

Modeling of bubble removal from glassmelts at refining temperatures

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A new model based on the quasi-stationary approximation is developed for removal of gas bubbles from glassmelts due to buoyant rise of bubbles. The growth and rising of multicomponent gas bubbles in glassmelts are examined from the view point of interfacial mass transfer. It is shown that the models for rising bubbles in glassmelts available in the literature are based on the quasi-steady approximation which is not very reasonable. The growth of a gas bubble initially consisting of nitrogen only is studied in a glassmelt whose diffusing gases are oxygen, water, carbon dioxide, sulfide and nitrogen. The proposed model based on the unsteady-state mass transfer (the quasi-stationary approximation) is compared with the model based on the steady-state mass transfer (the quasi-steady approximation). The former, which provides more rational and better descriptions of bubble behavior in refining processes compared with the latter, predicts rather shorter refining times than the latter.

Modell für das Entfernen von Blasen aus Glasschmelzen bei Läutertemperaturen

Auf der Grundlage der quasistationären Näherung wurde ein neues Modell für das Entfernen von Gasblasen aus Glasschmelzen mit Hilfe des statischen Auftriebs der Blasen entwickelt. Das Wachstum und der Aufstieg vielkomponentiger Gasblasen in Glasschmelzen werden vom Standpunkt des Grenzflächenstoffaustausches aus untersucht. Es wird aufgezeigt, daß die in der Literatur beschriebenen Modelle für aufsteigende Blasen in Glasschmelzen auf der Basis einer Gleichgewichtsnäherung nicht sehr sinnvoll sind. Das Wachstum einer zunächst nur aus Stickstoff bestehenden Gasblase wird in einer Glasschmelze untersucht, deren Diffusionsgase Sauerstoff, Wasser, Kohlendioxid, Sulfid und Stickstoff sind. Das vorgeschlagene Modell, das auf dem nichtstationären Stoffaustausch (quasistationäre Näherung) basiert, wird mit dem Modell auf der Grundlage des Stoffaustausches im Gleichgewicht (d.h. quasistatische Näherung) verglichen. Ersteres, das im Vergleich zu letzterem zu einer rationelleren und besseren Beschreibung des Blasenverhaltens bei Läuterprozessen führt, sagt sehr viel kürzere Läuterzeiten als das letztgenannte Modell voraus.

1. Introduction

The removal of gas bubbles from the glassmelt or refining is an important problem in the glass industry. The refining is required to produce high-quality glasses. Therefore, the rate of removal of gas bubbles has received extensive attention and several studies on this subject have appeared in the literature [1]. In order to analyze the behavior of the gas bubble in the melt some approximations have been applied [2]. Although the governing equations are well-known, exact analytical solutions cannot be obtained in general. Hence there are some approximate solutions such as quasi-stationary solutions [3 to 7], quasi-steady solutions [8], perturbation solutions [9] and finite-difference solutions [8 to 12]. The quasi-stationary approximation has been widely and successfully employed in treating dissolution and growth of bubbles. In this approximation, the motion of the bubble boundary is neglected in solving the convective diffusion equation and the simplified differential equation is used to determine the bubble boundary motion. The time-dependent concentration field of dissolved gas around the bubble is obtained by solving the diffusion equation for a fixed radius and the concentration gradient at the bubble surface is used to evaluate

the change in the bubble size. It has been found that in spite of its simplicity the quasi-stationary approximation is rather reasonable [2 and 8].

Two mechanisms are responsible for bubble removal from the glassmelt: bubble dissolution and buoyant rise of bubbles from the melt. Most published studies have been conceived to deal with stationary bubbles instead of moving bubbles and much progress has been made in understanding the dissolution and growth of stationary bubbles in the glassmelt. However, gas bubbles move along by currents in glass melting furnaces and relatively large bubbles are removed from the glassmelts by rising to the surface of the melts. In order to predict bubble trajectories in glass melting tanks with confidence, the modeling of the behavior of multicomponent gas bubbles rising through the glassmelts is required. The analysis of the growth of rising bubbles in the glassmelt is a problem of practical importance.

Nevertheless, progress in this area has been relatively slow. There is a clear need for more work on refining due to the rise of bubbles to the surface of the glassmelt. It should be emphasized that the case of the stationary bubble is considered as a first step before dealing with a translating bubble.

Němec [13 to 15] extensively examined the behavior of bubbles in the melt using Levich's solution for mass transfer from a rising bubble [16].

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Finite difference solutions of the mass transport equations governing the dissolution or growth of a rising gas bubble in a glassmelt were obtained by Onorato et al. [17]. They also examined the model based on the solution of the diffusion equation given by Levich [16]. Although they discussed a rising bubble in the melt, the change of the bubble location was not taken into account in the estimation of the bubble pressure as if the bubble was stationary.

Ramos [18 and 19] developed a mathematical model for the growth of multicomponent gas bubbles rising in the glassmelts. It is a simple model governed by an ordinary differential equation. The approximation used by Ramos [18 and 19] results in a considerable simplification of the labor involved and provides reasonable predictions.

