Evaporation, Diffusion and Convection in Containerless Melts at Low Gravity

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Nomenclature

D = diffusion coefficient
k = evaporation rate parameter; $k_0 = k(T_0)$
N_{Le} = α/D, Lewis number
N_{Ma} = $|(\partial\sigma/\partial T)\ (\partial T/\partial z)|R^2/\mu\alpha$, Maragoni number
N_{Sh} = $k_0 R/D$, Sherwood number
$N_{Sh}^{(1)}$ = $|(\partial k/\partial T)\ (\partial T/\partial z)|R^2/D$, modified Sherwood number
R = radius of the spherical melt
T_0 = average surface temperature
α = thermal diffusivity
μ = viscosity
σ = surface tension
τ = Dt/R^2, dimensionless time

Theme

SPACE with its vacuum and its near-zero gravity offers a place for containerless purification of melts. Nonconducting refractory materials can be levitated easily for containerless purification in a space laboratory, such as the Space Shuttle, thereby eliminating the earthbound problem of contamination by a container. These materials may find uses as analytical standards and as materials for research.

We will describe here a technique for estimating evaporative purification rates. This technique takes account of the chemical environment and evaporation at the melt surface and of the convective diffusion within the melt.

Contents

Our description of evaporative purification begins with the phenomenological expression

$$J_i = k_i c_i \tag{1}$$

relating the magnitude of the evaporative flux J_i to the surface concentration c_i of the component i. The rate parameter k_i depends upon the complex chemical equilibria within the melt, near the melt surface. By modifying the previous work on complex equilibria,[1] we have developed equations and a computer code for specifically handling the problems of evaporation into vacuum, and into a partial vacuum with a low pressure of an oxidizing or reducing gas. These calculations assumed a well-stirred liquid and provide an estimate of k_i which is used in the convective diffusion problem.

The general complex equilibria formalism of Kandiner and Brinkley,[1] upon which our adaptations are principally based, involves the use of a series of mass balance equations for the independent species of the system and a series of equilibrium constant equations for the dependent series. The equilibrium constant equations, in turn, involve relationships between the masses, the pressures and the activities of the various species. To describe the evaporation of a well-stirred melt into vacuum, we modified the formalism using the Knudsen equation and the ideal solution theory. The calculational approach is quite general and allows for relatively easy and direct modifications to describe a variety of situations of practical interest.

Our calculations show that for a well-stirred liquid rapid evaporative purification of refractories in vacuum may be obtained. Table 1 shows the results of calculations for Al_2O_3 evaporative purification in vacuum at 2400 K, where 10 mole-ppm FeO and 10 ppm SiO_2 impurities are initially present. Row 2 of the table shows that the rate of Al_2O_3 loss is very low, while rows 3 and 4 show that FeO and SiO_2 concentrations are approximately halved after only one second. In the table we also give the total pressure of the evaporated species (the computations yield the partial pressures of all gaseous species participating in the complex chemical equilibria[2]).

High rates of purification can result in a depletion of impurities at the surface and in concentration gradients within the melt. When homogeneity of the melt is desired, it can be accomplished by slowing the purification rates to allow time for better mixing. Slower purification of Al_2O_3 can be obtained by exposing the melt to a low ambient oxygen pressure. The pressure can be kept low enough to maintain molecular (Knudsen) flow conditions and yet can be high enough to shift chemical equilibria and slow the vaporization rates. Table 2 lists some results for the evaporative purification of molten Al_2O_3 containing 10 ppm CaO for evaporation into a vacuum and for evaporation into a partial vacuum containing 10^{-5} atm

Table 1 Vacuum evaporation of Al_2O_3 + 10 ppm FeO + 10 ppm SiO_2 (2400 K)

Elasped time,s	0.005	1.000
Moles of species present in melt		
Al_2O_3	1.00E+00	1.00E+00
FeO	9.98E-06	7.02E-06
SiO_2	9.97E-06	5.30E-06
Total pressure of gaseous species (atm)		
	8.11E-06	7.47E-06

Table 2 Vacuum evaporation of Al_2O_3 + 10 ppm CaO (2400K)

Esapsed time, s	0.005	60.000	0.005	60.000
	Absolute vacuum		Partial vacuum	
Al_2O_3 (Moles)	1.00E+00	9.99E-01	1.00E+00	1.00E+00
CaO	1.00E-05	8.04E-06	1.00E-05	9.34E-06

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oxygen. The higher oxygen pressure for the partial vacuum case shifts the equilibrium away from the reduced vapor species Ca(g) by the reaction $\mathrm{Ca(g)+O(g)\rightarrow CaO(\ell)}$, and this causes slower, more controlled, rates of purification. Some evaporative purification experiments may actually involve controlling the level of impurity or dopant within the sample.

Stirring is highly desirable since it improves sample homogeneity and aids in the purification process. It brings impurities to the surface where they can be expelled from the melt by vaporization. An actual melt may not be well-stirred, in which case the rate of purification will be less than in the "ideal" melt. In addition to the transport of material by convection, the nonhomogeneous concentrations in the actual melt will give rise to diffusion. Thus, the concentrations of a component at the surface will depend upon its rate of evaporation and upon its rate of transport to the surface by both convection and diffusion in the melt.

