a. Maximum of the transitional pressure difference $(\Delta P)_{max.}$ $(= P_{in.} - P_{ex.})_{max.}$ between the external phase (ex.) and the internal phase (in.) of a porous cylinder caused by an isothermal counter transport of two gases of different mean molar mass as function of the composition of the external phase. At the beginning of an experiment, the internal phase is formed by air $\langle M_{air}\rangle = 28.96$ g mol^{-1} and the external phase by a [air/CO$_2$] gas mixture; $M_{CO_2} = 44.01$ g mol^{-1} (i.e. $\langle M\rangle$ex > $\langle M\rangle$in).

Experiments with porous ceramic membranes: Transient volume flow out of the internal phase under isobaric conditions

To demonstrate a through-flow of gas caused by the counter diffusion of gaseous components across the porous cylinder for $[\langle M\rangle_{ex.}/\langle M\rangle_{in}] < 1$ the volume V(t) leaving the internal phase of the porous cylinder to maintain isobaric condition is measured as function of time.

Fig. 7 shows the total volume V_t of the gas leaving the internal phase as function of the composition of the internal phase for the system [air,CO$_2$]/air. The corresponding curve (not shown) for the system [air, CH$_4$]/air is similar but with negative values of V_t (i.e. gas flowing into the the internal phase). This is expected because the ratios $\langle M_{air}\rangle/M_{CO_2}$ and $M_{CH_4}/\langle M_{air}\rangle$ have similar values.

The maximum value of the total volume V_t of gas leaving the internal phase is about 1/2 of the volume of the internal phase ($V_{in} \approx 120$ cm^3; $x_{CO_2,in.} = 1$, $V_t \approx 50$ cm^3). The duration of the volume efflux is longer by a factor of about 2 than the equilibration time of the pressure difference $|\Delta P|$ under isochoric condition. This can be understood by taking into account the fact that the transient pressure difference $|\Delta P|$ observed under isochoric conditions acts as a

Fig. 6b. Corresponding experiments with the system [air, CH$_4$]/air. At the beginning of an experiment the internal phase is formed by air $\langle M_{air}\rangle = 28.96$ g mol^{-1} and the external phase by a [air/CH$_4$] gas mixture; $M_{CH_4} = 16.04$ g mol^{-1} (i.e. $\langle M\rangle_{ex.} < \langle M\rangle_{in}$). Also shown in both Figs. 6a and 6b is the mean molar mass $\langle M\rangle_{ex.}$ of the external gas mixture as function of composition. Parameter: volume flow $J_{v,ex.}$ through the external phase. $T = 25$ °C.
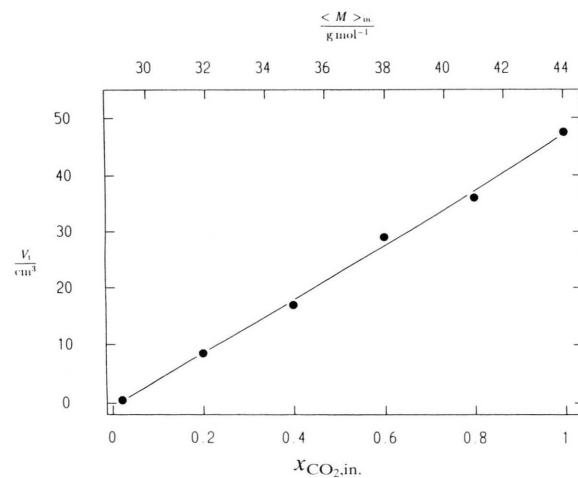

Fig. 7. Total volume of gas having left the internal phase of the porous ceramic cylinder during the counter transport of two gases of different molar mass under isobaric conditions as function of the composition of the internal phase ($P_{in.} = P_{ex.} \approx 1$ bar). The external phase is formed by air and the internal phase by a [air/CO$_2$] mixture (i.e. $\langle M\rangle_{ex.} < \langle M\rangle_{in.}$). $x_{CO_2,in.}$, mole fraction of CO$_2$ in the internal phase at the beginning of the experiment.

driving force of a volume flow across the wall of the ceramic cylinder. A rough estimate of the total volume leaving the internal phase across the porous wall of the cylinder during a isochoric experiment leads to a value ($V \approx 90$ cm³) which has the same order of magnitude as V_t (laminar flow, $V = (a\, r_m^2\, \varphi_m\, \Delta P\, t)/(8\eta\delta_m)$; with $\eta_{air}(20\,°C) = 1.8\cdot 10^{-11}$ $J\cdot s\cdot cm^{-3}$; $r_m \approx 0.2$ μm; $\delta_m = 0.35$ cm; $a = 150$ cm²; $\varphi_m = 0.2$).

