

THE APPLICATION OF THE CONTRACTING SPHERE EQUATION TO THE BEHAVIOUR OF OXYGEN BUBBLES IN MOLTEN GLASS

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ABSTRACT

In this study the contracting sphere equation is applied to the case of oxygen bubbles in molten glass. It is confirmed that in the cases studied for a freely moving bubble in the temperature range 950–1300°C the mechanism is isokinetic and reduced time plots indicate that the contracting sphere equation provides a very good description of the experimental data. The activation energy for the process is 202 kJ mol⁻¹.

INTRODUCTION

Attempts to follow the kinetics of bubble contraction of gases in molten glass have been made by Greene and co-workers^{1–4}, Doremus⁵, Frischat and Oel^{6,7}, and Nemeč^{8–10}, involving stationary bubbles, and part of Nemeč's study reported the use of equipment in which freely moving bubbles were observed.

In the case of a contracting bubble in a stationary bubble experiment there will be a concentration gradient as one considers positions removed from the surface of the bubble, whilst such a concentration gradient will tend to be minimised or absent in the case of moving bubbles. Some of the above authors have reported their experiments in terms of a parabolic diffusion law, whilst others reported a linear variation of bubble diameter with time.

In the work reported here the data on bubble contraction are first tested to indicate that it is isokinetic over the temperature range studied. The contracting sphere equation is shown to apply and the activation energy for the process established

EXPERIMENTAL

Materials

A soda-lime-silica glass was used and the gas was oxygen supplied from a cylinder.

Equipment

The apparatus is shown diagrammatically in Fig. 1. Each section will now be described.

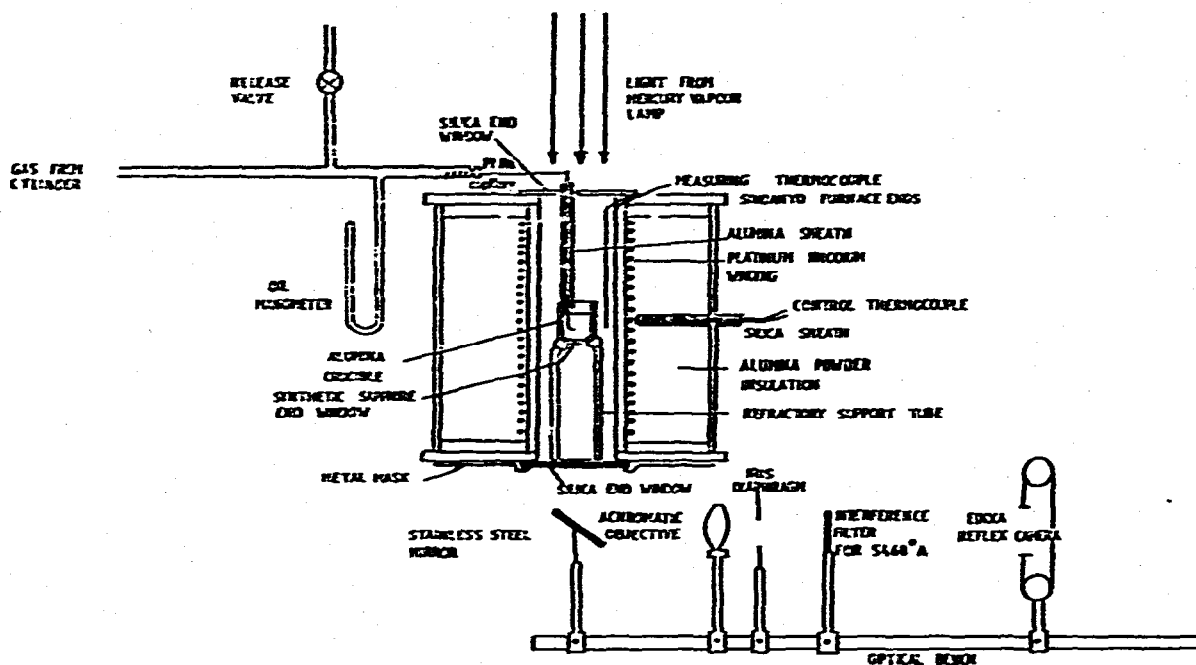


Fig. 1. Apparatus for study of bubble growth and decay.

