Volatilization of Volatile Constituent from Lead-glass Melts

By

Masanaga KUNUGI*, Hiroshi JINNO* and Ginjiro KAMBARA*

The kinetics of volatilization of a volatile constituent from the surface of glass melts containing lead oxide for the temperature range of 1100° to 1500°C have been studied with a thermal balance. From the results obtained, it was concluded that both the evaporation-rate coefficient at the surface of the glass melts and the diffusion coefficient of the volatile constituent in the glass melts are controlling factors of the overall rate of volatilization in the system.

1. Introduction

The kinetics of volatilization of a volatile constituent from the surface of glass melts containing lead oxide have been studied for the temperature range of 1100° to 1500°C.

2. Volatilization process from glass melts

The volatilization process from glass melts can be considered to consist of successive three steps. They are the diffusion in the melt, the evaporation at surface of the melt, and the flying away from the surface into atmosphere. Thus, the overall rate of the volatilization, V, is expressed by the rate of diffusion within the melt, D, the rate of the evaporation at surface, E, and the rate of the flying away into atmosphere, F, as shown in the following equation;

$$\frac{1}{V} = \frac{1}{D} + \frac{1}{E} + \frac{1}{F} \tag{1}$$

In general, the mass transportation in gaseous phase is so faster than the diffusion within the melt that we can neglect the term F. Then, the volatilization process can be expressed by the equation of diffusion with a boundary condition referring to the evaporation process at the surface.
Namely,

---

* Department of Industrial Chemistry.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

where C=concentration of the volatile constituent in the glass melt (g/cm³), t= time (sec), x=vertical distance from the bottom of the crucible (cm), D=diffusion coefficient of the volatile constituent in the melts (cm²/sec).

The boundary conditions are;

$$-D\frac{\partial C}{\partial x} = kC \quad \text{at the surface,} \ x = a \,,$$

and

$$\frac{\partial C}{\partial x} = 0 \quad \text{at the bottom,} \ x = 0 \,,$$

where k=rate coefficient for the evaporation process at the surface (cm/sec), a=depth of the glass melt (cm).

The initial condition is;

$$C = C_0 \quad \text{for} \quad t = 0$$

where C_0=original concentration of the volatile constituent (g/cm³).

By the use of the system of dimensionless variables,

$$\varphi = C/C_0 \,, \quad \alpha = ak/D \,, \quad \xi = x/a \,,$$

$$\tau = Dt/a^2 \,, \quad \varPhi = (\int_0^t kC_{x=a}\,dt)/aC_0 \,,$$

the solution for φ which satisfies the given conditions is obtained as

$$\varphi = \sum_{s=0}^{\infty} \frac{2 \exp\,(-m_s^2\tau)}{1+\alpha+\dfrac{m_s^2}{\alpha}} \cdot \frac{\cos m_s\xi}{\cos m_s} \,, \tag{3}$$

where m_s is the $(s+1)$-th root of the equation

$$m_s \tan m_s = \alpha \,.$$

Then, the ratio of the quantity of the volatile constituent volatilized up to the time t to its initial quantity in the melt, $\varPhi$, is given as

$$\varPhi = 1 - \sum_{s=0}^{\infty} \frac{2 \exp\,(-m_s^2\tau)}{\left(1+\alpha+\dfrac{m_s^2}{\alpha}\right)\dfrac{m_s^2}{\alpha}} \,. \tag{4}$$

From the above equation, the curves showing the relation between the relative volatilized quantity, $\varPhi$, and dimensionless time, $\tau = Dt/a^2$, are obtained for various values of the parameter, $\alpha = ak/D$, as shown in Fig. 1. In this figure,
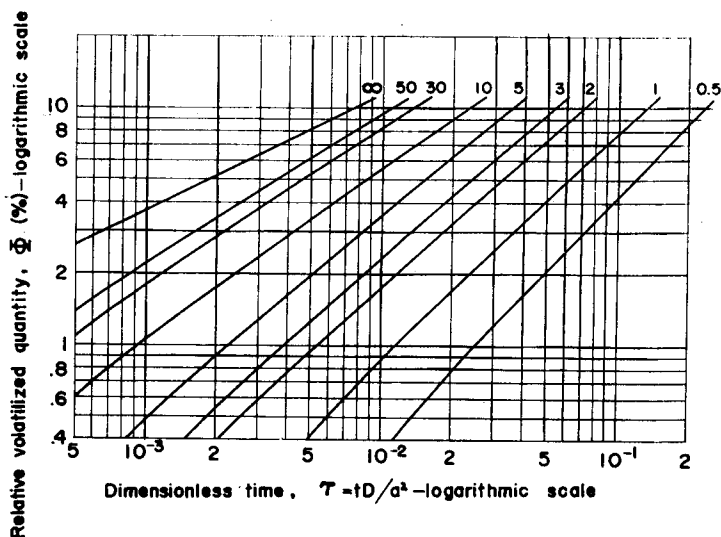
Fig. 1. The relative volatilized quantity against the dimensionless time.
Figures on the curves refer to the values of parameter, $\alpha = ak/D$.

