Rate of Volatilization of a Volatile Constituent from Surface of Glass Melts Containing Lead Oxide

By

Masanaga Kunugi*, Hiroshi Jinno* and Ginjiro Kambara*

A thermal balance technique has been used to study the kinetics of volatilization of a volatile constituent from the surface of glass melts containing lead oxide for extended periods of time in the temperature range 1100° to 1500°C. Distributions of density and refractive index of the glass after heat-treating at 1200–1300°C were also determined.

1. Introduction

The volatilization process from glass melts is interesting from both the theoretical and practical point of view. Several investigations concerning this problem have been published recently[1]−[4]. We believe, however, that further more quantitative data are necessary for the solution of this problem. The purpose of the present work is to evaluate the rate of volatilization of a volatile constituent from the surface of glass melts containing lead oxide and determine the distributions of density and refractive index in the glasses.

2. Experimental

As the samples, two commercial glasses were used. The nominal composition of the samples is shown in Table 1.

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

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

The quantities of the volatile constituent volatilized from the 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 details of the apparatus have

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* Department of Industrial Chemistry

been described previously[4]. The weighed sample was placed into a platinum crucible and suspended from the thermal balance in an electric furnace with silicon carbide heat elements. Four different depths, that is, 3, 6, 10 and 20 mm, of glass melts in the crucible were prepared. The emphasis was given to the study of the effect of temperature on the rate of volatilization. Density and refractive index of the glass samples after heat-treating at 1200–1300°C were also determined.

3. Experimental results and discussion

The theoretical equation expressing the volatilization process has been given in the previous report[4]. From the equation, the curves showing the relation between the ratio of the quantity of the volatile constituent volatilized up to time t to its intial quantity ϕ, and dimensionless time, $\tau = Dt/a^2$, are obtained for various values of the parameter, $\alpha = aK/D$, as shown in Fig. 1, where D=diffusion coefficient of the volatile constituent in the melts (cm^2/sec), t=time (sec), a=depth of the glass melts (cm), and k=rate coefficient for the evaporation process at the surface (cm/sec). In this figure, the numbers on the curves are the values of the parameter α. The curves in Fig. 1 show that the plotting of log ϕ versus log τ gives nearly straight lines. If we draw such a curve experimentally, we can determine the value of α from the slope of the line. Percentage ratio of the weight losses of the glass melts to their initial lead oxide contents as the functions of time and
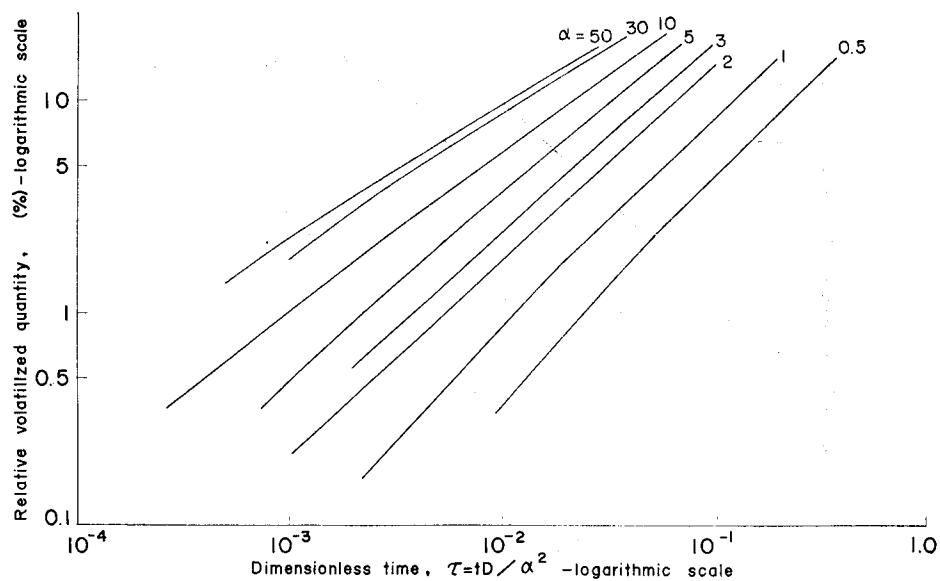

Fig. 1. The relative volatilized quantity against the dimensionless time.

temperature are shown in Fig. 2–Fig. 5.   The figures indicate that the rate of loss of constituent is a markedly temperature dependent.

