

MODEL CONCEPT OF VAPORIZATION FROM SILICATE MELTS

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The time course of vaporization of the volatile components from silicate melts is interpreted by means of model concepts derived from the two-film theory and the penetration theory. The model concepts are verified by means of experimental data on evaporation from the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ binary melt and from a multicomponent lead glass.

INTRODUCTION

Mathematical interpretation of experimental data obtained in the study of vaporization of volatile components of silicate melts is usually based on the assumption that the summary rate of vaporization depends on the rates of three partial processes [1]. The first of them is transport of the volatile component in the melt, the second a not closely defined process at the phase boundary, and the third process is transport of the vaporized component in the gaseous phase. The shares of these partial processes in the overall vaporization rate depend on the composition of the liquid and the gaseous phase and on the external conditions of vaporization.

Some of the studies published so far [2, 3] allow certain assumptions of the nature of the partial processes to be formulated. Transport of the volatile component in the melt and in the gaseous phase is generally assumed to take place by diffusion. The concept of the process at the phase boundary is unclear. In some cases it is regarded as a chemical reaction whose rate can be described by a first-order kinetic equation [2, 7].

These partial findings concerning the mechanism of vaporization gave rise to an attempt aimed at interpreting the experimental data obtained in vaporization studies by means of model concepts of mass transfer. Such concepts are expected to allow for a more precise description of the time course of vaporization under both laboratory and industrial conditions than the partial models used so far.

THEORETICAL CONCEPTS

Mass transfer from a flowing medium can be described mathematically on the basis of theoretical concepts presented in the literature under the terms two-film theory and penetration theory [4—6]. The two-film theory is based on the assumption that all the resistance to mass transfer is concentrated at the phase boundary in the form of two thin films of laminar boundary layers (Fig. 1). Inside the boundary layers, the mass transfer proceeds by molecular diffusion. It is further assumed that a local equilibrium is rapidly established at the phase boundary, i. e. steady-state, time-independent concentrations of the volatile component in the liquid and the gaseous phase are formed. Then it can be assumed that the mass transfer inside both films will take place by steady-state molecular diffusion.

The rate of mass transfer through the boundary layer in the gaseous phase is then described by the equation

$$\left(\frac{dm}{dt}\right)_G = AD_G \frac{C_{GS} - C_S}{\delta_G} = Ak_G(C_{GS} - C_G). \quad (1)$$

Similarly, the following equation holds for the rate of mass transfer through the boundary layer in the liquid:

$$\left(\frac{dm}{dt}\right)_L = AD_L \frac{C_L - C_{LS}}{\delta_L} = Ak_L(C_L - C_{LS}). \quad (2)$$

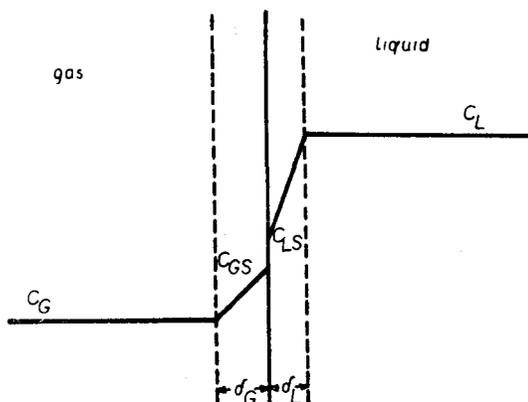


Fig. 1. Concentration distribution of the volatile component in the neighbourhood of the phase boundary according to the two-film theory.

These relationships define the coefficient of mass transfer in the gaseous phase, k_G , and in the liquid phase, k_L . The value of A represents the surface area of the phase boundary, D_L and D_G are the diffusion coefficients of the volatile component in the liquid and the gaseous phase respectively, and δ_L and δ_G are the thicknesses of the respective diffusion layers. On assuming further that Henry's law holds at the phase boundary, then

$$C_{GS} = HC_{LS}. \quad (3)$$

Similarly, the concentration of the volatile component in the gaseous phase at an adequate distance from the phase boundary can be substituted by the corresponding steady-state concentration in the liquid phase,

$$C_G = HC_{LR}. \quad (4)$$

In the steady state,

$$\left(\frac{dm}{dt}\right)_G = \left(\frac{dm}{dt}\right)_L = \frac{dm}{dt}, \quad (5)$$

on using equations (1)—(5) and e. g. by eliminating the concentration of the gaseous component in the liquid phase, one obtains the equation

$$\frac{dm}{dt} = A \frac{C_L - C_{LR}}{\frac{\delta_L}{D_L} + \frac{\delta_G}{HD_G}} = AK(C_L^* - C_{LR}), \quad (6)$$

which defines the overall (total) mass transfer coefficient,

$$K = \left(\frac{\delta_L}{D_L} + \frac{\delta_G}{HD_G} \right)^{-1}. \quad (7)$$

