# CHEMICAL REACTIONS TAKING PLACE DURING VAPORIZATION FROM SILICATE MELTS

JOSEF MATOUŠEK

*Department of Glass and Ceramics, Institute of Chemical Technology,*
*Technická 5, 166 28 Prague*

## INTRODUCTION

Vaporization of volatile components of silicate melts belongs among those high-temperature processes which significantly affect economy, ecology and technology of most industrially produced glasses. The older and the more recent professional literature contains a number of studies dealing with this issue [e.g. 1 - 5]. The gradually established experimental data allowed the basic concepts of the kinetics of vaporization from silicate melts to be formulated and subsequently the respective physico-chemical models of the processes, permitting their mathematical description, to be developed [3 -5]. At the same time, studies of thermodynamic equilibria during high-temperature vaporization and the first data on steady-state vapour pressures above silicate melts were published [6 - 7]. The findings were recently summarized in monograph [8]. The most recent works on the subject of vaporization are concerned with modelling the process in glass-making furnaces for the purpose of determining its course under the conditions corresponding to those of actual commercial glass-making processes [9 - 10].

Studies of vaporization soon revealed the influence of chemical reactions associated with the process. Apart from dissociative reactions of the volatile components there are also reactions between components of the melt and the reactive components of the gaseous phase above the melt. The latter reactions modify the thermodynamic equilibrium at the phase boundary, may interfere with the vaporization mechanism and thus affect significantly the kinetics of the process. This type of vaporization was given the name of reactive vaporization and is directly associated with high-temperature vaporization in glass furnaces.

The present contribution presents a description of reactions taking place during vaporization of the basic types of silicate and borosilicate glass melts. The most frequent volatile components of these melts are alkali oxides, lead oxide and boric oxide. Also other oxides come into consideration, such as $As_2O_3$, $Sb_2O_3$, ZnO, as well as other compounds (fluorides, sulphates, chlorides, ...), but their vaporization is significant only in the melting of special glasses.

## VAPORIZATION OF MELTS IN VACUO AND IN INERT ATMOSPHERE

The chemism of vaporization in vacuo can be studied by identifying the gaseous phase components following their vaporization from a glass melt sample placed in Knudsen's cell. High-temperature mass spectrometer can be used for identifying the steady-state composition of the vapours [8]. The composition of the gaseous phase above some melts is indicated by table 1.

Table 1. Equilibrium composition of vapours above model melts

| melt type | temperature (K) | composition of gaseous phase |
|---|---|---|
| $Na_2O.x\,SiO_2$ ($x = 1 - 4$) | 1163 - 1500 | Na, $O_2$ |
| $Na_2O - B_2O_3$ | 1248 | $NaBO_2$, $(NaBO_2)_2$ |
| $SiO_2 - B_2O_3$ | 1390 - 1590 | $B_2O_3$ |
| $Na_2O - CaO - SiO_2$ | 1240 - 1670 | Na, $O_2$ |
| $Na_2O - B_2O_3 - SiO_2$ | 1100 | Na, $NaBO_2$, $(NaBO_2)_2$ |
| $Na_2O - K_2O - CaO - SiO_2$ | 1240 - 1670 | Na, K, $O_2$ |
| $PbO - SiO_2$ | 1773 | PbO, $(PbO)_2$ |

The respective data show that at temperatures of up to about 1500 °C alkali oxides and lead oxide are virtually the sole volatile components of the silicate melts. Boric oxide and lead oxide vaporize from borate melts at these temperatures. No vaporization of $SiO_2$ at the temperatures involved was observed. Alkali oxides vaporize while dissociating according to the reaction

$$Na_2O\ (l) \longrightarrow 2\ Na\ (g) + 1/2\ O_2\ (g)$$
$$K_{1400\ °C} = 9.5 \times 10^{-5} \qquad (1)$$

$$K_2O\ (l) \longrightarrow 2\ K\ (g) + 1/2\ O_2\ (g) \qquad (2)$$
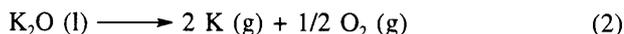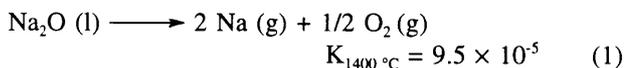
Lead oxide volatilizes in molecular form without decomposition, most frequently as monomer or dimer.

The values of equilibrium constants for reactions describing vaporization of various molecular forms of PbO do not show any major differences, as illustrated by table 2. Prevalence of this or that form depends on temperature. The representation of higher molecular forms increases with increasing temperature.

