DETERMINATION OF DIFFUSION COEFFICIENTS OF GASES IN GLASS MELTS USING THE METHOD OF ABSORBED GAS VOLUME

LUBOMÍR NĚMEC, JAROSLAV KLOUŽEK*

Laboratory of Glass and Ceramic Materials of ASCR and ICT,
**Department of Glass and Ceramic,*
Institute of Chemical Technology, Technická 5, 166 28 Prague

Received 2. 12. 1994

The values of diffusion coefficients of gases in glass melt represent a significant quantity when studying refining process and kinetics of gas dissolving in glass melt. As the determination of gas concentration profiles in glass is very difficult owing to the extremely low solubility of most gases in glass, the method following the rate of absorption of given gas volume in glass melt using the high temperature visual method has been developed. Special mesuring vessels from silica glass were applied to this purpose making it possible to follow the movement of phase boundary between measured gas and glass melt. The analysis of gas content of the measuring vessel after the experiment has been ensured. The equations were stated describing the absorption of pure gases as well as gas mixture into melt. Using the method, the temperature dependences of D_{O_2} *and* D_{H_2O} *have been obtained for soda-lime-silica glass in the temperature range 1200-1480 °C.*

INTRODUCTION

Diffusion coefficients of gases in glass melts play their important role when describing quantitatively the behaviour of gas phase during glassmelting process as is refining, foaming or bubble nucleation and growth. The progress in the mathematical modelling of glass melting process increased the need of mentioned quantity not only for research but also for industrial purposes. The contemporary methods are mostly using the determination of gas concentrations and concentration profiles of gases in glas melts after exposing the melt to the atmosphere of given gas [1-3]. The measurement of concentration gradients of physically soluble gases is, however, extremely difficult owing to their very low solubility being in the range of hundredths to thousandths percent. The visual methods following the kinetics of dissolution of gas phase in glass melts therefore spread over especially, thanks to preparation of artificial gas bubbles in glass [4]. The method of static gas bubbles has, however, its problem in comparatively laborious procedure and in arising new foreign bubbles at higher temperatures. The methods using the measurement of the size of freely rising artificial bubbles have their limitation for slowly diffusing gases and high measuring temperatures as the bubble residence time in the melt is too short to record any change of bubble size. The new method has been therefore proposed by authors consisting in visual recording the absorbed volume of measured gas being closed in a small cylindrical measuring vessel. The aim of this paper is the description of this method, the measurement of diffusion coefficients of water vapour (quickly diffusing gas) and physically soluble oxygen (slowly diffusing gas) in soda-lime-silica glass as well as discussion of method applicability.

METHOD DESCRIPTION AND THEORETICAL RELATIONS

The principle of proposed method is obvious from Figure 1. The measured gas is introduced by the Pt tube into the closed cylindrical silica glass vessel being suspended just above the glass level in the silica glass pot with glass. The cylindrical vessel with the measured gas is finally immersed into the glass melt. The gas absorption by the glass melt is indicated by the rising the glass level inside of the cylindrical vessel. The movement of the glass level is recorded by videocamera through the special opening in the furnace wall. The image analyzer or manual reading from the screen may be used for the evaluation of a measurement.

In Figure 2, there is detail of the glass level in the measuring cylindrical vessel. At given diameter of this vessel being less than 10 mm, the shape of glass level may be considered as spherical, thus being characterized by the radius of curvature r_a. The diffusion surface A between the glass and gas is given by:

$$A = 2\pi r_a^2 (1 - \sin\alpha) \qquad (1)$$

where α is the contact angle between glass and silica glass vessel. Using the solution of the second Fick's law