Capillary. Single bubbles were introduced into the melt from a platinum-10% rhodium tube of 0.5 mm internal diameter and 0.5 mm wall thickness which was supported along most of its length by an alumina sheath which was firmly clamped at the top.

The inlet gas was admitted to the capillary tube into the glass melt from a standard cylinder via a two-stage regulator. The pressure was measured by an oil manometer.

Crucible. The melt was contained in a Morgan XN50 alumina crucible in the bottom of which a hole 16 mm diameter had been drilled. A circular synthetic sapphire window 25 mm diameter and 2 mm thick was sealed on by means of sprayed alumina using the Rokide process. The finished crucible was mounted on a refractory pedestal in the centre of the vertical tube furnace.

Furnace and temperature control. The tube furnace was a normal cylindrical furnace with a platinum/rhodium winding. The ends were closed with silica sheet of optical quality to minimise optical disturbance due to convection currents in the air.

The control thermocouple was used with an Ether Transitrol saturable reactor controller which incorporates cold junction compensation. Control was continuous and being stepless was very smooth.

Optical system. The black body radiation from the crucible within the temperature range studied was quite appreciable, and even with mercury vapour lamp illumination would have been very much impaired without a suitable filter. An interference filter passing the green line at 546.1 nm of the mercury vapour spectrum was used. The use of monochromatic light had a further advantage; viewed through the molten glass the bubble appeared as a virtual image, the position of which depended on the refractive index of the glass which changes with wavelength, and with the filter a much sharper image could be obtained.

At the bottom of the furnace a stainless steel mirror reflected the light along a horizontal bench through an objective, iris diaphragm and interference filter on to the viewfinder of a 35 mm reflex camera with normal lens removed. The optical system was adjusted to give a 5× magnified image on 35 mm film. The optical system was enclosed to enable photographs to be taken in daylight. The photographs could be projected on a rigid screen for bubble diameter measurement.

Procedure

The crucible was loaded with small pieces of glass and installed in the furnace. The temperature was allowed to rise under control to 1050°C and this temperature maintained until any entrapped gas bubbles disappeared and the melt was clear. The platinum-rhodium capillary tube was then mounted in position in the crucible and connected to the gas cylinder to be used. The system was flushed out with the gas and, as soon as the mercury vapour lamp had been adjusted for maximum illumination and the chosen temperature reached, any air entrapped in the length of capillary tube immersed in the molten glass was removed by blowing a large bubble through the melt. Single bubbles of the gas to be examined were then blown and detached from the capillary tube. For each experimental run the bubble was introduced at 1050–1100°C and the temperature raised to that required and then maintained constant.

Once a bubble had been obtained it was photographed at intervals of time and the times were noted. Due to movement of bubbles through the melt, the position of the image constantly changed and for each photograph the camera position was adjusted to obtain the sharpest image. Each bubble was observed for as long as possible. The observation time depended on the bubble size and also the temperature. The smaller the bubble and lower the temperature the longer was the time for total observation. The observed quantities during each experimental run were:

- (a) the objective-image distance s (cm);
- (b) the projected image diameter d (cm);
- (c) the time the bubble had been in the melt.

If the focal length of the camera lens is f cm the true bubble size is given by the expression

$$D = \frac{df}{m(s-f)}$$

where m is the magnification of the system.