The relation between the total mass transfer coefficient K and those in the liquid and the gaseous phases is described by the equation

$$\frac{1}{K} = \frac{1}{K_L} + \frac{1}{HK_G}. \quad (8)$$

The overall resistance to mass transfer is thus given by the sum of partial resistances in the liquid and in the gaseous phases. If these are not commensurable, the rate of the mass transfer is given by the steady-state diffusion of the volatile component in that phase which exhibits a substantially higher resistance.

In agreement with the penetration theory, the second model concept assumes that non-equilibrium diffusion controls the vaporization process. The mathematical solution is based on Fick's law for unidirectional non-equilibrium diffusion of the volatile component in the liquid phase in the direction towards the phase boundary. On the condition that the initial and boundary conditions hold,

$$\begin{array}{lll} t = 0 & 0 \leq x \leq \infty & C_L = C_\infty \\ t > 0 & x = 0 & C_L = C_L^* = \text{const.} \\ t > 0 & x = \infty & C_L = C_{L\infty} \end{array}$$

where C_L is the concentration of the volatile component in the liquid, the total amount of the vaporized component can be described by the equation

$$m = 2(C_L^* - C_L) \left(\frac{D_L}{\pi t} \right)^{1/2}. \quad (9)$$

In contrast to the two-film theory, where the total vaporized amount was directly proportional to the value of the diffusion coefficient (cf. equation (2)), the penetration theory predicts the value of m to depend on the second root of the diffusion coefficient of the volatile component in the liquid phase.

There are several other theoretical approaches [4] which are aimed at harmonizing the two basic theories. To calculate the amount of vaporized volatile components from silicate melts, use was made of an approach considering non-equilibrium diffusion in the liquid phase and at the same time a process at the phase boundary. The rate of the process is directly proportional to the difference between the actual concentration of the volatile component at the phase boundary, C_{Ls} , and concentration C_{LR} which would be in equilibrium with the vapour pressure of the volatile component in the gaseous phase at an adequate distance from the phase boundary. In that case it holds that

$$-D \left(\frac{\partial C}{\partial x} \right)_{x=0} = \alpha(C_{LR} - C_{Ls}). \quad (10)$$

In this equation the proportionality constant α has the significance of the apparent rate constant of the process at the phase boundary. The amount of the component vaporized can then be determined from the equation

$$m = \frac{C_{LR} - C_L}{h} \cdot \left\{ \exp(h^2 D t) \operatorname{erfc}(h \sqrt{D t}) \right\} - 1 + \frac{2}{\sqrt{\pi}} h \sqrt{D t} \quad (11)$$

in which $h = \alpha/D_L$. The vaporization takes place when $C_{LR} < C_L$. In the opposite case the volatile component becomes dissolved in the melt. For very long periods of time, equation (10) can be simplified into the form

$$m = \frac{C_{LR} - C_L}{h} + 2(C_{LR} - C_L) \sqrt{\frac{D t}{\pi}} \quad (12)$$

VERIFICATION OF THE MODEL CONCEPTS

To verify the mathematical relationships derived in the previous paragraphs, use was made of experimental data obtained with the apparatus whose principle has already been described earlier [7]. For the sake of simpler interpretation, data on vaporization from the binary system $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ was selected. The vaporization proceeded isothermally at 1300°C under a variable water vapour pressure (0–69 kPa) in flowing nitrogen atmosphere. The details of the experimental conditions, the procedure and the data obtained are given in [3, 7]. Fig. 2 shows the time dependence of the total loss in weight for various partial water vapour pressures.