Table 2. Equilibrium constants of reactions involved in vaporization of lead oxide

| reaction | $K_{1400 \,°C}$ |
|---|---|
| PbO (l) ——► PbO (g) | $9.4 \times 10^{-2}$ |
| PbO (l) ——► 1/2 (PbO)$_2$ (g) | $3.0 \times 10^{-1}$ |
| PbO (l) ——► 1/3 (PbO)$_3$ (g) | $2.6 \times 10^{-1}$ |
| PbO (l) ——► 1/4 (PbO)$_4$ (g) | $3.4 \times 10^{-1}$ |

Volatile boric compounds vaporize congruently according to the reactions

$$B_2O_3 \text{ (l)} \longrightarrow B_2O_3 \text{ (g)} \qquad K_{1400\,°C} = 5.6 \times 10^{-4} \quad (3)$$

$$NaBO_2 \text{ (l)} \longrightarrow NaBO_2 \text{ (g)} \quad K_{1400\,°C} = 5.7 \times 10^{-2} \quad (4)$$
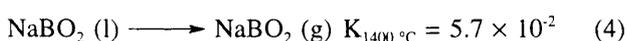
Also other components of melts become volatile at higher temperatures, including silicon dioxide, as shown by table 3.

Table 3. Equilibrium composition of vapours above model alkali-free melts

| melt type | temperature (K) | composition of gaseous phase |
|---|---|---|
| CaO - SiO$_2$ | 1933 - 2133 | Ca, CaO, SiO, SiO$_2$, O, CaSiO$_3$ |
| MgO - SiO$_2$ | 1873 - 1973 | Mg, O, Si |
| CaO - Al$_2$O$_3$ | 2060 | Ca, Al, O, Al$_2$O$_3$, AlO |
| CaO - Al$_2$O$_3$- SiO$_2$ | 1833 - 2033 | Ca, CaO, SiO, SiO$_2$, O, CaSiO$_3$ |
| CaO - MgO - Al$_2$O$_3$ | 1960 | Ca, Mg, O |

Also oxides usually regarded as stable volatilize at temperatures higher than about 1600 °C. Their vaporization mostly involves decomposition to the metal and oxygen, and in some instances also formation of less usual molecules in which the metal occurs in a lower oxidation valency. Apart from data on vaporization of two- and three-component melts, the literature also presents data on volatilization from multicomponent melts whose composition corresponds to commercially produced glasses [8]. This applies in particular to the following three types of glass:

Type I – glasses derived from the system Me$_2$O-CaO-SiO$_2$, among which belong sheet and container glasses. For example, during vaporization from a melt

having the composition 71.39 SiO$_2$, 12.75 Na$_2$O, 10.75 CaO, 2.78 Al$_2$O$_3$ and 2.02 K$_2$O (wt.%) over the temperature range of 1300 - 1800 K, elements Na, K and O$_2$ were identified in the gaseous phase. Vaporization of these melts thus involves the dissociative reactions observed with analogous binary and ternary melts.

Type II – glasses derived from the system Me$_2$O-B$_2$O$_3$-SiO$_2$, such as the Simax glass used widely in our laboratories. During vaporization of a melt having the composition 79.6 SiO$_2$, 12.1 B$_2$O$_3$, 1.0 Al$_2$O$_3$, 3.7 Na$_2$O and 1.7 K$_2$O (wt.%) over the temperature range of 1070 - 1473 K, sodium and potassium metaborate were identified in the gaseous phase, and in the case of melts with an elevated B$_2$O$_3$ content (above 30 wt.%), also dimers of these metaborates jointly with sodium-potassium metaborate NaK(BO$_2$)$_2$. The relative content of dimers grows with increasing vaporization temperature. The vaporization proceeds probably according to the following reaction schemes:

$$NaBO_2 \text{ (l)} \longrightarrow NaBO_2 \text{ (g)} \quad (5)$$

$$Na_2O \text{ (l)} + B_2O_3 \text{ (l)} \longrightarrow 2NaBO_2 \text{ (g)} \quad (6)$$

$$Na_2O \text{ (l)} + K_2O \text{ (l)} + 2B_2O_3 \text{ (l)} \longrightarrow 2NaK(BO_2) \text{ (g)} \quad (7)$$
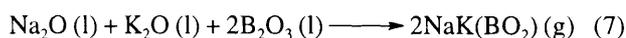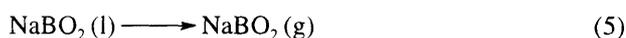
Type III – glasses derived from the system Me$_2$O-PbO-SiO$_2$, representing mainly lead crystal glasses. It was found that from a glass melt of the composition 59.9 SiO$_2$, 11.4 K$_2$O, 2.6 Na$_2$O, 0.6 CaO and 0.2 Al$_2$O$_3$ (wt.%) at 1187 - 1315 K, there vaporize Na, K, PbO and Pb$_2$O$_2$. The vaporization therefore involves the reaction PbO (l) $\rightarrow$ (PbO)$_n$ (g). The dissociative reactions yielding vapours of sodium and potassium and gaseous oxygen proceed at the same time.

The data on vaporization of commercial glasses in vacuo indicate that over the temperature range studied, no vaporization of silicon dioxide occurs, in spite of the fact that the compound SiO and oxygen was identified in the gaseous phase over a silica glass melt at temperatures of 1373 - 1673 K [8].

## REACTIVE VAPORIZATION OF MULTICOMPONENT MELTS

The chemism of vaporization of multicomponent melts may vary when the vaporization takes place in an atmosphere containing reactive components. This so-called reactive vaporization is that occurring most frequently in practice as the glass furnace atmosphere contains a number of compounds (H$_2$O, CO$_2$, SO$_x$, NO$_x$) which may react with some components of the melt [1, 11, 12].