Although it was not mentioned in the literature, the above models for bubbles rising in the melt are based on the quasi-steady approximation as described later in detail. The approximate solutions were obtained by solving the equations for the concentration distribution in the liquid when bubble boundary motion due to dissolution or growth was ignored and furthermore, a steady-state was assumed. This approximation seems to be an over-simplified model [8].

This paper is concerned with a spherical, multicomponent gas bubble rising in an infinite glassmelt. As mentioned above, the quasi-stationary approximation may give satisfactory results particularly when the driving force for growth is not too large [8]. In this work, therefore, this approximate procedure is used to develop a new model for the behavior of a gas bubble rising in the melt. First, the quasi-stationary and quasi-steady approximations for stationary bubbles in the melt will be re-examined. The stationary bubble has been examined as a first step before treating the rising bubble. Next, the authors will develop a model based on the quasi-stationary approximation for multicomponent bubbles rising in the melt. Finally, the computational results for multicomponent gas bubbles in the glassmelt will be investigated. The changes in mass transfer rate, bubble size, bubble location and gas content in bubbles with time are calculated.

2. Theory

2.1 Formulation of equations

The unsteady isothermal growth of a multicomponent bubble in a melt of large extent is considered (figure 1). The spherical bubble of initial radius a_0 is located at a depth H from the glassmelt surface. In this study, the following assumptions are made about the system:

- The mass transport is controlled by diffusion in the melt.
- The concentration field is spherically symmetric.
- The gases in the bubble are always perfectly mixed.

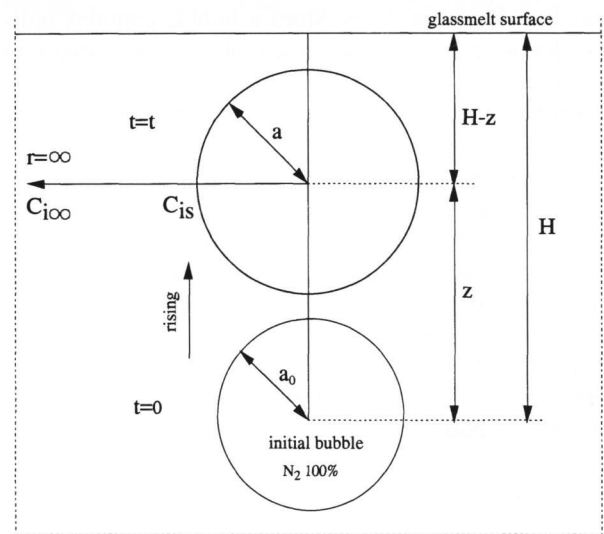


Figure 1. Schematic representation of the system.

- The diffusivities of the gases in the melt are independent of concentration.
- The density of the gases is negligible compared with the density of the glassmelt.
- The partial specific volume of the gases in the glassmelt is negligible.
- There are no chemical reactions.
- The gas mixture in the bubble is ideal.

The concentration of species i in the melt will be described by the following convective diffusion equation (1) and initial and boundary conditions (equations (2a to c)):

$$\frac{\partial C_i}{\partial t} + v(t, r) \frac{\partial C_i}{\partial r} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right); \quad (1)$$

$$C_i(0, r) = C_{i\infty} \quad \text{for } r > a, \quad (2a)$$

$$C_i(t, \infty) = C_{i\infty} \quad \text{for } t \geq 0, \quad (2b)$$

$$C_i(t, a(t)) = C_{is} \quad \text{for } t \geq 0. \quad (2c)$$

This partial differential equation (1), with the initial and boundary conditions, equations (2a to c), is a general description of the transport of dissolved gases in the melt to be solved.

The mass flow of any gas between bubble and glassmelt is given by the following ordinary differential equation [19]:

$$\frac{dn_i}{dt} = \frac{d}{dt} \left(\frac{p_i V}{R_g T} \right) = \frac{d}{dt} \left\{ \frac{p_i (4\pi a^3/3)}{R_g T} \right\} = 4\pi a^2 k_i (C_{i\infty} - C_{is}). \quad (3)$$

This equation states that the mass flux to the bubble being proportional to the concentration difference or driving force, $(C_{i\infty} - C_{is})$ is equal to the change in the

gas bubble composition. Since a bubble contains independently diffusing gases, each of them is subject to equation (3). This mass balance at the bubble surface leads to an expression for the rate of change of bubble radius.

In order to calculate the change in the number of moles of species i with time using equation (3), the concentrations of the species i at the bubble surface, C_{is} , must be known. Henry's law is used to determine C_{is} . In this study, the equilibrium according to Henry's law is assumed to be maintained at the gas/liquid interface. Therefore, the dissolved concentration of gas at the bubble surface, C_{is} , is related to the partial pressure of species i in the bubble, p_i , as:

$$C_{is} = L_i \cdot p_i \quad (4)$$

This law is valid if any interfacial processes occur more rapidly than the diffusion, i.e., diffusion is the rate-limiting process.