By comparing the experimental data with the theoretical curve for the rate of volatilization, the diffusion coefficient within the melt, D, and the rate coefficient
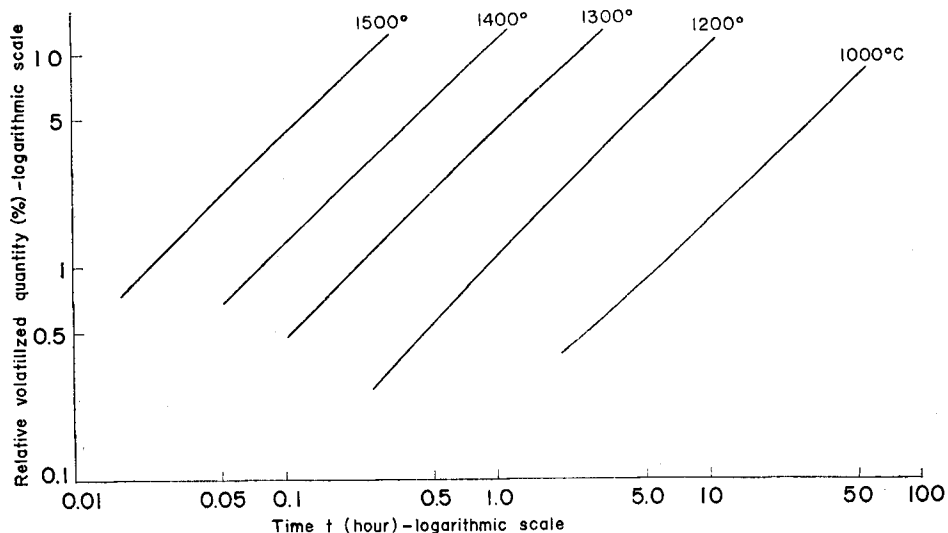

Fig. 2.   The relative volatilized quantity vs. the time (hour) at constant temperatures for Glass No. 1 with the depth of glass = 3 mm.
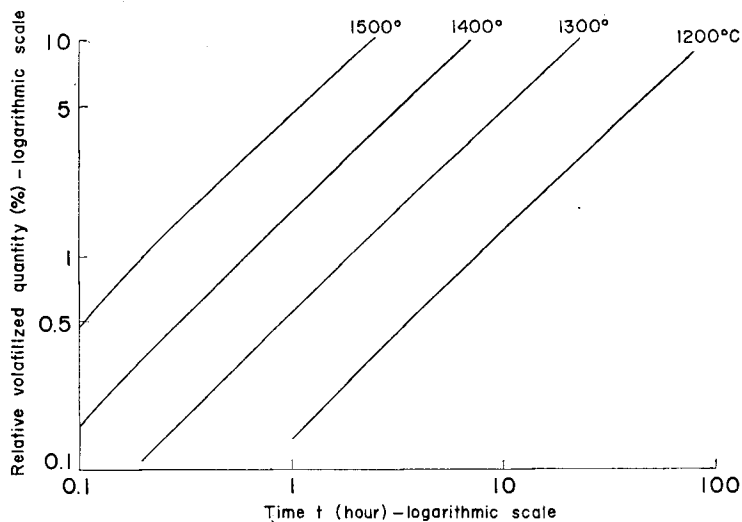