## Vaporization in an atmosphere containing water vapour

Water vapour affects significantly vaporization of volatile components of commercial glasses. The alkali oxides present in these melts react with water vapour according to the scheme

$$Na_2O \text{ (l)} + H_2O \text{ (g)} \longrightarrow 2NaOH \text{ (g)}$$
$$K_{1400\,°C} = 3.7 \qquad (8)$$

$$K_2O \text{ (l)} + H_2O \text{ (g)} \longrightarrow 2KOH \text{ (g)}$$
$$K_{1400\,°C} = 4.5 \times 10^3 \qquad (9)$$
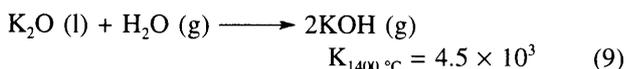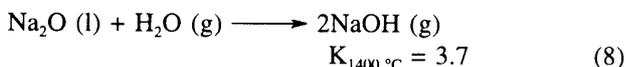
The equilibrium of these reactions is distinctly shifted in favour of alkali hydroxides. Monomers of their molecules were identified in the gaseous phase, but vaporization of pure hydroxides yields a monomer-dimer mixture at temperatures above about 600 °C. The relative proportion of dimer increases with increasing temperature. The steady-state vapour pressure above pure hydroxides is high even at relatively low temperatures, being equal to atmospheric pressure at the temperatures of glass melting (during vaporization of KOH the vapour pressure is 101.325 kPa at 1327 °C, and during vaporization of NaOH the same vapour pressure is attained at 1378 °C) [13]. From the point of view of thermodynamics, the vaporization of alkali hydroxides is substantially facilitated in comparison with that in an inert atmosphere. In view of the relatively ready diffusion of water vapour into the glass melt and of the relatively rapid diffusion of alkali ions in the glass melt, the glass melt offers no serious kinetic obstacles to this assumed rapid vaporization. These findings and considerations indicate that reactive vaporization due to water vapour is far faster than that associated with dissociation of sodium oxide. This conclusion is borne out by the time dependence of losses by weight due to vaporization of the $Na_2O.2SiO_2$ melt [14]. Figure 1 also shows that the vaporization rate increases with increasing partial pressure of water vapour in the inert carrier gas (nitrogen). A similar behaviour during vaporization in an atmosphere containing water vapour is shown by multicomponent commercial glass melts containing alkali oxides. This is demonstrated e.g. by data on vaporization of melted float glass in a moist air atmosphere (figure 2) and in nitrogen atmosphere (figure 3) [15].

Water vapour likewise influences to a significant degree vaporization of glass melts containing boric oxide. Molten boric oxide reacts with water vapour according to the following equations:

$$B_2O_3 \text{ (l)} + H_2O \text{ (g)} \longrightarrow 2HBO_2 \text{ (g)}$$
$$K_{1400\,°C} = 1.3 \times 10^{-2} \qquad (10)$$

$$B_2O_3 \text{ (l)} + 3H_2O \text{ (g)} \longrightarrow 2H_3BO_3 \text{ (g)}$$
$$K_{1400\,°C} = 1.2 \times 10^{-4} \qquad (11)$$
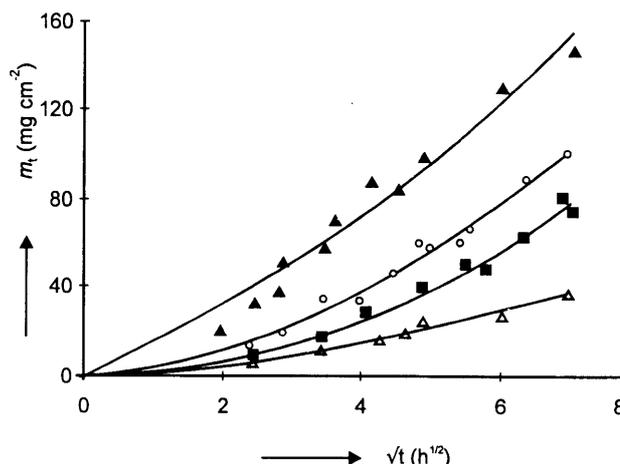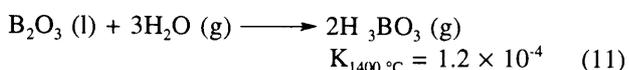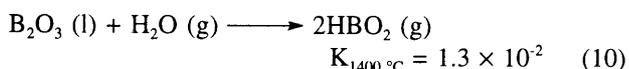