2.1.1 Stationary bubble

First, the quasi-stationary and quasi-steady models for stationary bubbles in the melt are examined to clarify the differences in these two approximations. Consider an isolated stationary gas bubble located at a depth H from the melt surface. Its initial radius is a_0 .

a) Quasi-steady model

The quasi-steady approximation is obtained by solving the equations for the concentration field in the melt when bubble boundary motion is ignored and a steady-state is assumed. Neglecting the convection transport and the accumulation terms in equation (1), the governing equation (5) for the quasi-steady approximation and the boundary conditions (equations (6a and b)) are obtained as:

$$\frac{D_i}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) = 0; \quad (5)$$

$$C_i(\infty) = C_{i\infty}, \quad (6a)$$

$$C_i(a) = C_{is}. \quad (6b)$$

The solution of equation (5) for the boundary conditions (6a and b) or the Sherwood number of steady-state mass transfer from a bubble may be written as [20]:

$$Sh_i \equiv \frac{k_i(2a)}{D_i} = 2. \quad (7)$$

The equation for the change in bubble radius may be given as [19 and 21]:

$$\begin{aligned} \frac{da}{dt} &= \frac{R_g T}{P} \sum_{i=1}^n D_i \left(\frac{\partial C_i}{\partial r} \right)_{t,a} \\ &= \frac{R_g T}{P} \sum_{i=1}^n k_i (C_{i\infty} - C_{is}). \end{aligned} \quad (8)$$

This equation is derived from the conservation of mass at the bubble surface per unit time or the sum of equation (3) for all species. In other words, equation (8) shows that the additional diffusion flux into or from the bubble (the right-hand side of equation (8)) is equal to the growth or shrinkage rate of the bubble (the left-hand side of equation (8)). Equation (8) yields the change in bubble size provided the concentrations of the species at the bubble surface, C_{is} , are known.

The pressure inside the bubble whose center of mass is stationary at $z = H$ is given as the sum of the gaseous species partial pressures by

$$P = \sum_{i=1}^n p_i = p_a + \rho_G g H + \frac{2\sigma}{a}. \quad (9)$$

This equation indicates that the total pressure for stationary bubbles changes with bubble radius. Substituting equations (7 and 9) into equation (8)

$$\frac{da}{dt} = \frac{R_g T \sum_{i=1}^n D_i (C_{i\infty} - C_{is}) (1/a)}{p_a + \rho_G g H + 4\sigma/(3a)} \quad (10)$$

is obtained. Using equations (3, 4, 7, 9 and 10), the changes in bubble size and gas concentrations in the bubble with time can be estimated.

b) Quasi-stationary model

In the quasi-stationary approximation, the moving bubble boundary is ignored in solving the convection diffusion equations. Therefore, only the convective transport term in equation (1) is neglected. The resulting model for the concentration fields is:

$$\frac{\partial C_i}{\partial t} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_i}{\partial r} \right); \quad (11)$$

$$C_i(0, r) = C_{i\infty} \text{ for } r > a, \quad (12a)$$

$$C_i(t, \infty) = C_{i\infty} \text{ for } t \geq 0, \quad (12b)$$

$$C_i(t, a) = C_{is} \text{ for } t \geq 0. \quad (12c)$$

It should be emphasized here that the bubble radius a is treated as a constant in solving the convective diffusion equation (11). The solution of equation (11) for the relevant conditions (equations (12a to c)) or unsteady-state mass transfer from a sphere is written in the form of the Sherwood number [20]:

$$Sh_i = 2 \left(1 + \frac{a}{\sqrt{\pi D_i t}} \right). \quad (13)$$

From equations (8, 9 and 13), the following equation for the rate of change of bubble size:

$$\frac{da}{dt} = \frac{R_g T \sum_{i=1}^n D_i (C_{i\infty} - C_{is}) \left(\frac{1}{a} + \frac{1}{\sqrt{\pi D_i t}} \right)}{p_a + \rho_G g H + \frac{4\sigma}{3a}} \quad (14)$$

is obtained. When $t \rightarrow \infty$, the quasi-stationary solution, equation (14), reduces to that of the quasi-steady solution, equation (10).

2.1.2 Rising bubble

Next, the quasi-steady and quasi-stationary models for the behavior of rising bubbles in refining processes are considered which is a problem of practical importance. The stationary bubble approximation sometimes provides inadequate description of the actual phenomena. As mentioned previously, however, only a few studies on the growth of gas bubbles rising through glassmelts have been published [13 to 15, and 17 to 19].

a) Quasi-steady model

Ramos [18] evaluated the mass transfer coefficient in equations (3 and 8) using the following correlation:

$$Sh_i = 2 + 0.60 Re^{1/2} Sc_i^{1/3}. \quad (15)$$

It should be noted that the coefficients in [18, equation (6)] should be twice as many. Later, Ramos [19] used the following equation instead of equation (15):

$$Sh_i = 1 + (1 + Pe_i)^{1/3}. \quad (16)$$

It is to be pointed out that the equation for the change in bubble radius in [19, equation (6)] includes an error. These correlations for the Sherwood number used by Ramos [18 and 19], equations (15 and 16), are solutions for steady-state mass transfer from a solid sphere in creeping flow [20]. When a solid sphere is stationary ($Re = 0$ or $Pe_i = 0$), equations (15 and 16) reduce to equation (7) which is the quasi-steady model for a stationary bubble in the glassmelts.