the numbers on the curves are the values of the parameter α. The infinity of α means a case controlled by only the diffusion process. That is the case with a very small value of diffusion coefficient, D, compared with the rate coefficient of evaporation, k, or the case for a very large value of the depth of the melt, a.

The curves in Fig. 1 show that the plotting of log Φ versus log τ gives nearly straight lines and the slope of these lines becomes smaller with increasing value of α. Therefore, if we draw such a curve experimentally, we can determine the value of α from the slope of the line obtained experiemntally. And we can determine get the value of diffusion coefficient, D, from the ratio of dimensionless time τ to real time, t, at a certain value of Φ.

3. Experimental

As the samples, two commercial lead glasses containing approximately 57 and 68 weight per cent of lead oxide, respectively, were used. The nominal composition of the samples is shown in Table I.

A rough sketch of the experimental apparatus is shown in Fig. 2. The weighed sample was placed into a platinum crucible having 20 mm in diameter, and suspended from the thermal balance in an electric furnace with silicon carbide heat elements. The depth of one crucible was 25 mm and the depth of glass melt in it was 20 mm. The other crucible had a depth of 12 mm, and the depth of glass melt in it was 6 mm. The quantities of the volatile constituent volatilized from the

Table 1. Nominal composition of the samples (Weight per cent).

Glass no.	1	2
SiO_2	29.0	34.0
Al_2O_3	0.4	0.3
B_2O_3	1.0	2.0
PbO	67.6	56.6
Na_2O	—	2.1
K_2O	2.0	5.0

A : direct reading balance

B : 20%Rh-Pt wire (1mm in diameter)

C : electric furnace

D : 13%Rh-Pt/Pt thermocouple

E : silicon carbide heater

F : Pt crucible

G : alumina crucible
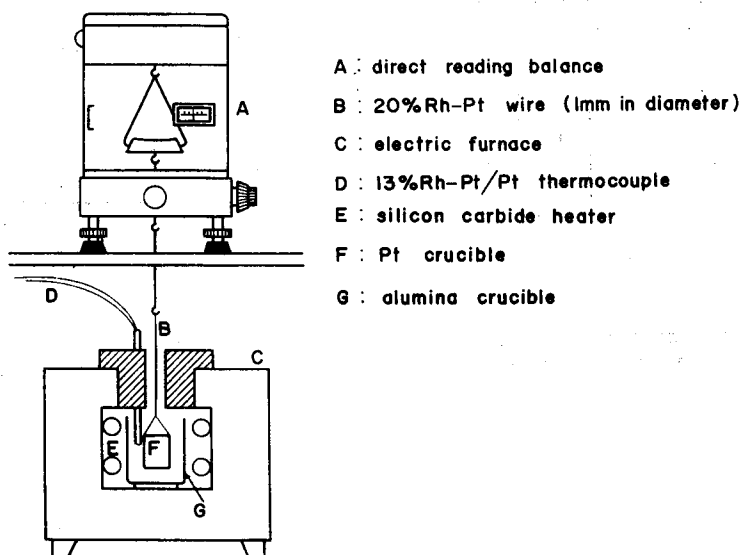
Fig. 2. Sketch of experimental apparatus.

sample in the temperature range of 1100° to 1500°C were determined by measuring the loss in weight of the sample with the thermal balance. The particular emphasis was given to the studies of the influence of temperature and of the depth of the glass melt on the rate of volatilization.

4. Experimental results and discussion

Percentage ratios of the weight losses of the glass melts to their initial lead oxide contents as the functions of time and temperature are shown in Fig. 3–Fig. 6. It can be seen from the figures that the rate of volatilization is most strongly influenced by temperature.