Fig. 3.   The relative volatilized quantity vs. the time (hour) at constant temperatures for Glass No. 1 with the depth of glass = 10 mm.
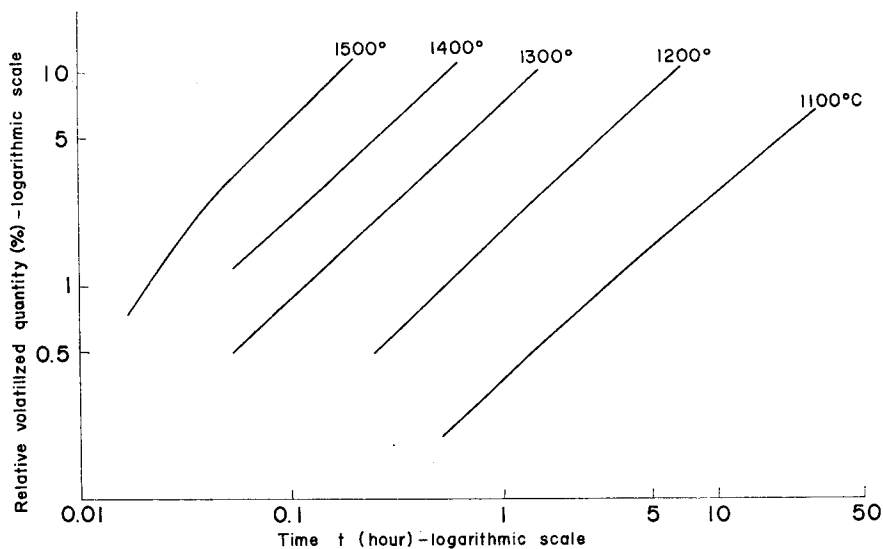
Fig. 4. The relative volatilized quantity vs. the time (hour) at constant temperatures for
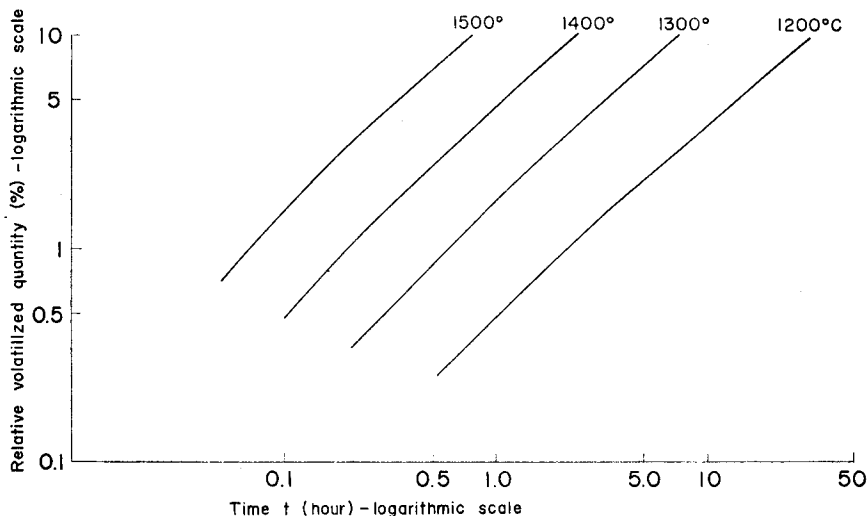Glass No. 2 with the depth of glass=3 mm.

Fig. 5. The relative volatillzed quantity vs. the time (hour) at constant temperatures for
Glass No. 2 with the depth of glass=10 mm.

of evaporation process at the surface of the melt, k, can be estimated at various
temperatures.   From the values of the diffusion coefficient and evaporation rate
coefficient for the temperature range of 1100° to 1500°C, the activation energies for
the volatilization process were calculated.   Their values are given in Table 2.

Table 2. Kinetics constants for volatilization process.

Glass No. 1

depth of melts (mm)	E_D (kcal/mole)	E_k (kcal/mole)
3	68	66
6	62	62
10	59	68
20	55	68

Glass No. 2

depth of melts (mm)	E_D (kcal/mole)	E_k (kcal/mole)
3	69	56
6	70	60
10	64	68
20	55	70

E_D; activation energy for diffusion in melts.
E_k; activation energy for the evaporation at the surface.

As shown in the Table, the values of activation energies for different depth of melts are almost the same. This result would suggest that both the evaporation rate coefficient at the surface of the melts and the diffusion coefficient of the volatile

Table 3. Initial rate of volatilization, J_0 (gr/cm²·sec). Comparison of theory with experiment.

Glass No. 1

depth of melts (mm)	temperature (°C)	α	J_0 calc.	J_0 obs.
3	1500	1.1	5.9×10^{-5}	6.3×10^{-5}
3	1300	2.1	5.9×10^{-6}	5.3×10^{-6}
6	1400	2.1	1.6×10^{-5}	1.7×10^{-5}
6	1100	1.0	2.6×10^{-7}	2.6×10^{-7}
10	1400	1.9	1.2×10^{-5}	1.1×10^{-5}
20	1150	3.1	0.7×10^{-7}	7.9×10^{-7}

Glass No. 2

depth of melts (mm)	temperature (°C)	α	J_0 calc.	J_0 obs.
3	1500	3.0	6.1×10^{-5}	5.8×10^{-5}
3	1400	1.0	2.1×10^{-5}	2.1×10^{-5}
6	1350	2.0	1.1×10^{-5}	1.1×10^{-5}
6	1300	2.0	4.9×10^{-6}	4.3×10^{-6}
10	1400	3.0	2.4×10^{-5}	2.5×10^{-5}
20	1100	3.0	3.0×10^{-7}	2.9×10^{-7}

constituent in the melts are controlling factors of the overall rate of volatilization process in the system.