Němec [13 to 15] applied Levich's correlation for Sh_i [16 and 20]

$$Sh_i = 0.991 Pe_i^{1/3}. \quad (17)$$

This is an asymptotic solution for a solid sphere which is valid at $Pe_i \rightarrow \infty$. Levich [16] solved the convective diffusion equation including the angular velocity component using the thin concentration boundary layer assumption and obtained equation (17).

Onorato et al. [17] applied Levich's solution for a gas bubble. Because the angular velocity distributions are considered in the convective diffusion equation, they employed the equation for local $Sh_i(\theta)$. An expression for the average Sh_i value corresponding to the local $Sh_i(\theta)$ value used by Onorato et al. [17] may be written as

$$Sh_i = \sqrt{\frac{2}{\pi}} Pe_i^{1/2}. \quad (18)$$

This equation is applicable when $Pe_i \rightarrow \infty$ as well as equation (17). It should be mentioned, incidentally, that the equation for the rate of bubble radius change in [17, equation (12)] includes errors. Equations (17 and 18) are also the solutions of the steady-state convective diffusion equation as well as equations (15 and 16).

Although the models for rising bubbles in the literature consider the forced convection due to bubble rising, the correlations for mass transfer coefficient k_i were obtained by solving the steady-state convective diffusion equation. Therefore, the models of Ramos [18 and 19], Němec [13 to 15] and Onorato et al. [17] are based on the quasi-steady approximation.

b) Quasi-stationary model

In the case of stationary bubbles, the quasi-stationary approximation provides better estimations of bubble growth or dissolution rates compared with the quasi-steady approximation [8]. Considering this fact, a model based on the quasi-stationary approximation is expected to provide satisfactory solutions for the growth or dissolution of rising bubbles in the melt. However, no models based on the quasi-stationary approximation for dissolution or growth of a multicomponent gas bubble rising in the glassmelts have been reported so far. Therefore, the authors develop a new quasi-stationary model for the growth of a gas bubble rising in the melts.

As well as in the studies of Němec [13 to 15] and Ramos [18 and 19] the additional assumption on the cause of the rise of bubbles is that a bubble behaves like a rigid sphere ($Re \ll 1$). When the liquid contains small amounts of surface-active materials, these materials tend to suppress the motion on the surface of bubbles and the bubbles obey Stokes' law. Therefore, the bubble rise velocity is given by Stokes' equation:

$$U = - \frac{d(H-z)}{dt} = \frac{2}{9} \cdot \frac{\rho_G g a^2}{\mu}. \quad (19)$$

Hornyak and Weinberg [22] found the bubble rising velocities were correlated by the Hadamard-Rybczynski equation rather than the Stokes equation. It is well-known, as noted by them, that when the melt contains small amounts of surface-active materials bubbles behave like solid particles. This situation may be more practical.

The pressure inside the bubble rising in the melt is given as the sum of the gaseous species partial pressures by the following equation instead of equation (9):

$$P = \sum_{i=1}^n p_i = p_a + \rho_G g (H-z) + 2\sigma/a. \quad (20)$$

Using equations (3, 19 and 20), the following equation for the change in bubble radius can be obtained [19]

$$\frac{da}{dt} = \frac{R_g T \sum_{i=1}^n k_i (C_{i\infty} - C_{is}) + a Q_G g U/3}{p_a + Q_G g (H - z) + 4\sigma/(3a)} \quad (21)$$

An expression of mass transfer coefficient k_i or Sherwood number Sh_i for unsteady-state mass transfer from a solid sphere is introduced instead of steady-state solutions, equations (15 to 18).

In this study, the following correlation for unsteady-state mass transfer from a solid sphere at $Pe_i \rightarrow \infty$ [20] is used.

$$Sh_i = \frac{k_i \cdot (2a)}{D_i} \quad (22)$$

$$= Pe_i^{1/3} \left[0.956 + \left(\frac{2a}{\sqrt{\pi D_i t Pe_i^{1/3}}} \right)^5 \right]^{1/5}$$

The above approximate correlation is valid only when the Peclet number is large. This limitation will be discussed later.

2.2 Solution procedure

In the case of the quasi-stationary model for a rising bubble, equations (3, 4 and 19 to 21) are simultaneously solved to obtain the values of a , p_i , U and z at $t = t$ (arbitrary) by means of the fourth-order Runge-Kutta method. The ordinary differential equations are numerically integrated along with the initial conditions. The time step, Δt , was varied to ensure that values obtained from integration were independent of the step size. The increment of t selected in this study was 0.001 s.

3. Results and discussion

As a numerical example, the growth of a gas bubble is discussed that initially contains nitrogen only in a glassmelt whose diffusing gases are oxygen ($C_{O_2\infty} = 250 \cdot 10^{-3} \text{ kg m}^{-3}$), water ($C_{H_2O\infty} = 425 \cdot 10^{-3} \text{ kg m}^{-3}$), carbon dioxide ($C_{CO_2\infty} = 175 \cdot 10^{-3} \text{ kg m}^{-3}$), sulfur trioxide ($C_{SO_3\infty} = 6200 \cdot 10^{-3} \text{ kg m}^{-3}$) and nitrogen ($C_{N_2\infty} = 0.45 \cdot 10^{-3} \text{ kg m}^{-3}$). The initial radius of the bubble is 0.001 m and the initial location is 1 m below the glassmelt surface. The physical properties used in the calculations are those presented in the paper of Ramos [19]. At present, accurate gas diffusivity and solubility data in the glassmelts are not available. It should be noted that most of the measurements of physical properties include the influence of refining agents or chemical reaction and hence they are apparent values. It implies that the effects of chemical reactions are indirectly included in the concentration $C_{i\infty}$ and as a result the estimated diffusivities and Henry's constants are apparent rather than actually physical.