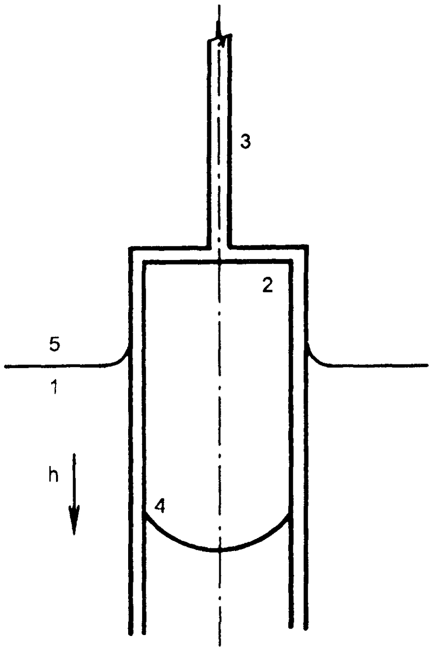


Figure 1. The scheme of the experimental arrangement
1 - the special silica glass pot with measured glass, *2* - the cylindrical closed silical glass vessel with measured gas, *3* - the holder of the cylindrical vessel, *4* - the moving phase boundary between glass and gas, *5* - the glass level in the silica glass vessel

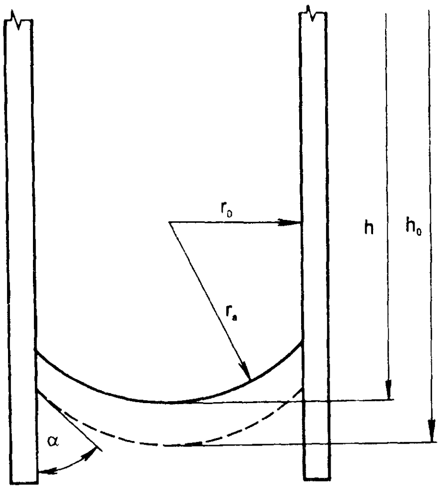


Figure 2. The detail of the glass level in the cylindrical measuring glass vessel
r_0 - radius of the cylindrical vessel, r_a - radius of the interface gas-glass melt, h_0 - initial vertical coordinate, h - vertical coordinate, α - contact angle

in spherical coordinates [5], following equation is valid for the mass balance at the phase boundary:

$$\frac{dh}{dt} = - \frac{DRT}{pM} \frac{2r_a^2}{r_0^2} (1 - \sin\alpha)(c_i - c_b) \left[\frac{1}{r_a} + \left(\frac{1}{\pi D t} \right)^{1/2} \right] \tag{2}$$

with initial conditions $t = 0$, $h = h_0$. Here h is the vertical coordinate of the shifting phase boundary, D is the diffusion coefficient of the measured gas, R is the gas constant, r_0 is the radius of the cylindrical vessel, T is temperature, p is pressure, M is molecular mass of the measured gas, c_i is interface concentration of the gas in glass melt and c_b is its bulk concentration in the melt. The solutation of Equation (2) is:

$$h - h_0 = - \frac{DRT}{pM} \frac{2r_a^2}{r_0^2} (1 - \sin\alpha)(c_i - c_b) \left[\frac{t}{r_a} + 2 \left(\frac{t}{\pi D} \right)^{1/2} \right] \tag{3}$$

where h_0 is the initial vertical coordinate of the phase boundary. The simple calculation procedure has been prepared to evaluate D from Equation (3).