Figure 1. Vaporization loss from $Na_2O.2SiO_2$ melt at 1300 °C vs. second root of time in nitrogen - water vapour mixture.
$\triangle$ - $p_{H2O}$ = 0 kPa, $\blacksquare$ - $p_{H2O}$ = 12 kPa, $O$ - $p_{H2O}$ = 31 kPa, $\blacktriangle$ - $p_{H2O}$ = 69 kPa
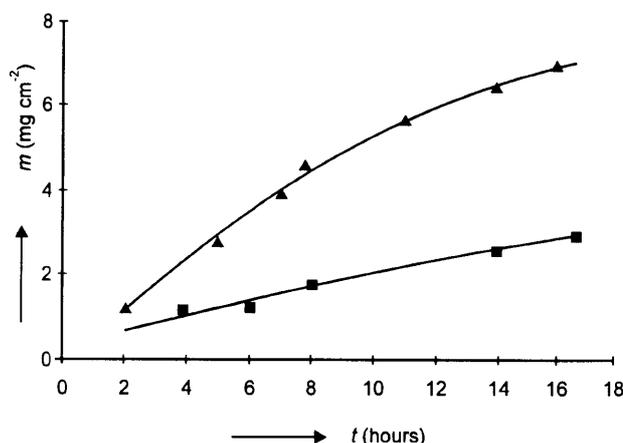


Figure 2. Vaporization loss from float glass melt at 1450 °C vs. time in air atmosphere and in an air-water vapour mixture.
$\blacksquare$ - $p_{H2O}$ = 0 kPa, $\blacktriangle$ - $p_{H2O}$ = 29 kPa
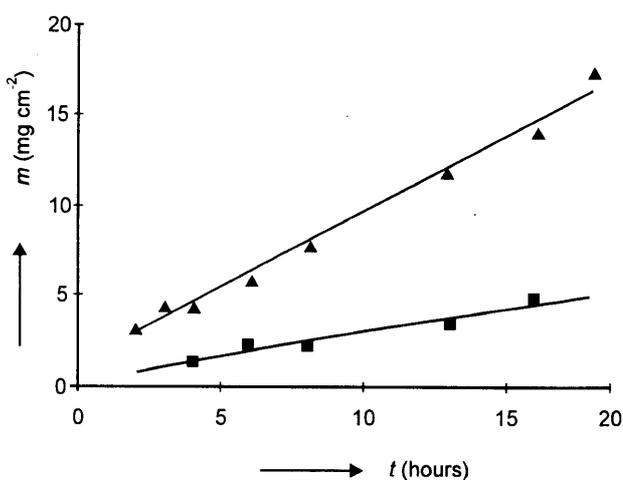


Figure 3. Vaporization loss from float glass melt at 1450 °C vs. time in an atmosphere of nitrogen and in a mixture of nitrogen and water vapour.
$\blacksquare$ - $p_{H2O}$ = 0 kPa, $\blacktriangle$ - $p_{H2O}$ = 29 kPa

The values of equilibrium constants and those of other data from the literature [8, 11] allow to assume that metaboric acid in gaseous form is formed preferentially at higher temperatures. This may also be why on vaporization of boric and borosilicate melts the losses in weight are lower in an atmosphere containing water vapour than on vaporization in a non-reactive atmosphere. Figure 4 demonstrates the effect of water vapour on vaporization of the Simax glass melt. For the sake of completeness it should be pointed out that the effect of water vapour on vaporization of borate melts depends on the composition of the melt, in particular on the content ratio $Na_2O/B_2O_3$. Vaporization of melts richer in sodium oxide is not very sensitive to water vapour content. This is probably due to the preferential vaporization in the form of metaborates and/or in the form of NaOH molecules. On the other hand, water vapour affects strongly vaporization of melts with a higher content of $B_2O_3$ (starting from the ratio $Na_2O/B_2O_3 = 1:4$) [16, 17]. With such melts there dominates vaporization of boric acid in the form of $HBO_2$ molecules.
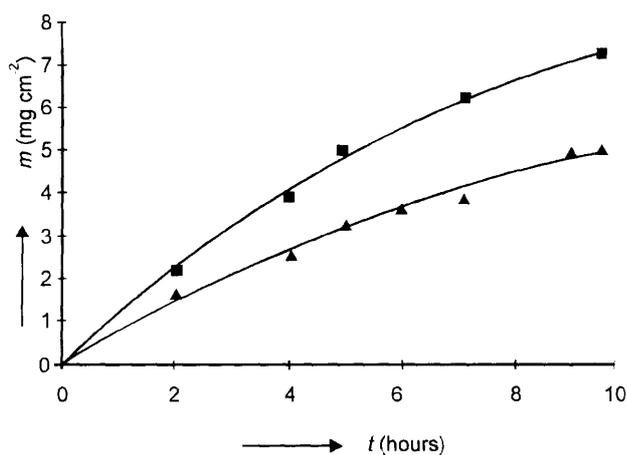


Figure 4. Vaporization loss from Simax glass melt vs. time in carbon dioxide atmosphere, and in a $CO_2$ - water vapour mixture at 1400 °C.
■ - $p_{H2O} = 0$ kPa, ▲ - $p_{H2O} = 29$ kPa