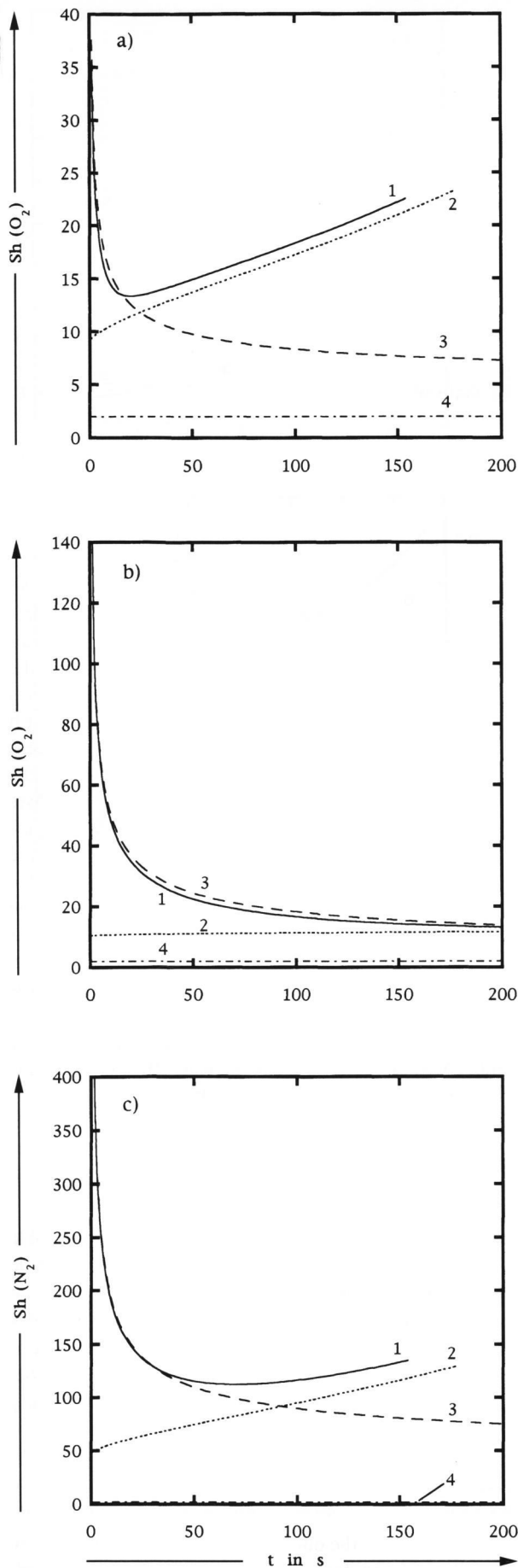
Figure 2a shows the values of Sherwood number Sh_i for oxygen at 1773.15 K as a function of time. The Sherwood number is a dimensionless number of the mass transfer coefficient k_i representing mass transfer rates. In

this study, the mass transfer coefficient during the refining process is evaluated using equation (22). As mentioned previously, equation (22) is a correlation at sufficiently larger values of Pe_i . Since the range of Pe_i in the numerical examples is from 558 to $2.29 \cdot 10^6$, the application of equation (22) may be acceptable. Incidentally, the correlation of Sh_i for a stationary solid sphere ($Pe_i = 0$) is equation (13). For the shrinkage of a very small bubble rising in the melt with very low velocity, equation (13) should be used instead of equation (22) because Pe_i is very small. In order to estimate Sh_i for the growth of a rising bubble in the whole range of Pe_i , equations (13 and 22) must be interpolated. This problem will be discussed in a future work dealing with the simulation of glass melting tanks in which both growth and shrinkage of bubbles occur.

In figure 2a the solid line is the quasi-stationary result for a rising bubble. Since the initial content of O_2 gas in the bubble is zero, O_2 diffuses toward the bubble. The Sherwood number rapidly decreases in the initial stages of growth and a minimum value of $Sh(O_2)$ occurs at $t = 20$ s. With the further increase in time, the Sh number gradually increases. The minimum in the Sherwood number can be interpreted as follows. At shorter times, the mass transfer coefficient decreases because the driving force decreases with time. The O_2 concentration gradient at the bubble surface decreases sharply with time due to the decreased dissolved oxygen concentration in the melt near the surface. It is found, on the other hand, that the mass transfer coefficient increases at longer times. It is because that the bubble size increases and hence, the bubble rising velocity and the mass transfer coefficient increase. The increase in k_i due to an increase of bubble rising velocity overcomes the decrease in k_i due to a decrease of the driving force at longer times. Ramos' model [19], the quasi-steady model for a rising bubble, predicts a rather smaller mass transfer coefficient than the quasi-stationary model for $t < 10$ s. In the initial stages of growth, the quasi-steady model underestimates the mass transfer coefficient for O_2 because in the model the large driving force at shorter times is taken into account. The predictions of these two models are relatively close to each other for $t > 50$ s. For longer times, as a matter of course the unsteady-state value reduces to that of the steady-state.