At zero-g, if surface tension gradients (surface transactions) are present to drive convection, mass transport from the interior of the melt to the surface will occur by convective diffusion. Surface tractions may arise from either temperature gradients or concentration gradients along the surface. We treat here the case of dilute impurity concentrations and assume that for this case a thermal surface traction can be imposed which predominates over the solutal surface traction.

Our model of convective diffusion in a spherical melt assumes a steady nonconvective temperature field with a constant temperature gradient—the gradient defining the z-axis. The evaporation rate parameter is assumed to depend linearly on the surface temperature. An Arrhenius relation which gives a more correct temperature-dependence for k improves the estimated evaporation rates by less than 0.2% in our case of CaO evaporating from molten alumina. The steady fluid velocity field is described by formulas adapted from the work of Young, et al.[3] The method of Green's functions[4] is used to integrate the convective diffusion equation, and the expansion of the solution as a series of spherical harmonics is terminated at the first-order terms. The series expansion of the concentration function can be substituted into Eq. (1), and the resulting expression can be integrated over the surface of the melt to obtain the evaporation rate. The total evaporation rate consists of 3 components: a pure radial diffusion component (V_{1D}) given by Crank,[5] a correction (V_{2D}) for the asymmetry of the radial concentration gradient, and a convective component (V_{2U}). The details of the last two terms are given elsewhere.[6] For $(\partial T/\partial z) \leq 10$ K/cm and $\tau < 10^{-2}$, V_{2D} and V_{2U} can be taken as proportional to $\tau \cdot V_{1D}$. In this approximation, V_{2U} exceeds V_{1D} when $\tau > 18\pi^4/N_{Sh}N_{Sh}^{(1)}N_{Ma}N_{Le}$. Also, for CaO in molten alumina, $N_{Ma}N_{Le} > N_{Sh} > N_{Sh}^{(1)}$ so that $V_{2U} > V_{2D}$.

By integrating the evaporation rate with respect to time from 0 to τ, the fractional impurity loss $M_{\mathrm{tot}}/M_\infty$ can be obtained. Approximately,

$$M_{\mathrm{tot}}/M_\infty = M_{1D}/M_\infty + [-(N_{Sh}^{(1)})/^{2}6\pi N_{Sh} + N_{Sh}N_{Sh}^{(1)}N_{Ma}N_{Le}/18\pi^4] \cdot \left[M_{1D}/M_\infty - M_\infty^{-1}\int_0^\tau d\tau' \int_0^{\tau'} d\tau''\, V_{1D}(\tau'')\right] \tag{2}$$

where M_{1D}/M_∞ is obtained from V_{1D}. For $N_{Sh} > 10$, the integral in Eq. (2) can be evaluated as if N_{Sh} were infinite.

Estimates of the fractional loss of CaO impurity from molten alumina at two values of T_0, 2400 and 2600 K, are plotted in Fig. 1 against the elapsed time τ. M_{1D}/M_∞, $M_{\mathrm{tot}}/M_\infty$ and the fractional loss M_{WS}/M_∞ for a well-stirred drop are shown in the figure. The differences between $M_{\mathrm{tot}}/M_\infty$ and M_{1D}/M_∞ is approximately the value of the convective component. The data for the calculation of these curves is from the following sources: 1) k and $(\partial k/\partial T)_{T_0}$ from the present complex equilibria analysis: 2) μ from Bates, et al.;[7] and 3) $(\partial\sigma/\partial T)$ and D as order of magnitude estimates, -0.1 dyn/cm$\cdot K$ and 10^{-5} cm^2/sec, respectively. A possible temperature dependence of D is ignored resulting in only one curve for M_{1D}/M_∞. A temperature gradient of 1 K/cm is used. Using these data the dimensionless groups N_{Sh}, $N_{Sh}^{(1)}$ and $N_{Ma}\cdot N_{Le}$ have the following values: 700, 10, and 4×10^4 at 2400 K; and 2700, 40 and 8×10^4 at 2600 K.

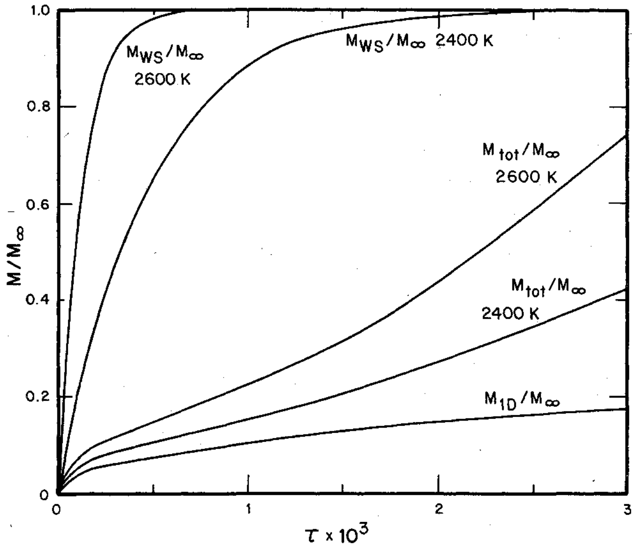

Fig. 1 Fractional loss of CaO from a spherical melt of $\mathrm{Al_2O_3}$.

Figure 1 shows that a very modest temperature gradient of 1 K/cm can produce sufficient circulation to raise the purification rate appreciably above the diffusion-controlled rate. A larger temperature gradient would bring the purification rate closer to the limiting rate obtained with the well-stirred melt.

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