Vaporization of melts containing lead oxide is likewise sensitive to water vapour content [1, 18]. In that instance the effect of water vapour can be attributed to the reaction

$$PbO \text{ (l)} + H_2O \text{ (g)} \longrightarrow Pb(OH)_2 \text{ (g)}$$
$$K_{1400 °C} = 4.7 \times 10^{-1} \quad (12)$$
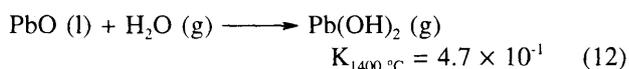
the equilibrium constant of which indicates a somewhat more extensive vaporization of PbO in moist atmosphere than in an inert one. This assumption is borne out by the

experimental data plotted in figure 5 which shows the effect of water vapour on vaporization of commercial glass melt of type III while using various carrier gases. The effect of water vapour at its higher partial pressure becomes dominant regardless of the carrier gas type. With type III melt one can of course expect that water vapour will also contribute to faster vaporization of alkali oxides in the form of hydroxides. In order to distinguish the two effects, i.e. vaporization of PbO in the form of hydroxide and that of alkali oxides in the form of hydroxides, the effect of water vapour was also studied on the $PbO.SiO_2$ binary melt. Vaporization speeded up by the effect of water vapour was established even in this instance so that the accelerating effect of water vapour on vaporization of PbO was thus borne out [18].
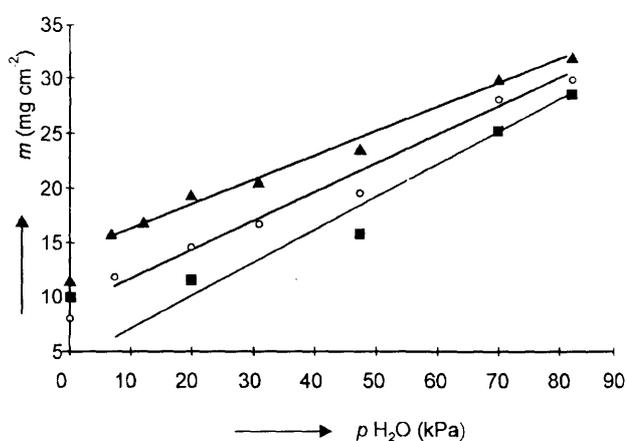


Figure 5. Vaporization loss from lead glass melt (24 wt.% PbO) in an atmosphere of air, nitrogen and carbon dioxide at 1140 °C vs. partial pressure of water vapour.
■ - $N_2 + H_2O$, ○ - $CO_2 + H_2O$, ▲ - air + $H_2O$

At higher temperatures (above 1200 °C) water vapour reacts with silica glass [19], possibly yielding volatile silicate compounds by the reactions

$$SiO_2 \text{ (s)} + H_2O \text{ (g)} \longrightarrow SiO(OH)_2 \text{ (g)} \quad (13)$$

$$SiO_2 \text{ (s)} + 2H_2O \text{ (g)} \longrightarrow SiO(OH)_4 \text{ (g)} \quad (14)$$

$$2SiO_2 \text{ (s)} + 3H_2O \text{ (g)} \longrightarrow Si_2O(OH)_6 \text{ (g)} \quad (15)$$
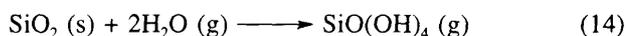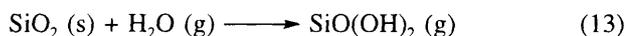
At lower partial pressures of water vapour the compound $SiO(OH)_2$ was determined in the gaseous phase by the high-temperature mass spectrometer. $Si(OH)_4$ is formed preferentially at higher pressures and temperatures (above 1300 °C) while the first of the reactions is of only marginal significance. The last reaction probably does not take place under the given conditions, as its product was not detected in the gaseous phase.

During vaporization occurring in the course of melting of commercial glasses (such as types I - III),

formation of volatile silicon compounds has not so far been proved. However, it is likely that at high temperatures, in particular in the case of melts with a higher content of $SiO_2$, water vapour may bring about vaporization of this otherwise poorly volatile component.

### Vaporization in $CO_2$ atmosphere

According to the literature, the presence of carbon dioxide in the gaseous phase should not affect the course of vaporization of melts containing alkali oxides. If the respective carbonate is formed on the melt surface, its decomposition at the usual glass-melting temperatures would proceed in two stages:

$$Na_2CO_3 \text{ (l)} \longrightarrow Na_2O \text{ (l)} + CO_2 \text{ (g)} \qquad (16)$$

$$Na_2O \text{ (l)} \longrightarrow 2Na \text{ (g)} + {}^{\sim}O_2 \text{ (g)} \qquad (17)$$
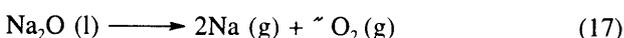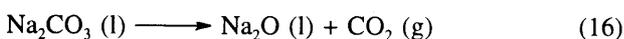
There is the key question whether and to what extent sodium carbonate can be formed at high temperatures and how stable it would be. In this connection, the inhibiting effect of $CO_2$ on vaporization of PbO from multicomponent melts is of interest [11, 18]. However, the mechanism of the effect of $CO_2$ has not so far been satisfactorily explained in this case either.