EXPERIMENTAL PART

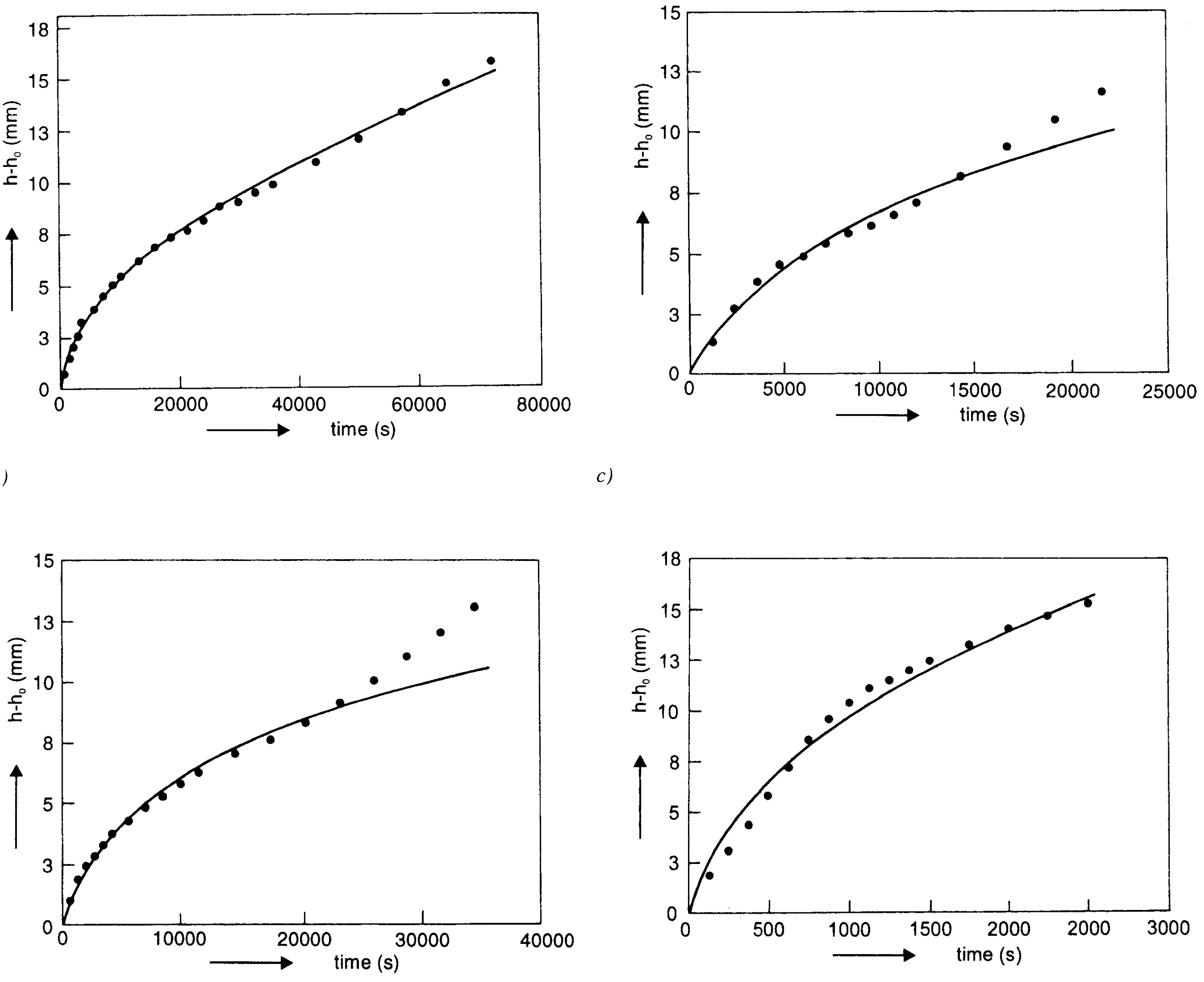
The glass used in this study was soda-lime-silica glass (74.2 SiO_2, 16.2 Na_2O, 9.6 CaO, wt.%) prepared by melting analytically pure raw materials for 10 hours at 1350 °C, without any refining agent. The iron content was up to 0.005 wt.% Fe_2O_3. The glass composition was determined by AAS after the sample decomposition with the mixture HF and H_2SO_4.