The quasi-stationary model for a stationary bubble (equation (11)) agrees well with that for a rising bubble at shorter times. When $t \rightarrow 0$, both equation (22) for a rising bubble and equation (13) for a stationary bubble approach to $Sh_i = 2a/\sqrt{\pi D_i t}$. At the early stage of bubble growth, the effect of bubble rising is very slight because the bubble size is small and then the bubble rising velocity is small. Consequently, these two models coincide with each other. Deviations between the quasi-stationary model for a rising bubble and that for a stationary bubble increase with time.

In the case of the quasi-steady model for a stationary bubble, it is seen from equation (7) and figure 2a that



Figures 2a to c. Sherwood number for a bubble initially containing 100% N₂; a) oxygen at 1773.15 K, b) oxygen at 1473.15 K, c) nitrogen at 1773.15 K. Curve 1: quasi-stationary model for a rising bubble, curve 2: quasi-steady model for a rising bubble (Ramos' model), curve 3: quasi-stationary model for a stationary bubble, curve 4: quasi-steady model for a stationary bubble.

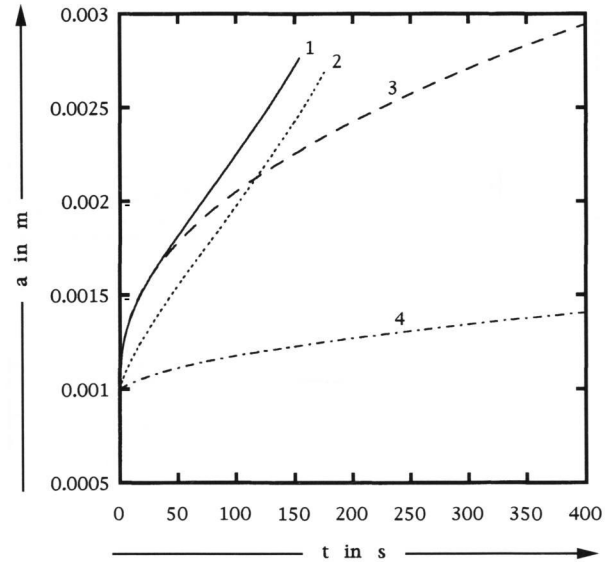


Figure 3. Bubble radius versus time for a bubble initially containing 100% N₂ at 1773.15 K. Curve 1: quasi-stationary model for a rising bubble, curve 2: quasi-steady model for a rising bubble (Ramos' model), curve 3: quasi-stationary model for a stationary bubble, curve 4: quasi-steady model for a stationary bubble.