In nitrogen atmosphere, and/or at low values of partial water vapour pressures, the vaporization takes place at a constant rate. At higher water vapour pressures and after a certain time, the rate of vaporization starts gradually to decrease with time. In all instances, there was always a sufficiently long period of time during which the vaporization rate was constant. This fact allows the vaporization kinetics

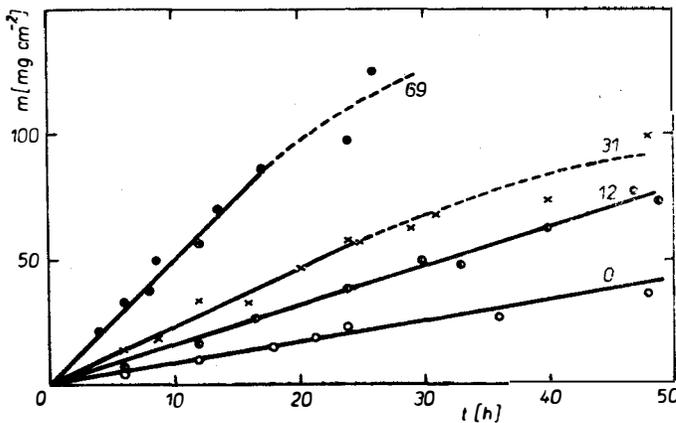


Fig. 2. Loss in weight due to vaporization from $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ melt in terms of time at 1300°C under variable water vapour pressure (0–69 kPa) in nitrogen atmosphere.

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to be interpreted in agreement with the two-film theory. The overall mass transfer coefficient K can be calculated from equation (6). In view of the conditions of vaporization, it holds approximately that $C_G = 0$ and thus $C_{LR} \ll C_L$. The value of C_L can be determined by means of the density of the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ melt, which amounts to 2.20 g cm^{-3} at 1300°C [8]. In view of the fact that the values of both A and K are likewise constant, equation (6) indicates a linear dependence of the total amount vaporized in terms of time:

$$m = AKC_L t. \quad (13)$$

Equation (13) permits the total mass transfer coefficient to be calculated, as the remaining parameters are easy to determine. The K values are listed in Table I.

Table I

The overall mass transfer coefficients for vaporization from $\text{Na}_2\text{O} \cdot \text{SiO}_2$ melt at 1300°C

$p_{\text{H}_2\text{O}}$ (kPa)	0	12	12	69
K (cm s^{-1})	3.2×10^{-7}	5.8×10^{-7}	7.9×10^{-7}	1.9×10^{-6}

The model concept based on the two-film theory describes very satisfactorily the time course of vaporization in an inert dry atmosphere. The presence of water vapour causes the period of time, during which the rate of vaporization is constant, to be shortened. This is probably due to the fact that at a higher rate of vaporization, the concentration of the volatile component in the surface layer decreases so rapidly that the concept of steady-state diffusion in the boundary layer no longer holds. The volatile component is then transported to the surface by non-equilibrium diffusion and the time course of vaporization is better described by the model based on the penetration theory. The validity of this model for mathematical description of the time course of vaporization has already been derived earlier [3]. The kinetic constants, determined by means of equation (12), were also taken over from the study quoted and are listed in Table II.

It is obvious that both the value of the diffusion coefficient D_L and the apparent rate constant α increase with increasing partial pressure of water vapour in the atmosphere. However, the value of the diffusion coefficient is always substantially lower, so that non-equilibrium diffusion of the volatile component in the melt will be the controlling process of vaporization. The process at the phase boundary,

Table II

Kinetic constants for vaporization from $\text{Na}_2\text{O} \cdot \text{SiO}_2$ melt, calculated from equation (12)

$p_{\text{H}_2\text{O}}$ (kPa)	$10^7 D_L$ ($\text{cm}^2 \text{s}^{-1}$)	$10^7 \cdot \alpha$ (cm s^{-1})
0	0.21	6.7
0.12	1.5	9.0
0.31	2.0	16.0
0.69	3.3	43

characterized by the apparent rate constant α , will play a significant role in the initial stages of vaporization, where, as follows from equation (12), the amount of the volatile component transported by non-equilibrium diffusion will be small.

The model concepts of vaporization were further verified on a multicomponent glass having the composition 59.4 SiO₂, 25.3 PbO, 9.6 K₂O, 4.3 Na₂O, 0.6 CaO, 0.6 Al₂O₃ (wt. %). The method for, and results of measuring the time course of vaporization from melt of this composition were given in [7, 9]. For the purpose of a discussion of the data obtained, Fig. 3 shows the time course of the amount vaporized at 1200°, 1300° and 1400°C. At 1200°C, the vaporization takes place at a constant rate. The data obtained at the higher temperatures indicate an unequalized course of vaporization. Analogously to the previous case, steady-state diffusion can be assumed at 1200°C and the vaporization interpreted by means of the two-film theory. For temperatures of 1300° and 1400°C, this kind of interpretation is formal and can be employed e. g. for calculating the initial rate of vaporization. The values of the total mass transfer coefficient listed in Table III have this kind of significance.