For the evaluation of D_{H_2O}, the experiments at 1200, 1300, 1400 and 1480 °C, respectively, have been performed. The concentration of hydroxyl groups in the soda-lime-silica glass has been measured using IR spectroscopy at absorption band 2.8 µm. The values of the water vapour solubilities in the glass at $p_{H_2O} = 100$ kPa were taken from [6]. The glass used for the experiment with oxygen has been evacuated to about 1 kPa for 2 hours at 1400 °C in order to decrease the level of dissolved oxygen. The glass after evacuation contained 75.6 % of SiO_2, 9.9 % CaO and 14.5 % Na_2O (wt.). The diffusion experiments have been performed at 1200, 1300 and 1400 °C, respectively. The initial oxygen concentration in glass has been measured using gas chromatografic method [7]. After saturation of glass by oxygen at $p_{O_2} = 100$ kPa and different temperatures, the values of oxygen saturation concentrations have been evaluated using the mentioned gas chromatographic method. The initial (bulk) and saturation concentrations of both gases are presented in Table I. In Figures 3a - d, there are results of experiments for water vapour diffusion in glass in form of dependence between glass level

Table I. The initial and saturation concentrations of water vapour and oxygen in soda-lime-silica glass (74 SiO_2, 16 Na_2O, 10 CaO, wt. %).

Gas	Temperature (°C)	Saturation Gas Conc. at 100 kPa (kg m^{-3})	Initial (Bulk) Conc. (kg m^{-3})*
Water Vapour	1200	2.10	0.67
	1300	2.24	1.21
	1400	2.34	1.93
	1480	2.42	0.67
Oxygen	1200	5.5×10^{-2}	0
	1300	6.2×10^{-2}	0
	1400	8.4×10^{-2}	0

* after 30 min by water vapour before the dıffusion experiment



a) c)

b) d)

Figure 3. The dependence between the glass level shifting, $h - h_0$, and time for the water vapour diffusion in glass ——— theoretical solution of Equation (3) using the average value of D_{H_2O}, • - experimental points, a) 1200 °C, b) 1300 °C, c) 1400 °C, d) 1480 °C

Table II. The values of the diffusion coeficients of water vapour in the soda-lime-silica glass calculated from Equation (3)

1200 °C		1300 °C		1400 °C		1480 °C	
t(s)	D(m^2 s^{-1})	t(s)	D(m^2 s^{-2})	t(s)	D(m^2 s^{-1})	τ(s)	D(m^2 s^{-1})
720	3.1541×10^{-12}	720	9.5331×10^{-12}	1200	5.5470×10^{-11}	125	5.1795×10^{-11}
1440	6.2759×10^{-12}	1440	1.5702×10^{-11}	2400	9.7398×10^{-11}	250	6.7294×10^{-11}
2160	7.1930×10^{-12}	2160	1.7021×10^{-11}	3600	1.1734×10^{-10}	375	8.7601×10^{-11}
2880	9.1184×10^{-12}	2880	1.7371×10^{-11}	4800	1.1903×10^{-10}	500	1.1262×10^{-10}
3600	1.0557×10^{-11}	3600	1.8305×10^{-11}	6000	1.0890×10^{-10}	625	1.3666×10^{-10}
4320	1.1154×10^{-11}	4320	1.8901×10^{-11}	7200	1.0752×10^{-10}	750	1.5467×10^{-10}
5760	9.6657×10^{-12}	5040	1.8655×10^{-11}	8400	1.0525×10^{-10}	875	1.6537×10^{-10}
6480	9.7800×10^{-12}	5760	1.8605×10^{-11}	9600	1.0181×10^{-10}	1000	1.6764×10^{-10}
7200	9.9759×10^{-12}	6480	1.8380×10^{-11}	10800	1.0154×10^{-10}	1125	1.6844×10^{-10}
8640	1.0129×10^{-11}	7200	1.8490×10^{-11}	12000	1.0345×10^{-10}	1250	1.6263×10^{-10}
10080	1.0130×10^{-11}	7920	1.8060×10^{-11}	14400	1.0758×10^{-10}	1375	1.5989×10^{-10}
11520	9.9908×10^{-12}	8640	1.7928×10^{-11}	16800	1.1634×10^{-10}	1500	1.5635×10^{-10}
12960	9.9053×10^{-12}	10080	1.8542×10^{-11}	19200	1.2158×10^{-10}	1750	1.5001×10^{-10}
14400	9.9091×10^{-12}	11520	1.8673×10^{-11}	21600	1.2911×10^{-10}	2000	1.4439×10^{-10}
15840	9.9538×10^{-12}	14400	1.8570×10^{-11}		$\boxed{\bar{D} = 1.07 \times 10^{-10} \pm 1.72 \times 10^{-11}}$	2250	1.4048×10^{-10}
17280	9.6471×10^{-12}	17280	1.7827×10^{-11}			2500	1.3679×10^{-10}
18720	9.5905×10^{-12}	20160	1.7953×10^{-11}				$\boxed{\bar{D} = 1.35 \times 10^{-10} \pm 3.64 \times 10^{-11}}$
20160	9.2200×10^{-12}	23040	1.8489×10^{-11}				
21600	8.9033×10^{-12}	25920	1.9512×10^{-11}				
24480	8.8257×10^{-12}	28800	2.0778×10^{-11}				
27360	9.0881×10^{-12}	31680	2.1777×10^{-11}				
30240	8.7064×10^{-12}	34560	$2.2965 \,.\, 10^{-11}$				
33120	8.6482×10^{-12}		$\boxed{\bar{D} = 1.83 \times 10^{-11} \pm 2.48 \times 10^{-12}}$				
36000	8.5118×10^{-12}						
43200	8.5438×10^{-12}						
50400	8.6590×10^{-12}						
57600	9.0874×10^{-12}						
64800	9.6412×10^{-12}						
72000	9.7615×10^{-12}						
	$\boxed{\bar{D} = 9.09 \times 10^{-12} \pm 1.49 \times 10^{-12}}$						