In technological practice, $CO_2$ acts usually jointly with water vapour. The chemism of vaporization is then complicated by hydrolytic reactions and the effect of water vapour on vaporization is very probably of determining significance. Reactions between gaseous phase components and those of the melt may be followed by reactions in the gaseous phase. For example, vaporization of PbO from type III glass melts yielded basic lead carbonate $Pb_3(CO_3)_2(OH)_2$ and lead-potassium hydroxy carbonate $KPb_2(CO_3)_2OH$, whose formation is attributed to the following reactions in gaseous phase [18]:

$$3PbO \text{ (g)} + 2 CO_2 \text{ (g)} + H_2O \text{ (g)} \longrightarrow$$
$$\longrightarrow Pb_3(CO_3)_2(OH)_2 \text{ (g)} \qquad (18)$$

$$4 PbO \text{ (g)} + 2 KOH \text{ (g)} + 4 CO_2 \text{ (g)} \longrightarrow$$
$$\longrightarrow 2 KPb_2(CO_3)_2 \text{ (g)} \qquad (19)$$
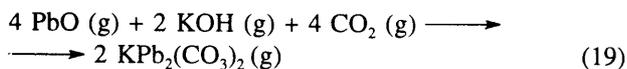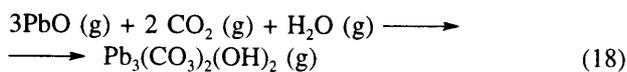
### Vaporization in an atmosphere containing $SO_2$

The effect of sulphur dioxide contained in gaseous phase on vaporization of both model and commercial melts is not very distinct. With melts containing alkali oxides the effect of $SO_2$ can be derived e.g. in the case of sodium oxide from the assumed reaction

$$Na_2O \text{ (l)} + SO_2 \text{ (g)} + 1/2 O_2 \text{ (g)} \longrightarrow Na_2SO_4 \text{ (l)} \quad (20)$$
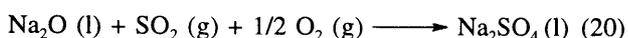
The sodium sulphate can vaporize without decomposing according to the reaction

$$Na_2SO_4 \text{ (l)} \longrightarrow Na_2SO_4 \text{ (g)}$$
$$K_{1400 \text{ °C}} = 1.8 \times 10^{-4} \qquad (21)$$
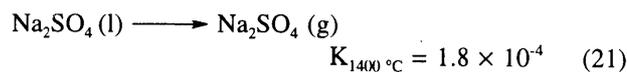
or with decomposition according to the reaction

$$Na_2SO_4 \text{ (l)} \longrightarrow 2Na \text{ (g)} + SO_2 \text{ (g)} + O_2 \text{ (g)} . \qquad (22)$$
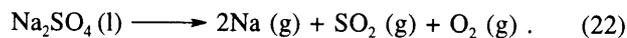
The experimental data [20] show that at low partial pressures of $SO_2$ (< 500 Pa), $Na_2SO_4$ molecules vaporize slowly and congruently, the contribution of the decomposing reaction being negligible. In the presence of water vapour, the following hydrolytic reaction is viable:

$$Na_2SO_4 \text{ (l)} + H_2O \text{ (g)} \longrightarrow 2 NaOH \text{ (g)} +$$
$$+ SO_2 \text{ (g)} + O_2 \text{ (g)} \qquad (23)$$
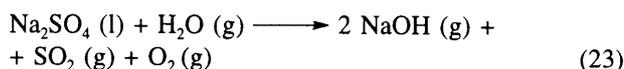
according to which vaporization of sodium sulphate is substantially promoted in contrast to a dry atmosphere. Some authors [21] assume that in the presence of water vapour, sulphate ions interfere with the Si-O bond by the reaction

$$Na_2SO_4 \text{ (l)} + 3 \equiv Si\text{-}O\text{-}Si\equiv + 2 H_2O \longrightarrow$$
$$\longrightarrow SO_3 + 4 \equiv Si\text{-}OH + 2 \equiv Si\text{-}ONa \qquad (24)$$
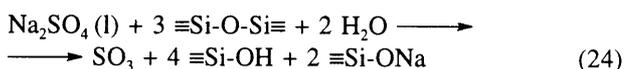
In view of the low content of sodium sulphate in the melts the contribution of these reactions to the overall vaporization of sodium oxide is mostly negligible. However, the vaporization loss of this compound, in particular in a moist atmosphere, becomes more significant as illustrated by figure 6 [22].

### CHEMICAL REACTIONS OF VAPORIZATION AND ITS KINETICS

The chemical processes taking place between the components of the melt and those of the gaseous phase at the phase boundary respect one of the partial processes comprising the vaporization process. As a rule, the kinetic model of vaporization considers in all three such partial processes (cf. figure 7). The remaining two are transport processes by which volatile components are carried towards the phase boundary (diffusion in melt) or away from the phase boundary (diffusion in gaseous phase) [3, 5]. Most of the mathematical models attempting to describe the vaporization kinetics are based on these physico-chemical concepts.