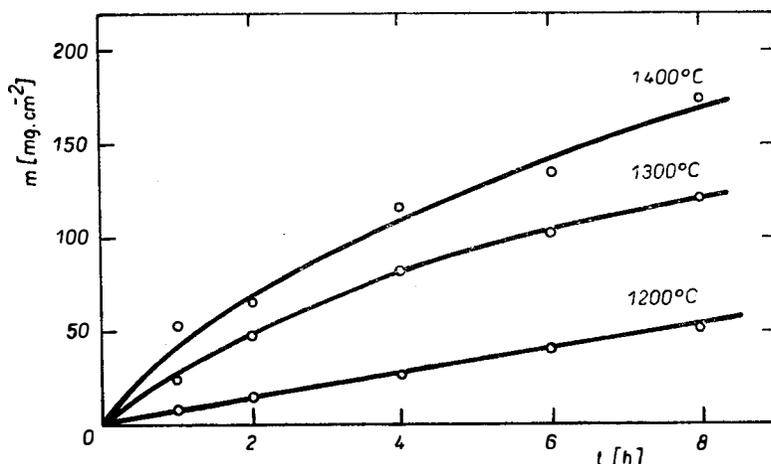


Fig. 3. Loss in weight due to vaporization from the melt of a multicomponent lead glass at 1200°C, 1300°C and 1400°C.

Table III

The overall mass transfer coefficient for vaporization from a multicomponent lead glass

Temperature (°C)	1 200	1 300	1 400
K (cm s ⁻¹)	2.4×10^{-6}	8.9×10^{-6}	1.7×10^{-5}

Throughout the entire time range, the two-film theory and thus also the value of the total mass transfer coefficient can be applied only to the temperature of 1200°C. At higher temperatures, the time dependence of the amount vaporized is parabolic in shape and non-equilibrium diffusion can thus be logically assumed

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Table IV

Kinetic constants for vaporization from a lead glass melt, calculated from equation (12)

Temperature (°C)	D_L (cm ² s ⁻¹)	α (cm s ⁻¹)
1 200	2.7×10^{-7}	5.4×10^{-6}
1 300	1.3×10^{-6}	2.6×10^{-5}
1 400	3.0×10^{-6}	3.0×10^{-5}

to be the controlling process. Equation (12) yields the values of the kinetic constants D_L and α listed in Table IV.

The value of the diffusion coefficient as well as that of the apparent rate constant increase with temperature. However, it holds again that the value of D_L is substantially lower which indicates that the vaporization process is controlled by diffusion of the volatile component in the melt. At the higher vaporization rates determined at 1300 °C and 1400 °C, there arises a surface layer depleted of the volatile component, and non-equilibrium diffusion takes place through this layer.

CONCLUSION

Two mathematical models describing the time dependence of the loss in weight due to vaporization of volatile components from the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ binary glass, and from a multicomponent lead glass were verified.

Vaporization was found to take place at a constant rate when this rate was low. The process can be described mathematically by a relationship derived from the theory of steady-state diffusion through a boundary layer in liquid and gaseous phase. According to this relationship, the dependence of weight loss due to vaporization is directly proportional to time.

At the higher vaporization rates, the time course of vaporization can be described by an equation based on the assumption that the process is controlled by non-equilibrium diffusion of the volatile component in the melt. This equation predicts direct proportionality between the weight loss due to vaporization and the second root of time.

Both models allow the time course of vaporization to be described mathematically on the basis of relatively readily available kinetic constants and concentration parameters.

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MODELOVÉ PŘEDSTAVY O VYPAŘOVÁNÍ SILIKÁTOVÝCH TAVENIN

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Časový průběh vypařování těkavých složek silikátových tavenin lze matematicky popsat pomocí teoretických představ o přestupu hmoty z proudícího média. Tyto představy jsou ověřovány pomocí experimentálních dat o časové závislosti úbytků hmotnosti při vypařování v binární soustavě $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ a ve vícerozložkové tavenině o složení 59,4 SiO_2 ; 25,3 PbO ; 9,6 K_2O ; 4,3 Na_2O ; 0,6 CaO ; 0,6 Al_2O_3 (hmot. %).

Při konstantní rychlosti vypařování lze experimentální data popsat pomocí vztahu (13), který vychází z představ o existenci tenkých laminárních filmů v kapalně a v plynné fázi, v nichž nastává transport těkavé složky ustálenou molekulární difúzí. V binární soustavě $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ lze takto interpretovat časový průběh vypařování za teploty 1 300 °C, jestliže vypařování probíhá v suché inertní atmosféře. U vícerozložkové taveniny s relativně vysokým obsahem PbO probíhá vypařování konstantní rychlostí a tedy ve shodě s teorií dvou filmů za teploty 1 200 °C.