By comparing the experimental data with the theoretical curves for the rate of volatilization, the diffusion coefficient within the melt, D and the rate coefficient of evaporation process at the surface of the melt, k, can be estimated at various
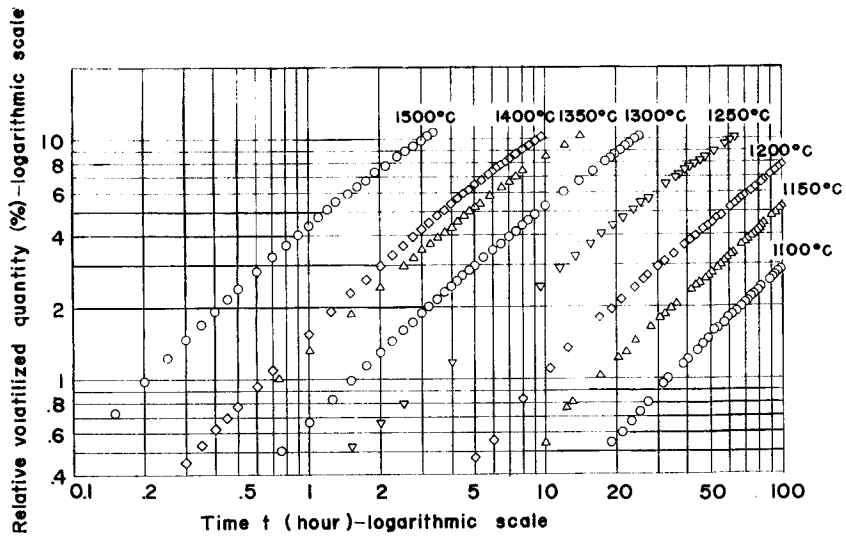
Fig. 3.   The relative volatilized quantity against the time (hour) at constant temperatures for the lead-glass melt containing approximately 57% lead oxide with the depth of 20 mm.
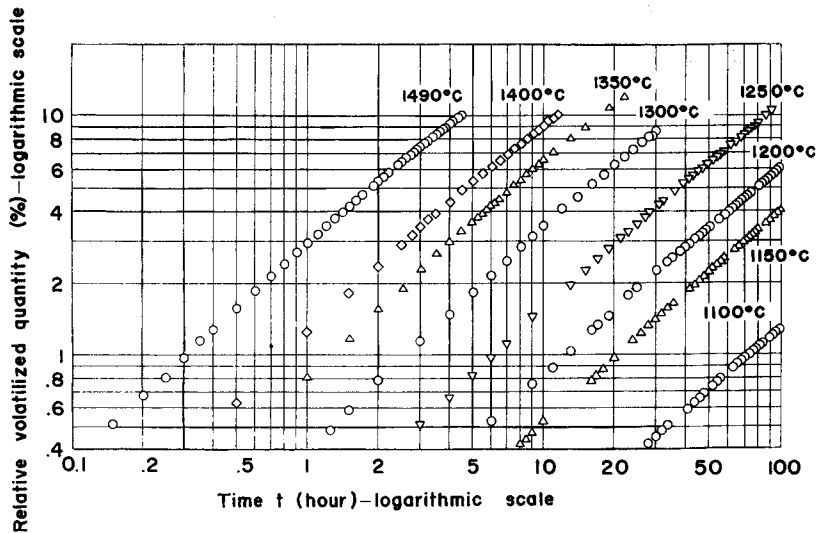

Fig. 4.   The relative volatilized quantity against the time (hour) at constant temperatures for the lead-glass melt containing approximately 68% lead oxide with the depth of 20 mm.
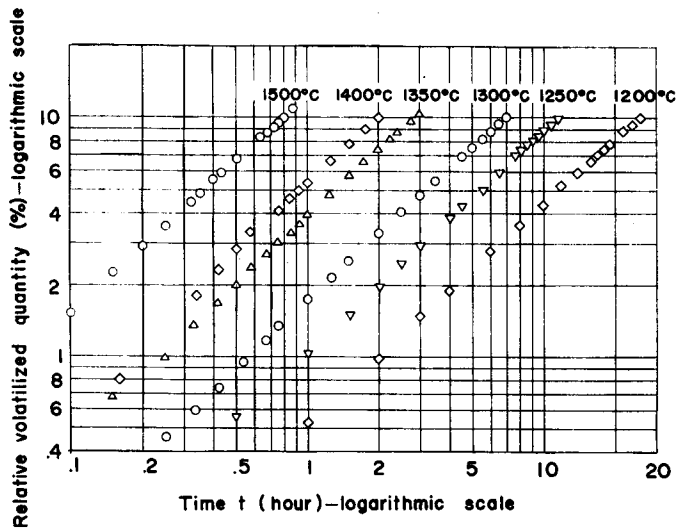
Fig. 5. The relative volatilized quantity against the time (hour) at
constant temperatures for the lead-glass melt containing
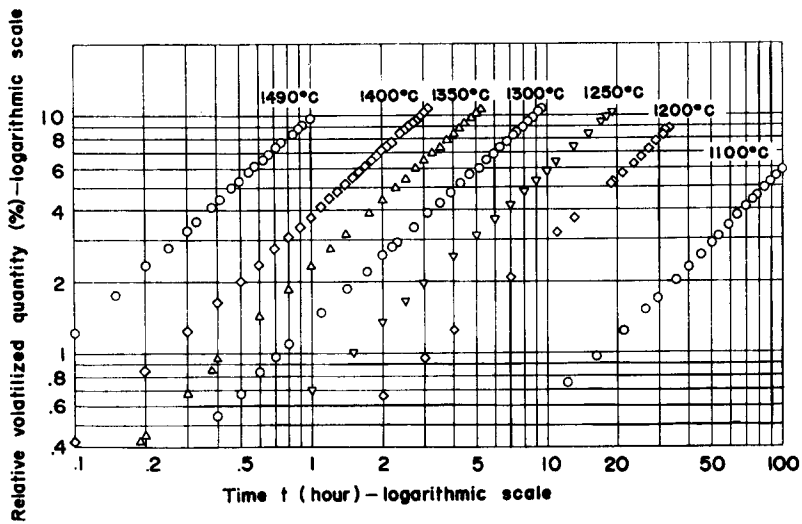approximately 57% lead oxide with the depth of 6 mm.