Table III. The values of the diffusion coefficients of oxygen in the soda-lime-silica glass calculated from Equation (3)

1185 °C		1290 °C		1400 °C	
t(s)	D(m^{2}s^{-1})	t(s)	D(m^{2}s^{-1})	t(s)	D(m^{2}s^{-1})
3200	1.9954×10^{-10}	2960	2.8140×10^{-10}	7200	3.2775×10^{-10}
7120	2.9272×10^{-10}	7200	2.9973×10^{-10}	9600	3.9228×10^{-10}
17160	2.2530×10^{-10}	12000	2.9320×10^{-10}	12000	4.5890×10^{-10}
26400	2.1639×10^{-10}	16800	2.9752×10^{-10}	14400	5.0842×10^{-10}
36000	1.8103×10^{-10}	24000	2.9613×10^{-10}	16800	5.2354×10^{-10}
45600	1.9730×10^{-10}	28800	3.4941×10^{-10}	19200	5.4298×10^{-10}
55200	2.2503×10^{-10}	33600	3.9383×10^{-10}	21600	5.4499×10^{-10}
64800	2.3391×10^{-10}	38400	3.8661×10^{-10}	24000	5.4803×10^{-10}
74400	2.3565×10^{-10}	43200	3.8710×10^{-10}	26400	5.3630×10^{-10}
101920	2.0343×10^{-10}	48000	3.9646×10^{-10}	28800	5.3956×10^{-10}
	$\boxed{\bar{D} = 2.21 \times 10^{-10} \pm 3.07 \times 10^{-11}}$	52800	4.1269×10^{-10}		$\boxed{\bar{D} = 4.92 \times 10^{-10} \pm 7.60 \times 10^{-11}}$
		59600	4.2671×10^{-10}		
			$\boxed{\bar{D} = 3.52 \times 10^{-10} \pm 5.45 \times 10^{-11}}$		