Jestliže rychlost vypařování s časem klesá, vystihuje lépe experimentální data představa založená na předpokladu neustálené molekulární difúze těkavé složky v kapalně fázi. Časový průběh vypařování vykazuje parabolickou závislost a lze jej popsat vztahem (12). Takto lze interpretovat vypařování binární soustavy $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, jestliže probíhá v atmosféře obsahující vodní páru. Rovněž časový průběh vypařování vícerozložkové taveniny za vyšších teplot (1 300 °C, 1 400 °C) dobře vystihuje rovnice (12).

Pro uvedené soustavy byly stanoveny příslušné kinetické parametry (úhnný koeficient přestupu hmoty, difúzní koeficient těkavé složky v tavenině, zdánlivá rychlostní konstanta děje na fázovém rozhraní). Použitím těchto parametrů a kombinací obou modelových představ v závislosti na podmínkách vypařování lze dobře popsat časový průběh vypařování těkavých složek v uvedených soustavách. Modelové představy jsou natolik obecné, že lze předpokládat jejich úspěšnou aplikaci při matematickém popisu vypařování i v dalších silikátových soustavách.

Obr. 1. Distribuce koncentrace těkavé složky v okolí fázového rozhraní podle teorie dvou filmů.

Obr. 2. Úbytek hmotnosti při vypařování taveniny $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ v závislosti na čase za teploty 1 300 °C při proměnném parciálním tlaku vodní páry (0—69 kPa) v atmosféře dusíku.

Obr. 3. Úbytek hmotnosti při vypařování taveniny vícerozložkového olovnatého skla za teplot 1 200, 1 300 a 1 400 °C.

МОДЕЛЬНОЕ ПОНИМАНИЕ ИСПАРЕНИЯ СИЛИКАТНЫХ РАСПЛАВОВ

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Временный ход испарения летучих веществ силикатных расплавов можно математически описать с помощью теоретических предположений о массопередаче из проточной среды. Приводимые предположения проверяются с использованием экспериментальных данных относительно временной зависимости убыли массы при испарении в бинарной системе $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ и во многокомпонентном расплаве составом 59,4 SiO_2 , 25,3 PbO , 9,6 K_2O , 4,3 Na_2O , 0,6 CaO , 0,6 Al_2O_3 (% по весу).

При постоянной скорости испарения можно экспериментальные данные описать с помощью отношения (13), исходящего из представления существования тонких ламинарных пленок в жидкой и газообразной фазах, в которых проходит перемещение летучего компонента устойчивой молекулярной диффузией. В бинарной системе $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ можно таким образом объяснить временный ход испарения при температуре 1 300 °C в том случае, когда испарение протекает в сухой инертной среде. В случае многокомпонентного расплава с относительно высоким содержанием PbO испарение

проходит постоянной скоростью, а следовательно в согласии с теорией двух пленок при температуре 1 200 °С.

Если скорость испарения в зависимости от времени понижается, то экспериментальные данные больше отвечают представлению, основывающемуся на предположении постоянной молекулярной диффузии летучего компонента в жидкой фазе. Временный ход испарения характеризует параболическая зависимость и можно его описать отношением (12). Таким образом можно объяснить испарение бинарной системы $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ тогда, когда оно проходит в среде, содержащей водяной пар. Также временному ходу испарения многокомпонентного расплава при более высоких температурах (1 300 °С, 1 400 °С) хорошо соответствует уравнение (12).

Для приводимых систем устанавливаются соответствующие кинетические параметры (общий коэффициент массопередачи, коэффициент диффузии летучего компонента в расплаве, кажущаяся константа скорости процесса на разделе фаз). Используя данные параметры и комбинируя оба модельных представления в зависимости от условий испарения, можно хорошо описать временный ход испарения летучих компонентов в приводимых системах. Модельные представления оказываются настолько общими, что можно предполагать их успешное применение при математическом описании испарения даже в дальнейших силикатных системах.

- Рис. 1. Распределение концентрации летучего компонента вблизи раздела фаз согласно теории двух пленок.*
- Рис. 2. Убыль массы при испарении расплава $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ в зависимости от времени при температуре 1 300 °С при переменном парциальном давлении водяного пара (0—69 кПа) в среде азота.*
- Рис. 3. Убыль массы при испарении расплава многокомпонентного свинцового стекла при температурах 1 200, 1 300 и 1 400 °С.*