Fig. 6. The relative volatilized quantity against the time (hour) at constant
temperatures for the lead-glass melt containing approximately 68% lead
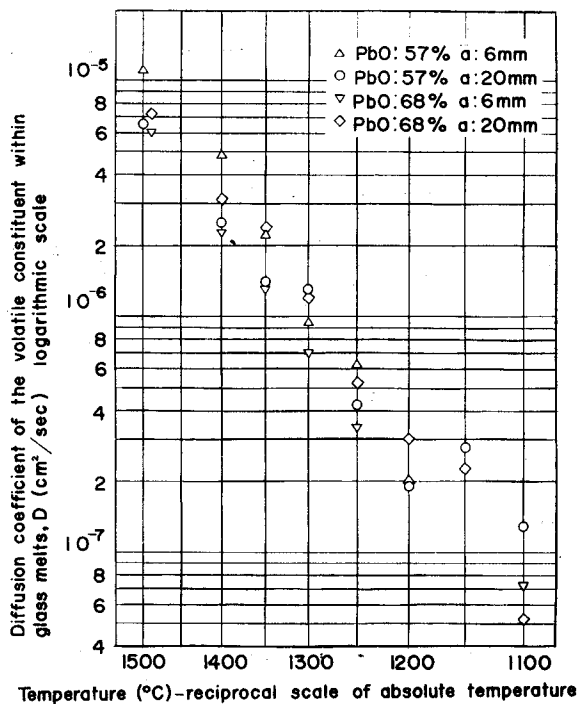oxide with the depth of 6 mm.

Fig. 7.   Diffusion coefficient of the volatile constituent within glass melts as a function of the reciprocal of the absolute temperature.
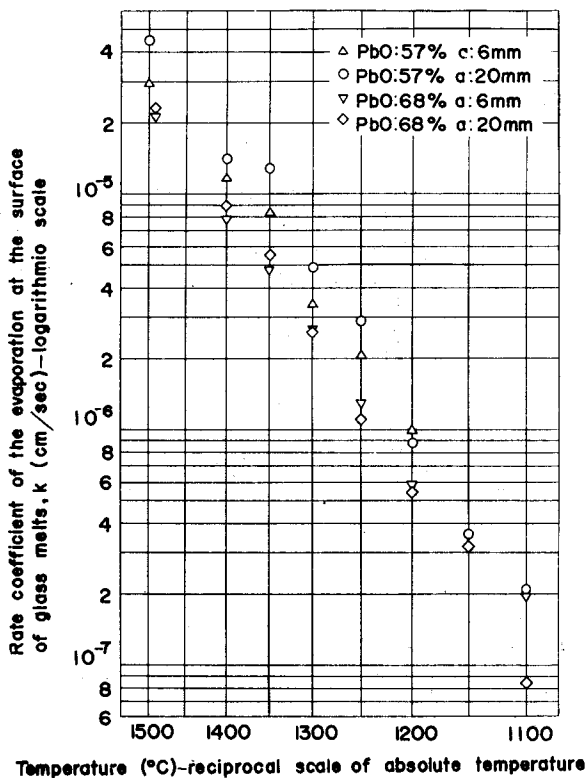