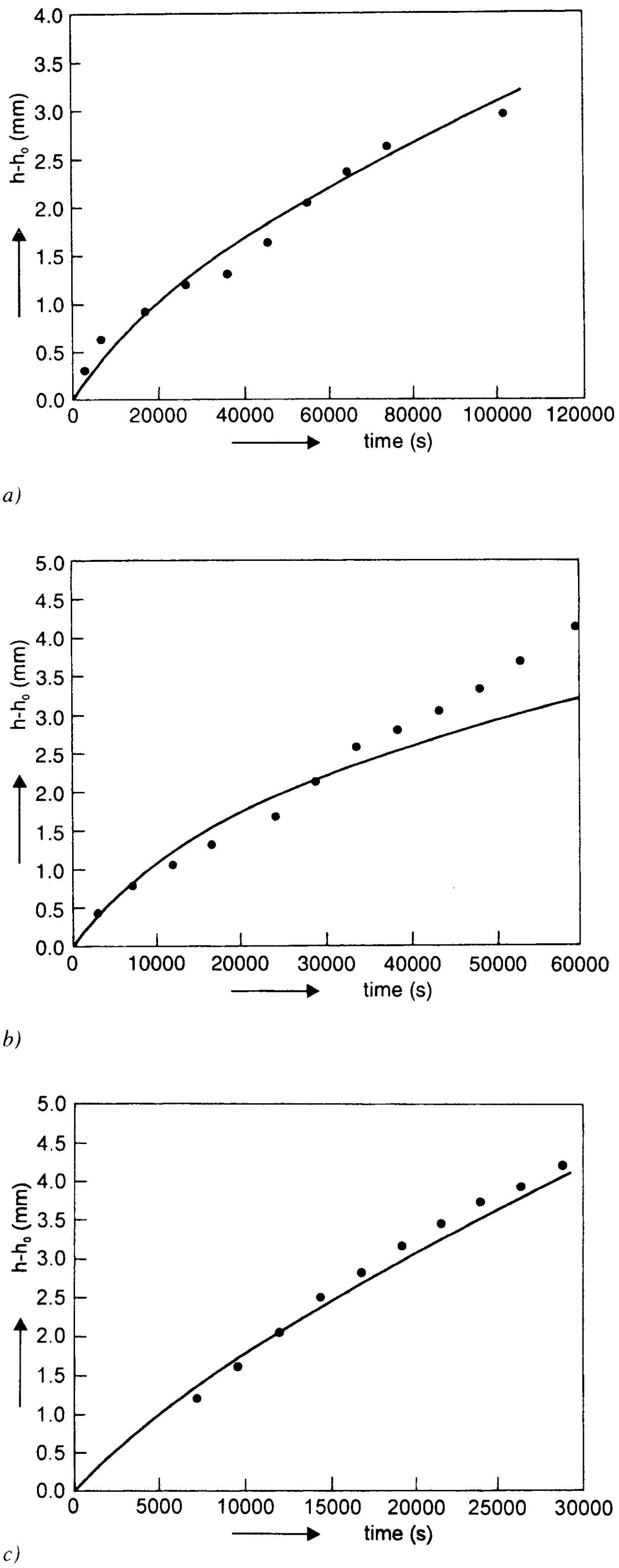


Figure 4. The dependence between the glass level shifting, h - h_0, and time for the oxygen diffusion in glass
—— theoretical solution of equation (3) using the average value of D_{O_2}, ● experimental points, *a)* 1185 °C, *b)* 1290 °C, *c)* 1400 °C

shifting, h - h_0, and time (see Equation (3)). The full line is indicating the solution of Equation (3) using the average value of diffusion coefficient. Table II presents the values of diffusion coefficient during the course of the experiment together with the average value as the result of the measurement. The appropriate values of oxygen diffusion are given in Figures 4a - c and Table III, respectively.

