

Gas exchange between bubbles and molten glass¹⁾

Jan Matthijs Hermans and Adriaan Cornelis Verbeek
Philips Display Components, Eindhoven (The Netherlands)

Knowledge about the exchange of gases between bubbles and molten glass is of vital importance for bubble diagnosis. This process was studied using melting trials with very well-defined test bubbles (tracer bubbles), and bubble analysis. These experiments enable the direct determination of the gas permeability (the product of solubility and diffusivity) which describes the rate of gas exchange. In literature, little reliable data on the permeability can be found due to experimental problems with the most common method of studying gas exchange, gas extraction. For CO₂ in television screenglass a permeability of about $2 \cdot 10^{-17}$ mol/(m s Pa) at 1305 °C was found.

Gasaustausch zwischen Blasen und geschmolzenem Glas

Für die Diagnose von Glasfehlern ist das Verständnis des Gasaustauschs zwischen Blasen und geschmolzenem Glas notwendig. Der Gasaustauschprozeß wurde mit Hilfe von sogenannten Tracerblasen, d.h. Blasen mit sehr gut definierter Ausgangszusammensetzung, untersucht. Tracerblasenversuche ermöglichen die direkte experimentelle Bestimmung der Permeabilität (= Produkt aus Diffusions- und Henryschem Koeffizienten), die die Geschwindigkeit des Gasaustauschs beschreibt. Verlässliche Daten über die Permeabilität sind wegen der experimentellen Schwierigkeiten mit der üblichen Analysenmethode zur Untersuchung des Gasaustauschs, der Gasextraktion, in der Literatur nur schwer zu finden. Aus den Versuchen ergab sich für CO₂ in Fernsehschirmglas eine Permeabilität von $2 \cdot 10^{-17}$ mol/(m s Pa) bei 1305 °C.

1. Introduction

Bubbles are the most important defect category in the production of television screenglass. Television screens are a very critical product with respect to bubbles: A rate of 6 bubbles/t glass already leads to 10 % reject. Recent developments concerning increased contrast and future developments concerning High-Definition Television (HDTV) and monitor glass will even make the product more sensitive, since the maximum allowable bubble size is becoming smaller and smaller.

The composition of the gases in a bubble gives very important clues about the source and the residence time of that bubble. To be able to make full use of the results of bubble analysis, knowledge about gas exchange rates and equilibria in molten glass is needed. Theoretically, the process of gas exchange between bubbles and molten glass is relatively well known. However, obtaining the correct physical constants for a good description is a very big problem. There is no agreement in literature, not even about the order of magnitude of these constants.

2. Theory

In principle, the gas exchange process between bubbles and molten glass is described by Fick's law:

$$J = D \cdot dC/dx . \quad (1)$$

The most important restriction for mass transfer lies in the glass phase. At the interface bubble/glass equilibrium is assumed, according to Henry's law ($C = k_H \cdot p$). Combination of Fick's and Henry's law yields:

$$J = -D \cdot k_H \cdot dp/dx . \quad (2)$$

The product diffusivity · Henry coefficient is called the permeability. This product determines the rate at which gas diffuses into or out of a bubble. Combination of equation (2) with the ideal gas law leads to:

$$d(p \cdot V/R \cdot T)/dt = -D \cdot k_H \cdot 4\pi r^2 \cdot \Delta p/\delta . \quad (3)$$

Only under certain assumptions equation (3) can be solved analytically. The most important cases are:

a) isothermic, constant volume (a minor component diffusing into an inert bubble):

dV/dt and dT/dt can be neglected, so equation (3) becomes:

$$\begin{aligned} V \cdot dp/dt &= -D \cdot k_H \cdot R \cdot T \cdot 4\pi r^2 \cdot \Delta p/\delta , \\ 1/\Delta p \cdot dp/dt &= -3 \cdot D \cdot k_H \cdot R \cdot T/r \cdot \delta , \\ \ln \Delta p/dt &= \text{constant} . \end{aligned} \quad (4)$$

Relation (4) means that the partial pressure of the minor component will approximate the equilibrium pressure in an exponential way.

Received July 16, 1993.

¹⁾ Presented in German at the 67th Annual Meeting of the German Society of Glass Technology (DGG) on May 19, 1993 in Königswinter (Germany).

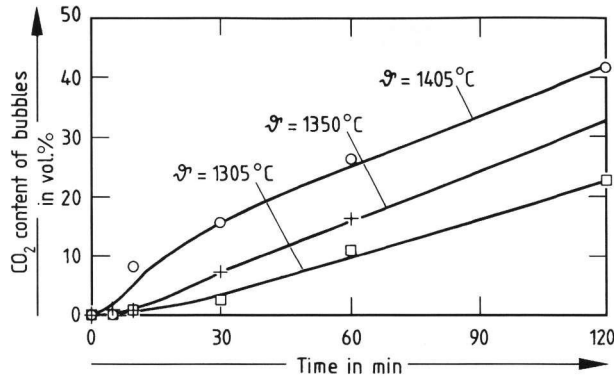


Figure 1. CO₂ exchange in 100 % argon bubbles in television screenglass at various temperatures.