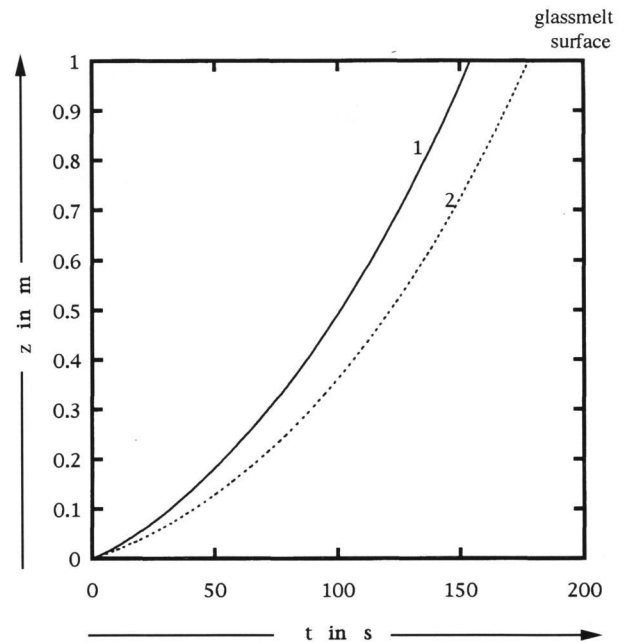
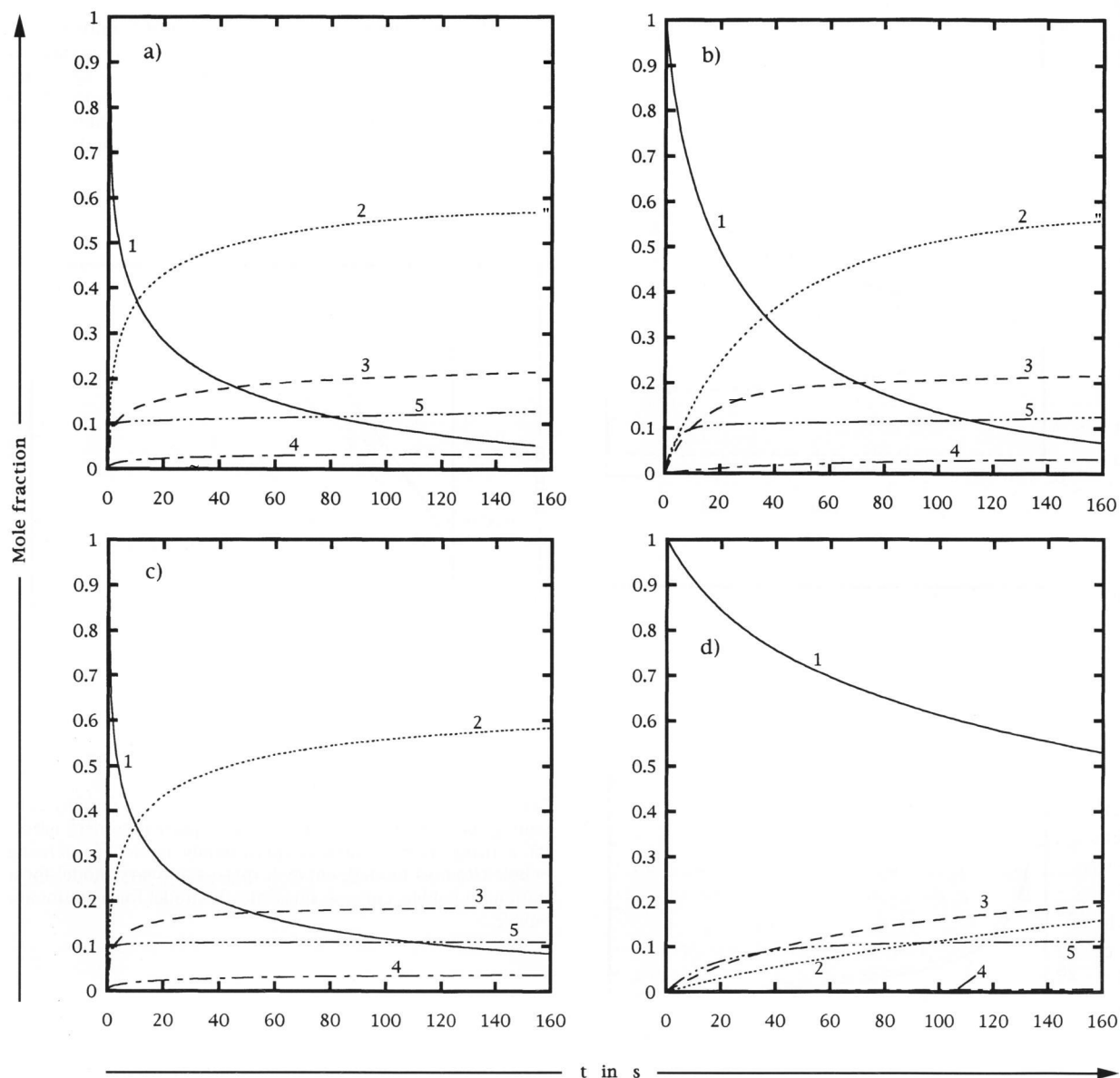


Figure 4. Bubble location versus time for a bubble initially containing 100% N₂ at 1773.15 K. Curve 1: quasi-stationary model, curve 2: quasi-steady model.



Figures 5a to d. Mole fractions of gases in a bubble versus time at 1773.15 K for a bubble initially containing 100% N_2 ; a) quasi-stationary model for a rising bubble, b) quasi-stationary model for a rising bubble (Ramos' model), c) quasi-stationary model for a stationary bubble, d) quasi-stationary model for a stationary bubble. Curve 1: N_2 , curve 2: SO_3 , curve 3: O_2 , curve 4: CO_2 , curve 5: H_2O .

the Sherwood number is constant. Since the model assumes a steady-state and no bubble rising, Sh_i does not change with time. The quasi-stationary model for the stationary bubble can be found to underestimate the mass transfer coefficient for O_2 significantly.

The Sherwood numbers for oxygen at 1473.15 K are shown in figure 2b. The $Sh(O_2)$ number for the rising bubble monotonically decreases with time and has no minimum value unlike the result at 1773.15 K. The quasi-stationary model for the stationary bubble predicts only a slightly increase in $Sh(O_2)$. It is found that the predictions of the quasi-stationary models for the rising bubble and the stationary bubble agree well with each

other. Since the temperature of the melt is low, the growth rate of bubble and hence the bubble rising velocity are very slow as if the stationary bubble.

As shown in figure 2c, the change in $Sh(N_2)$ at 1773.15 K with time is similar to that in $Sh(O_2)$. However, a minimum value of $Sh(N_2)$ occurs at $t = 70$ s. Because the bubble initially contains N_2 only, N_2 diffuses away from the bubble.