Fig. 8.   Rate coefficient of the evaporation process at the surface of glass melts as a function of the reciprocal of the absolute temperature.
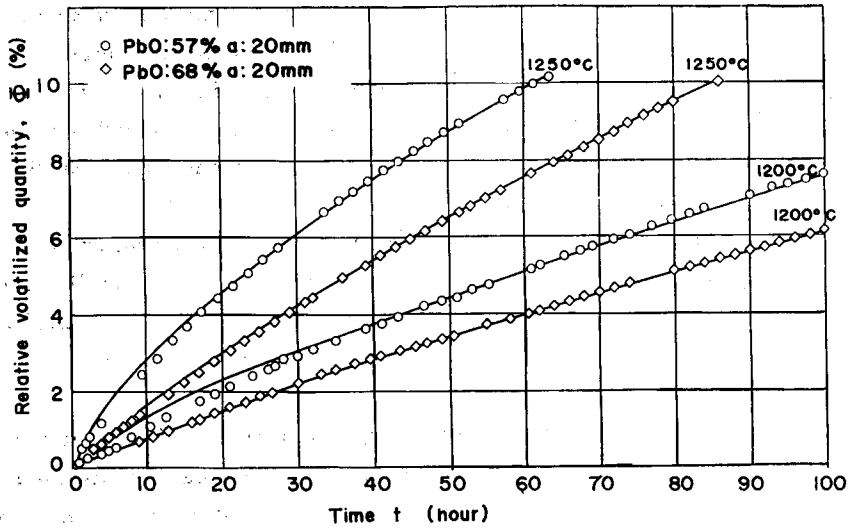
Fig. 9. Experimental plots and theoretical curves of the relative volatilized quantity against the time at constant temperatures for the lead glass melts.
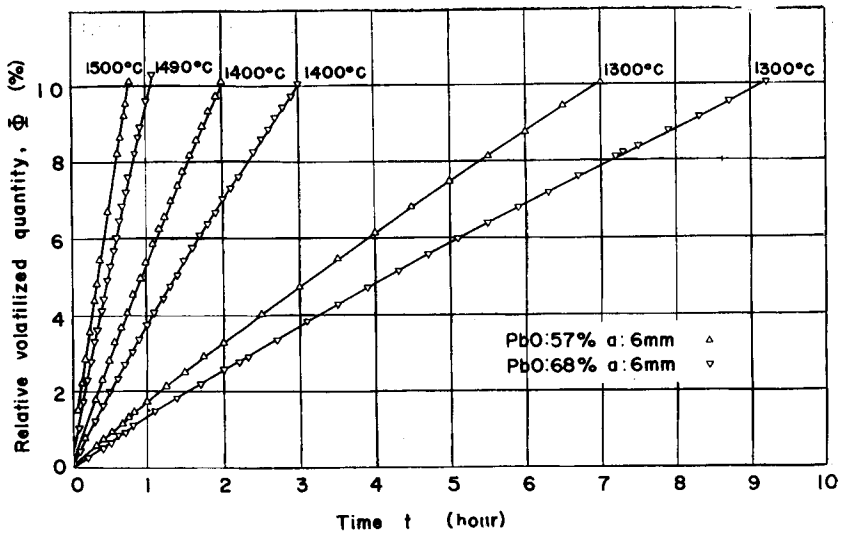

Fig. 10. Experimental plots and theoretical curves of the relative volatilized quantity against the time at constant temperatures for the lead glass melts.

temperatures. Their values are plotted in Fig. 7 and Fig. 8. As shown in the figures, the values of D or k obtained for definite temperatures are almost the same.

From the values of the evaporation-rate coefficient and the diffusion coefficient for the temperature range of 1100° to 1500°C, the activation energies of the processes, which are proportional to the slopes of the lines in Fig. 7 and Fig. 8, were calculated. The value of the activation energy for the rate coefficient of evaporation at the surface was estimated to be about 65 kcal/mole and that for the diffusion coefficient about 60 kcal/mole.

To examine the suitability of the theory to the real volatilization process we computed and drew the volatilization curve with constants, k and D, obtained as above. Some comparison of the curve with the experiment is given in Fig. 9 and Fig. 10, and good agreement between the experiment and theory was found as shown in the figures.

This would suggest that both the evaporation rate coefficient at the surface of the glass melts and the diffusion coefficient of the volatile constituent in the glass melts are controlling factors of the overall rate of volatilization in the system.

5. Conclusion

The rate of volatilization of a volatile constituent from the surface of glass melts containing lead oxide for the temperature range of 1100° to 1500°C can be considered to be governed by both the evaporation-rate coefficient at the surface of the glass melts and the diffusion coefficient of the volatile constituent in the melts.