In the sum of partial processes, the chemical reactions are considered when they proceed at a rate lower than, or commensurable with, that of the diffusion processes. In the case of reactive vaporization the chemical processes whose course changes the vaporization mechanism, are in some models regarded as decisive ones for calculation of the overall vaporization losses. This procedure implies the assumption of a negli-
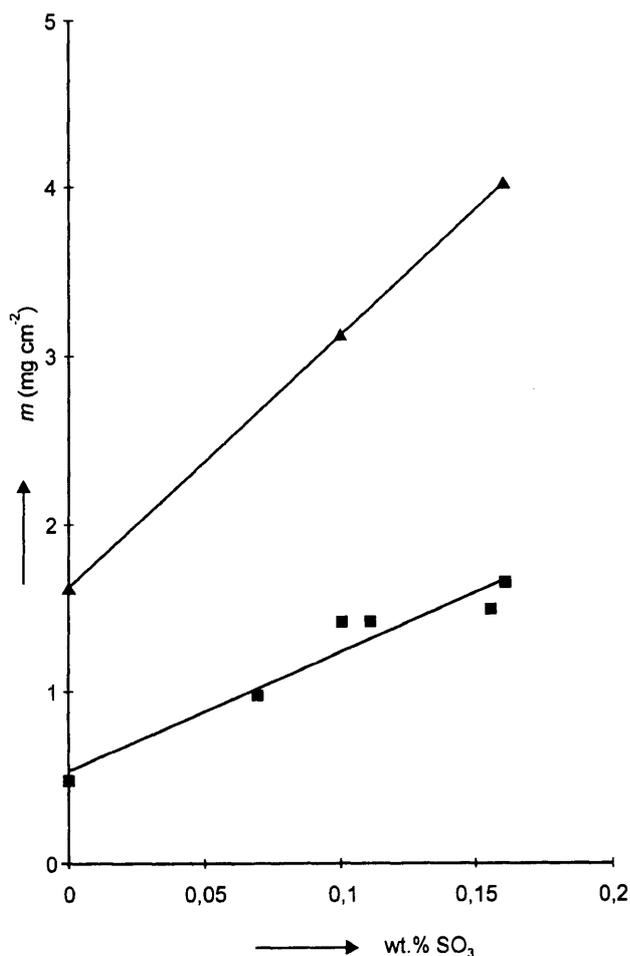
Figure 6. Vaporization loss from float glass melt in an atmosphere of air and in a mixture of air and water vapour at 1450 °C vs. $SO_3$ content in the melt.

■ – $p_{H2O}$ = 0 kPa, ▲ – $p_{H2O}$ = 29 kPa

gible diffusion resistance in both the liquid and the gaseous phases. The mathematical model of vaporization is then reduced to mere description of the kinetics of the chemical reaction at the phase boundary. The simplest case is represented by kinetic description of a first-order reaction, where the reaction rate is directly proportional to concentration of the volatile component in the liquid phase at the phase boundary,

$$dc \ / \ dt = k_1 c_s \ . \tag{25}$$

Unless the concentration $c_s$ is constant, it can be expressed by means of a relationship describing its variability in terms of diffusion resistance in the melt. Such a model, covering two partial processes, often corresponds quite well to experimental data obtained in laboratory. The calculation can be further simplified on assuming a steady state at the phase boundary, i.e. when it holds that

$$j_d = -DS \ dc/dx = k_1 c_s \ . \tag{26}$$

On the other hand, when desiring to make the calculation more precise, one can consider a more complex form of the kinetic equation. The calculation retains its character of simulation and is not based on exact knowledge of the kinetics of the respective chemical reaction. This also applies to models which consider diffusion resistance in the gaseous phase in addition to the chemical reaction.

The vaporization process is further complicated by the fact that in practice it takes place under non-isothermal conditions. The partial processes mentioned so far are thus supplemented with heat transfer. A complete mathematical model describing volatilization in an actual glass furnace includes three main sub-models:

1. Model of heat transfer in melt

2. Model of rate field in melt

3. Model of the combustion space, i.e. the velocity model in gaseous phase and the kinetic model of reactions taking place in gaseous phase and at the boundary between the gaseous phase and the melt.
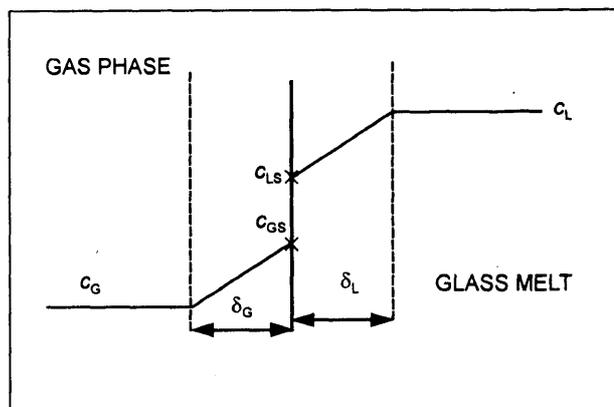


Figure 7. Kinetic model of vaporization from silicate melts.

$c_G$ – concentration of the volatile component in gaseous phase at adequate distance from phase boundary

$c_{GS}$ – concentration of the volatile component in gaseous phase at phase boundary

$c_L$ – concentration of the volatile component in melt at an adequate distance from phase boundary

$c_{LS}$ – concentration of the volatile component in melt at phase boundary;

The submodels of temperature and velocity fields are the starting points for the solving of diffusion equations and for the acquiring of data on the concentration distribution of the volatile component in the combustion space of the glass furnace [9, 10].