DISCUSSION OF RESULTS

The relatively good consistency between the theoretical solution and experimental results is demonstrated in Figures 3*a* - *d* and 4*a* - *c*. The agreement is better for water vapour where the bigger values of h - h_0 were more advantageous for the manual reading of the glass level. The deviations from Equation (3) may arise in the very early stages of the experiment when the curvature of glass level is still developing (see Figure 3*d*) and at very late stages and for relatively fast diffusion of gas into glass. In the latter case, the radial convection under glass curvature - being the concequence of the already developed glass velocity profile inside of diffusion vessel - is distorting the concentration gradient accelerating thus the penetration of gas in glass melt (see Figures 3*b* - *c*). Nevertheless, maximum standard deviation of single results being 26.9 % for water vapour at 1480 °C and the average value for all measurements being 16.8 % give evidence of good applicability of the method.

The temperature dependence of D_{H_2O} (m^2 s^{-1}) has the following form:

$$D_{H_2O} = 1.89 \times 10^{-3} \exp\left(- \frac{28500}{T} \right) \qquad (4)$$

and is plotted in Figure 5 as the relation between ln D_{H_2O} and $1/T$. The present values are compared with these ones obtained for the float glass using the method of artificial static bubble in the temperature interval 930 - 1180 °C [8]. As is obvious from this comparison, the values of diffusion coefficients obtained by the presented method are lower in the temperature interval between 1200 - 1300 °C and the exponential factor being - 28500 K is greater than this one presented in [8] and being - 18300 K. The differences in glass composition may probably bring about also differences in D_{H_2O}, however, the relatively great dispersion of the initial water vapour concentration in glass (see Table I) resulting probably in the low homogenity of glass as for water content, could unfavourably influence the results, especially at lower temperatures.

The temperature dependence of D_{O_2} (m^2 s^{-1}) having the form

$$D_{O_2} = 1.55 \times 10^{-7} \exp\left(- \frac{9550}{T} \right) \qquad (5)$$

is presented in Figure 6 together with the values of Doremus [4]. The agreement between both methods is good at higher temperatures, at lower ones however, the values of D_{O_2} obtained by the presented method are lower. In accordance with this fact, the value of the exponential factor being - 9550 K in this measurement is much lower than this one presented by Doremus and being - 26600 K.

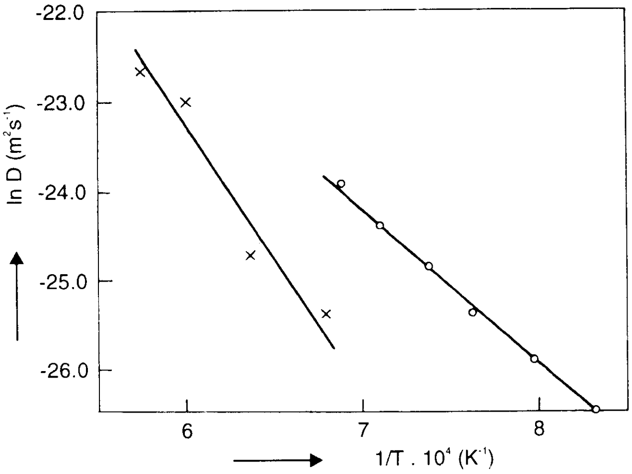


Figure 5. The temperature dependence of D_{H_2O} in the logaritmic form
o values for flat glass from [8], × this measurement

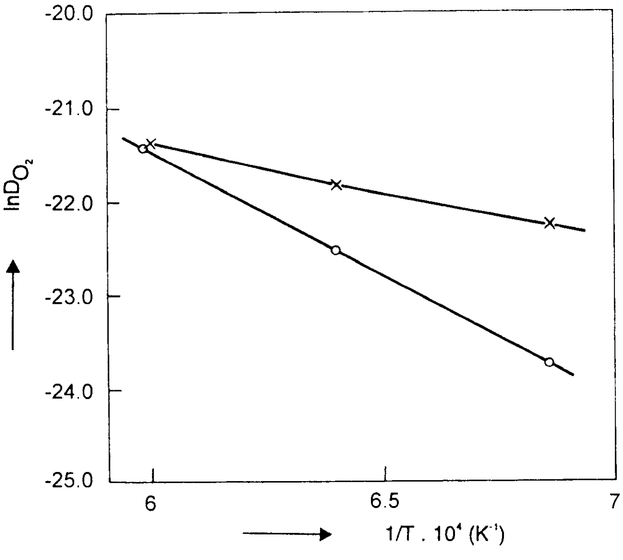


Figure 6. The temperature dependence of D_{O_2} in the logaritmic form
o Doremus' data, × this measurement