Calculating $d\phi/d\tau$ for $\tau=0$, the initial rate of volatilization (gr/cm². sec) for the very early stage of volatilization can be obtained. The values obtained are given in Table 3 with experimental values for different runs in the temperature range 1100 to 1500°C. Good agreement between the theoretical and experimental values is found as shown in the Table.
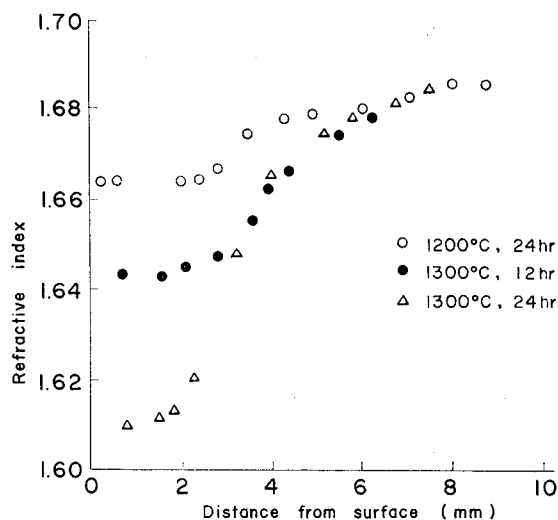

Fig. 6.   Distribution of refractive index of Glass No. 2 after heat-treating at 1200° or 1300°C for a period of 12 or 24 hr.
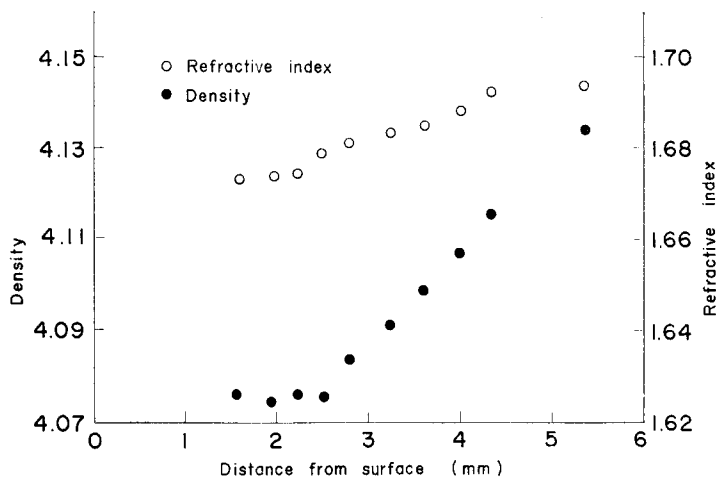

Fig. 7.   Distributions of density and refractive index of Glass No. 2 after heat-treating at 1200°C for a period of 30 hr.

Refractive index and density of the glass samples after heat-treating at 1200–1300°C were also determined. The distributions of these values in the glasses are given in Fig. 6 and Fig. 7. From the figures it is seen that loss of the volatile results in changes of refractive index and density from the depths of the glass melt to the glass surface.

4. Summary

The results obtained may be summarized as follows:

(1)   The volatilization of lead oxide from the glasses containing about 56 or 67% lead oxide obeys the kinetics for the process controlled by both the evaporation-rate coefficient at the surface of the glass melt and the diffusion coefficient of the volatile in the melt.

(2)   The value of the activation energy for the rate coefficient of evaporation at the surface was estimated to be 56–70 kcal/mole and that for the diffusion coefficient 55–70 kcal/mole.

(3)   The initial rate of volatilization J_0 (gr/cm². sec) was evaluated in the temperature range 1100° to 1500°C as given in Table 3.

(4)   Distributions of refractive index and density in the lead glass after heat-treating at 1200–1300°C were determined.

References

1)   L.F. Oldfield, R.D. Wright, Glass Tech., **3**(2) 59 (1962). Advances in Glass Tech., p. 35 (1962) Plenum Press.
2)   R. Terai & T. Ueno, J. Ceram. Assoc. Japan, **74**(9) 283 (1966)
3)   M. Shinbo, J. Ceram. Assoc. Japan, **74**(11) 346 (1966)
4)   M. Kunugi, H. Jinno & G. Kambara, Memoirs Faculty Eng., Kyoto Univ., **26**(3) 336 (1967)