Figure 3 illustrates the time dependence of the bubble radius. The initially sharp concentration gradients at the bubble surface which contribute to the rapid growth for short time in the quasi-stationary approximation do not contribute to the quasi-steady solution. In the earlier

stages of the bubble growth, the quasi-steady approximation underestimates the concentration gradient or the driving force of mass transfer at the surface and as a result the bubble growth rate by ignoring the transient mass transfer regime. For this reason, the quasi-stationary model proposed in this study appears to give superior results as compared with the quasi-steady models in the literature. For $t > 50$ s, the quasi-stationary model predicts that the bubble radius increases nearly linearly with time. The bubble grows continuously until the bubble reaches the glassmelt surface. The quasi-stationary solution for a rising bubble is in good agreement with the quasi-stationary solution for a stationary bubble during an initial period of bubble growth ($t < 50$ s) and at longer times agrees reasonably with the quasi-steady model of Ramos [19]. It is clear from figure 3 that the rates of bubble growth for the rising bubble are larger as compared with those for a stationary bubble.

The bubble location is illustrated as a function of time in figure 4. The quasi-stationary model predicts that the refining time defined as the time required for the bubble to reach the glassmelt surface is 154 s. The refining time evaluated by Ramos' model is 178 s which is about 15% larger than that obtained by the quasi-stationary model.

In figure 5a, the mole fractions of nitrogen, oxygen, carbon dioxide, water and sulfur trioxide in the bubble predicted by the quasi-stationary model for the rising bubble are shown as a function of time. During the refining process, the mole fraction of N_2 always decreases, whereas the mole fractions of O_2 , SO_3 , CO_2 and H_2O increase with time. It should be noted that the number of moles of nitrogen in the bubble is almost constant because its diffusivity and solubility are very small. Sulfur trioxide, water and oxygen the diffusivities of which are large diffuse from the glassmelt to the bubble. As a result, the mole fraction of N_2 decreases with time. In the case of the present numerical examples, the bubble growth occurs mainly due to the entrance of SO_3 and O_2 . Since the solubility and the driving force of SO_3 in the melt are quite large, the SO_3 diffusion is rather faster than the diffusions of other species. During the first few ten seconds rapid growth occurs mainly due to the entrance of SO_3 into the bubble.

Figure 5b depicts the predictions obtained by the quasi-steady model of Ramos [19] for the mole fractions of the species in the bubble. It is apparent from figures 5a and b that at short times the quasi-steady model underestimates the mass transfer rates. According to the quasi-stationary model, as shown in figure 5a, the nitrogen concentration in the bubble decreases quite rapidly at the beginning. At about 10 s the mole fraction of N_2 decreases to 0.35. However, the quasi-steady model predicts rather slow change in nitrogen concentration in the bubble. As seen in figure 5b, the quasi-steady model predicts that the decrease in the N_2 mole fraction from 1 to 0.35 requires about 35 s.

In figure 5c the mole fractions in the bubble calculated by the quasi-stationary model for the stationary bubble are given. It can be found from figures 5a and c that the transitional motion of the bubble only slightly affects the change of mole fractions with time.

As shown in figure 5d the predictions of the quasi-steady model for the stationary bubble are quite different from those obtained by other models shown in figures 5a to c. The quasi-steady model predicts considerably slow diffusion of species as compared with the results of the quasi-stationary model shown in figure 5c.

4. Conclusions

From the viewpoint of mass transfer at the bubble surface, the quasi-stationary and quasi-steady approximations were examined. A quasi-stationary model for the growth of a multicomponent bubble rising in a glassmelt has been developed. The quasi-stationary model based on unsteady-state mass transfer is more rational compared with the quasi-steady model based on steady-state mass transfer. Numerical results indicate that the quasi-steady model may underestimate the mass transfer coefficient and overestimate the refining time both for the rising bubble and the stationary bubble. The quasi-stationary model proposed in this study may be superior to the quasi-steady models in the literature to describe the behavior of multicomponent bubbles rising in the glassmelts. This work was undertaken as a starting point for the simulation of the glass refining processes.

5. Nomenclature

5.1 Symbols

a	bubble radius in m
C	concentration in glassmelt in mol m^{-3}
D	diffusivity in $\text{m}^2 \text{s}^{-1}$
g	gravitational acceleration in m s^{-2}
H	bubble location at $t = 0$ in m
k	mass transfer coefficient in m s^{-1}
L	Henry's law constant in $\text{mol m}^{-3} \text{Pa}^{-1}$
n	number of moles in mol
P	bubble pressure in Pa
Pe	Péclet number ($= 2aU/D$)
p	partial pressure in Pa
p_a	atmospheric pressure above the glassmelt in Pa
R_g	gas constant in $\text{J mol}^{-1} \text{K}^{-1}$
Re	Reynolds number ($= 2aU/v_G$)
r	radial coordinate in m
Sc	Schmidt number ($= v_G/D$)
Sh	Sherwood number ($= 2ak/D$)
T	temperature in K
t	time in s
U	bubble rising velocity in m s^{-1}
V	bubble volume in m^3
$v(t,r)$	radial velocity in m s^{-1}
z	bubble location with respect to the initial bubble location in m
θ	angular coordinate in rad
μ	dynamic viscosity in Pa s
ν_G	kinematic viscosity in $\text{m}^2 \text{s}^{-1}$
ρ_G	density in kg m^{-3}
σ	surface tension in N m^{-1}

5.2 Subscripts

i	species
s	surface
∞	value at large r values

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