Experiments with leaves of Nymphaea alba L.

To evaluate the physical effect of Graham's law of diffusion for generating gas flows through aquatic plants, the artificial porous partition is replaced by an excised floating leaf of the *Nymphaea* species. Preliminary studies with excised leaves of *Nymphaea lotus* var. *lotus* and *N. alba* have shown that the gas exchange between the internal gas phase of the leaf and the outer atmosphere can be manipulated by ventilation of the surface of the leaf with pure gases of different molar mass. For experimental reasons, a pair of gases is chosen with a large difference between their molar masses to generate sufficiently high transitional gas flows through the leaf (N_2/He: $M_{N_2} = 28$ g mol⁻¹, $M_{He} = 4$ g mol⁻¹). Similar to the experiments with the ceramic cylinders, the exchanged gas volumes depend on the total volume of the leaf's arenchyma.

The isobaric $J_v(t)$ curve shown in the first part of Fig. 8 refers to a situations in which the external N_2 gas atmosphere with which the leaf of *Nymphaea alba* is in gas exchange equilibrium is replaced by He gas. At the upper surface of the leaf blade a counter diffusion of N_2 and He takes place. According to Graham's law of diffusion (see Equ. (1)) the molar flow density of He into the interior of the leaf (i.e. the leaf's aerenchyma) is larger than that of N_2 which is directed outward through the leaf's surface following their concentration gradients. Consequently, a transient pressure difference develops (i.e. $(P_{in.} - P_{ex.}) > 0$). This pressure difference leads to a transient gas flow from the interior of the leaf through the air channels of the petiole into the outer atmosphere ($J_v(t) > 0$). This observation is taken as evidence that the resistance of these air channels of the petiole to the gas flow is lower than that of the cuticula with its stomata. With a gas flow through the gas space above the leaf of about 100 cm³ min⁻¹ and a value this gas space of $V_{ext.} \approx 186$
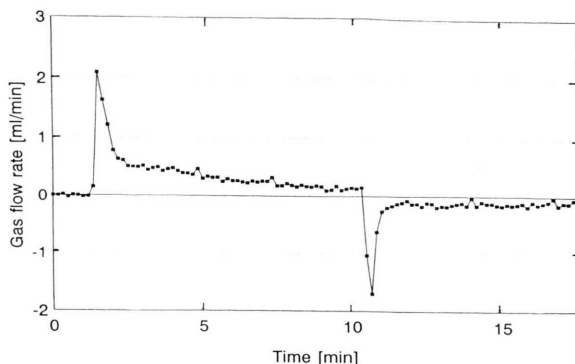

Fig. 8. Records of the direction and the value of the volume flow J_v of gas through the leaf and its petiole of *Nympha alba* contained in a acrylglass chamber as function of time t. The composition of the gaseous atmosphere above the leaf surface within the acrylglass chamber at a pressure at 1 bar is changed consecutively ($N_2 \rightarrow$ He $\rightarrow N_2$). *T*, room temperature. Positive and negative values represent efflux and influx of gas, respectively at the cut petiole.

cm³ it is estimated that during an experiment the gas in the chamber is mostly replaced within the first minute. Caused by the interdiffusion process the mean molar mass of the internal gaseous phase of the leaf formed by N_2 and He decreases. Finally, the leaf is in gas exchange equilibrium with He. Therefore, $J_v(t)$ goes through a maximum and decreases again. It is expected to reach the value $J_v(t) = 0$. This is not observed experimentally. The base line of $J_v(t)$ curve before starting a counter diffusion experiment (i.e. $t = 0$: $J_v = 0$) and that after a time sufficiently long so that the counter diffusion process can be expected to have stopped, is slightly different from zero (i.e. $|J_v| \neq 0$). This could be caused by the fact that the gas flowing through chamber is not completely saturated with water vapour. Water evaporates from the tissues inside the leaf keeping the ratio of the molar masses $[\langle M_{He}\rangle_{ext}/\langle M_{He,H_2O}\rangle]$ smaller than 1. This keeps the system from reaching its equilibrium (i.e. $J_v = 0$) state.