As the value of Doremus´ exponential factor is the more reasonable one, the courses of found discrepancy should be discussed. The first reason may be in the relatively low attainable accuracy when measuring the very low concentration differences of physically dissolved oxygen in glass. The second reason seems to be more important revealing probably the influence of chemically bound oxygen in glass melt being a consequence of the very low concentrations of iron in glass. In this case, the chemical reaction between Fe^{2+} and Fe^{3+} influences the diffusion of oxygen from diffusion vessel into glass [9]:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} + P(t) \qquad (6)$$

where $P(t)$ is the source of oxygen by the chemical reaction in equilibrium. To remove the problem, the concentration of iron in glass must be more lowered or the influence of appropriate chemical reaction must be considered in the diffusion equation. The second solution seems to be more exact one, however, the equilibrium data of the appropriate oxidation - reduction pair are required.

CONCLUSION

The described and discussed method shows a good aplicability for different gases over the whole temperature interval of glass melting. The gas mixtures may be applicated too providing appropriate theoretical description is used. The results show that there is a good coincidence with theoretical equation except for fast diffusing gases in later stages of experiment. The average standard deviation of results being ± 16.8 % confirms the already mentioned facts. The accuracy of measurement for slowly diffusing gases may be increased using image analyser instead of manual reading from the screen. The precission of the diffusion measurement is especially influenced by the initial concentrations of gases in glass, which should be very low and by the values of saturation concentrations of mentioned gases. The glass degasing before experiment joint with cautious homogenization of glass after saturation experiments is necessary. If the concentration of oxidation - reduction pairs is not negligible with respect to the physical solubility of oxygen, the influence of the appropriate chemical relation must be taken into account. The analysis of gas content of the diffusion vessel after experiment is desirable to control the respective influence of another gas. In these experiments, no influence of foreign gas has been found.

Acknowledgement

This work was supported by Czech Grant Agency for Science (Grant No 106/93/1289)

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Submitted in English by the authors

STANOVENÍ DIFÚZNÍCH KOEFICIENTŮ PLYNŮ VE SKLOVINÁCH METODOU ABSORBOVANÉHO OBJEMU

LUBOMÍR NĚMEC, JAROSLAV KLOUŽEK*

Laboratoř skelných a keramických materiálů,
**Ústav skla a keramiky,*
Vysoká škola chemicko-technologická,
Technická 5, 166 28 Praha 6

Znalost hodnot difúzních koeficientů je důležitým faktorem při studiu čeřícího procesu a kinetiky rozpouštění plynů ve sklovinách. Dříve používané metody stanovení byly založeny na sledování rychlosti růstu bublin čistých plynů. Přesnost těchto metod však byla omezena na poměrně krátkou dobu setrvání bubliny ve sklovině. Proto byla vyvinuta metoda stanovení difúzních koeficientů plynů ve sklovinách využívající absorpce objemu plynu umístěného ve shora uzavřené nádobce z křemenného skla. Difúzní koeficient je řešením integrovaného tvaru diferenciální rovnice popisující pohyb fázového rozhraní plyn-sklovina. Rychlost posuvu rozhraní je měřena přímým odečtem z obrazovky monitoru nebo s použitím analyzátoru obrazu. Metodu je možné využít i pro sledování rychlosti rozpouštění směsi plynů. Článek uvádí stanovené teplotní závislosti difúzních koeficientů kyslíku a vodní páry v sodnovápenatokřemičité sklovině pro teplotní rozmezí 1200 - 1480 °C.