Table 1. Fit parameters determined from the results in figure 1

temperature in °C	equilibrium pressure of CO ₂ in 10 ⁵ Pa	$D \cdot k_H$ in mol/(m s Pa)
1305	0.4	$2 \cdot 10^{-17}$
1350	0.5	$2.4 \cdot 10^{-17}$
1405	0.6	$3 \cdot 10^{-17}$

b) Constant concentrations (stationary diffusion)

$$p \cdot dV/dt = -D \cdot k_H \cdot R \cdot T \cdot 4\pi r^2 \Delta p/\delta, \quad (5)$$

$$r \cdot dr/dt = -D \cdot k_H \cdot R \cdot T \cdot \Delta p/(p \cdot \delta).$$

As an example equation (5) can be solved for the case of a pure bubble ($p_{\text{bubble}} = 1$ bar) dissolving in a strongly undersaturated melt ($p_{\text{equilibrium}} = 0$ bar). Assuming the boundary layer thickness to be equal to the bubble radius (Sherwood number = 2), the dissolution time becomes:

$$t_{\text{diss}} = r_0^2/(2 \cdot D \cdot k_H \cdot R \cdot T). \quad (6)$$

3. Experimental

Most literature sources use the diffusion coefficient and the solubility of the most important gases dissolved in glass to describe the gas exchange process. From the theory presented here, it can be concluded that the permeability and the equilibrium pressure suffice to give a full description. The effect of solubility and diffusivity is combined in the permeability. The advantage of such an

Table 2. CO₂ permeabilities at 1305 °C in comparison with literature values

reference	D in m ² /s	k_H in mol/(m ³ Pa)	$D \cdot k_H$ in mol/(m s Pa)
this work	=	=	$2 \cdot 10^{-17}$
Ramos [1]	$5 \cdot 10^{-11}$	$4.3 \cdot 10^{-5}$	$2.2 \cdot 10^{-15}$
Krämer [2]	$4.7 \cdot 10^{-11}$	$1.9 \cdot 10^{-6}$	$9 \cdot 10^{-17}$
Němec [3]	$2.7 \cdot 10^{-13}$	$4.3 \cdot 10^{-5}$	$1.2 \cdot 10^{-17}$

approach is that it is no longer necessary to extract all the gas from the glass in order to measure the solubility. This also evades fundamental problems like the definition of "chemically dissolved oxygen".

For the evaluation of the permeability and equilibrium pressures of CO₂, nitrogen, oxygen and argon in colour television screenglass, a method was used in which very well-defined bubbles, so-called „tracer bubbles“, were introduced into the glass to be investigated. The bubbles measured 100 to 200 μm in diameter and contained less than 0.5 vol% impurities. The glass was then subjected to a specific heat treatment, quenched and annealed, and the bubbles were analyzed. By filling the bubbles with an easily detectable, inert gas, like argon, they could be discriminated from the air and CO₂ bubbles that might have formed in the experiments.

Figure 1 shows the result of such a „tracer bubble experiments“ studying the CO₂ exchange between bubbles and glass in 100 % argon bubbles in television screenglass at various temperatures. The slope of the lines gives information about the diffusion rate of CO₂. From these results, and from the results of 6 h gas exchange experiments performed to determine the equilibrium pressure of CO₂, the permeabilities given in table 1 can be fitted. Using these data for the investigated glass between 1300 and 1400 °C, the error in predicted CO₂ content is about 25 % (relative).

4. Comparison with literature values

Table 2 summarizes the results of tracer bubble experiments in comparison with some literature values for the permeability of CO₂ in silicate glasses. It shows that there is very little agreement about the permeability of CO₂ in silicate glass. The fact that most literature data are based on separate measurements of the solubility and diffusivity, both very difficult measurements from an experimental view, might be one of the causes of the disagreement. Tracer bubble experiments, like the ones presented here, may help to resolve the uncertainties in solubility and diffusivity of gases in glass.

5. List of symbols

D	diffusion coefficient in m ² /s
J	mole flux in mol/(m ² s)
k_H	Henry coefficient in mol/(m ³ Pa)
p	partial pressure in Pa
Δp	difference in equilibrium partial pressure bubble/glass in Pa
R	gas constant in J/(mol K)
r	bubble radius in m
T	temperature in K
t	time in s
V	volume in m ³
x	distance in m
δ	boundary layer thickness in m

6. References

- [1] Ramos, J. I.: Behavior of multicomponent gas bubbles in glass melts. *J. Am. Ceram. Soc.* **69** (1986) no. 2, p. 149–154.
- [2] Krämer, F.: Bubble defect diagnosis by means of a mathematical model. in: XIV International Congress on Glass, New Delhi (India) 1986. Coll. pap. Vol. 2. Calcutta: Ind. Ceram. Soc. 1986. p. 288–295.
- [3] Němec, L.; Mühlbauer, M.: Verhalten von Gasblasen in der Glasschmelze bei konstanter Temperatur. *Glastech. Ber.* **54** (1981) no. 4, p. 99–108.

■ 0294R003