The isobaric $J_v(t)$ curve shown in the second part of Fig. 8 refers to a situations in which the external He gas atmosphere with which the leaf is in gas exchange equilibrium is replaced by N_2 gas. Again, at the upper surface of the leaf a counter diffusion of N_2 and He takes place, but the directions of the molar flow of the two gases are reversed because the sign of their concentration gradients are reversed.

According to Graham's law the molar flow of N_2 through the surface of the leaf into its interior is smaller than that of He which is directed out of the leaf. Consequently, a transient pressure difference develops (i.e. $(P_{in.} - P_{ex.}) < 0$). This pressure difference leads to a transient gas flow of air from the outer atmosphere through the petiole into the interior of the leaf ($J_v(t) < 0$) compensating the reduction of the gas volume in the aerenchyma. These N_2/He gas exchange cycles have been repeated at least 7 times with a given leaf. Although the shape of the $|J_v(t)|$ curves change slightly, the sign of $J_v(t)$ was always in agreement with the predictions of Graham's law. The total volume of gas leaving and entering a leaf, respectively, can be obtained from integrating the $J_v(t)$ curves measured in the series of N_2/He gas exchange cycles. For a leaf with an surface area of 186 cm^2 the mean value of the exchange volume during efflux is $\langle V_{eff} \rangle = (0.98 \pm 0.18)$ cm^3 and that of the exchange volume during influx is $\langle V_{in} \rangle = -(0.78 \pm 0.12)$ cm^3 at atmospheric pressure. The values refer to the exchanged volume at the peak of $J_v(t)$ curves within $t = 1$ min and correspond to about 20% of the total gas volume of the leaf. The shoulder of the $J_v(t)$ curves following the peak probably reflect the inhomogeneous internal pore structure of the leaf. It has to be taken into account also that the density of N_2 and He is different ($\varrho(\text{He})/\varrho(N_2) \approx 0.1$) this influences the mixing process of the gases within the leaf.

Conclusions

Graham's Law of diffusion (not to be confused with Graham's law of effusion) plays a role in generating convective gas flows in plant aeration. This is demonstrated by experiments carried out with porous ceramic membranes and with leaves of *Nymphaea alba L.* at atmospheric pressure. Porous partition with pore radii r in the range of the mean free path lengh λ of the gaseous molecules ($r/\lambda \approx 1$) separating two phases formed by gases of different molar mass are necessary to generate convective gas flows. At atmospheric pressure, λ has a value of the order of $\lambda \approx 0.1$ μm in air. Since plant surfaces are generally permeable to gas and the mean molar mass of gas mixtures with in plants and their environment are often different, transport of gases governed by Graham's law may be more common than usually thought.

Caused by CO_2 fixation and O_2 production in photosynthetic highly active leaves, the mean molar mass in the gas phase decrease there. This leads to a transient reduction of the pressure in the intercellular space when gas with the lower molar mass moves out faster than air with the higher mean molar mass enters the leaf. This could induce an inflow of CO_2 enriched gas from tissues with high respiratory activity. The CO_2 will be reused in photosynthesis.

Graham's law of diffusion may also play a role in the uptacke of O_2 by roots with a high CO_2 concentrations in the their intercellular gas spaces from well air aerated soil ($\langle M_{air} \rangle_{soil} < \langle M_{air,CO_2} \rangle_{root}$). The same may be true for the gas transport from the pore volume of sediments in freshwater lakes enriched with CH_4 into roots with a hight concentration of respiratory CO_2 in their intercellular space ($\langle M_{air,CH_4} \rangle_{sediment} < \langle M_{air,CO_2} \rangle_{root}$).

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