## CONCLUSION

The chemical reactions taking place at high temperatures during vaporization of the volatile components of silicate melts may significantly affect the mechanism and kinetics of this process. Vaporization most frequently involves dissociation of the volatilizing compounds, but the process may also include degradative reactions and finally also reactions which, although not bringing about any changes in the composition of the vaporizing products, may create kinetic obstacles to their volatilization. Study of the high-temperature heterogeneous reactions between components of melts and those of the gaseous phase provides additional information on the chemism of changes taking place in the melts and thus influencing their behaviour and properties. Knowledge of the thermodynamics and kinetics of high-temperature reactions is a prerequisite for obtaining data required for mathematical modelling of the vaporization process.

### Acknowledgement

### References

1. Conradt R., Scholze H.: Glastechn.Ber. *59*, 34 (1986).
2. Matoušek J., Hlaváč J.: Sklář a keramik *24*, 258 (1974), (in Czech).
3. Hermans J.M.: Glastechn.Ber. *63K*, 342 (1990).
4. Beerkens R.G.C.: Glastech.Ber. Glass Sci.Technol. *68*, 369 (1995).
5. Matoušek J.: Ceramics - Silikáty *17*, 201 (1991), (in Czech).
6. Piacente V., Matoušek J.: Silikáty *17*, 269 (1973), (in Czech).
7. Matoušek J., Piacente V., Ferro D., Nappi B.: Glass Technology *19*, 158 (1978).
8. Stoljarova V.L., Semenov G.A.: *Mass Spectrometric Study of the Vaporization of Oxide Systems*, John Wiley & Sons, Chichester 1994.
9. Beerkens R.G.C., Kobayashi H.: Glastech.Ber. Glass Sci.Technol. *68C2*, 111 (1995).
10. Kobayashi H., Wu K.T., Richter W.: Glastech.Ber. Glass Sci.Technol. *68C2*, 119 (1995).
11. Hanke K.P., Scholze H.: Glastechn.Ber. *50*, 271 (1977).
12. Sanders D.M., Schaeffer H.A.: J.Am.Ceram.Soc. *59*, 96 (1976).
13. Ohe S.: *Computer Aided Data Book of Vapor Pressure*, Data Book Publishing Company, Tokyo 1976
14. Holá M., Matoušek J., Hlaváč J.: Silikáty *18*, 209 (1974), (in Czech).
15. Matoušek J.: Sklář a keramik *41*, 3 (1991), (in Czech).
16. Fernandes M.H.V., Cable M.: Glass Technol. *34*, 26 (1993).
17. Fernandes M.H.V., Cable M.: Bol.Soc.Esp.Ceram.Vid.: *31C*, 161 (1992).
18. Matoušek J., Paurová D.: Proc. Fundamentals of Glass Science and Technology, pp. 65-71, Glafo, The Glass Research Institue, Vaxjo , Sweden 1997.
19. Opila J.E., Fox D.S., Jacobson N.S.: J.Am.Ceram.Soc. *80*, 1009 (1997).
20. Sanders D.M., Wilke M.E., Hurwitz S., Haller W.K.: J.Am.Ceram.Soc. *64*, 399 (1981).
21. Hanke K.P., Scholze H.: Glastechn.Ber. *43*, 475 (1979).
22. Matoušek J.: Glass *58*, 22 (1981).

*Submitted in English by the author.*

---

## LASER CLEANING IN CONSERVATION
### An Introduction

*Edited by Martin Cooper,*
*Butterworth-Heinemann, Oxford 1998*
*98 pp, 90 figures, hardcover, price £ 30.00*
*ISBN 0 7506 3117 1*

The book, based on experience gained during the past seven years, summerizes the theory and practice of the use of lasers for cleaning in conservation of materials from a wide range of works of art. Within that time period, commercial laser cleaning systems were developed through cooperation of scientists and conservators from Great Britain and Greece.

The book is divided into seven chapters: 1. Introduction; 2. Basic principles of a laser; 3. Removal of surface layers by laser radiation; 4. Practical cleaning with a Q-switched Nd:YAG laser; 5. Case studies; 6. Lasers in the conservation of painted artworks; 7. Future developments.

Chapter 1 discusses the differences between laser cleaning and more conventional methods, incl. a brief history of laser cleaning since 1972, and presents a review of research on the use of lasers for cleaning stone, terracotta, textiles, paper, stained glass and paintings. Chapter 2 summarizes basic principles and information about different types of lasers. Chapter 3 describes the interaction of a laser beam with a surface and the resulting effects. Chapter 4 reviews some of the practical techniques using a laser operating in the near infrared, with emphasis laid on the Nd:YAG laser which is most commonly used in conservation studios. Chapter 5 presents a series of studies devoted to cleaning of various artworks using a Nd:YAG laser. The text includes case studies on marble, limestone, sandstone, terracotta, plaster, aluminium, ivory, bone, parchment and wood. In Chapter 6, special attention is given to the use of lasers in the conservation of painted artworks. The last chapter 7 discusses some of the possible future developments in the field of laser cleaning.

The text of the book is accompanied by instructive drawings and figures. It is supplemented by a glossary of specific technical terms. The authors present a well balanced survey of principles, facts and experience, based on a systematic approach. The book - the first one written on this subject - can be recommended to all readers interested in conservation of various types of artworks and materials, incl. glass, ceramics, mosaics etc.

*J. Hlaváč*

---