RESULTS

Figure 2 indicates typical plots of bubble diameter against time. On the scale on which this appears the relationship is approximately linear. On the same scale, data of Greene et al.¹⁻⁴ is also linear and other investigations⁵⁻⁸ have established a similar behaviour. The data reported here were collected at temperatures of 950-1300°C. The data were replotted on a reduced time scale (Fig. 3). In this diagram the ordinate is represented by the fractional volume contracted α and the abscissa by $t/t_{0.5}$, where t was recorded and $t_{0.5}$ the time when $\alpha = 0.5$.

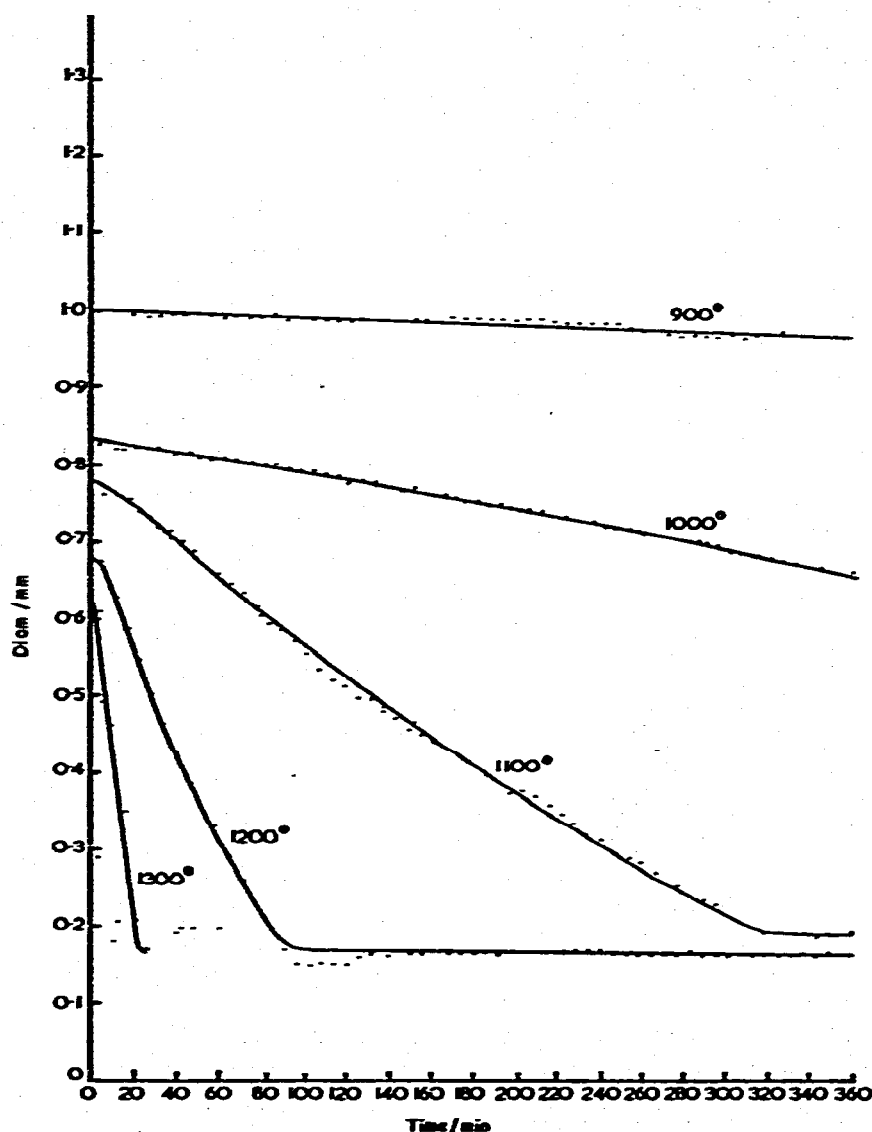


Fig. 2. Typical data for contraction of oxygen bubbles in molten soda-lime glass. Similar data were also obtained at temperatures of 950, 1050, 1150 and 1250°C. V_t was determined experimentally on all runs.

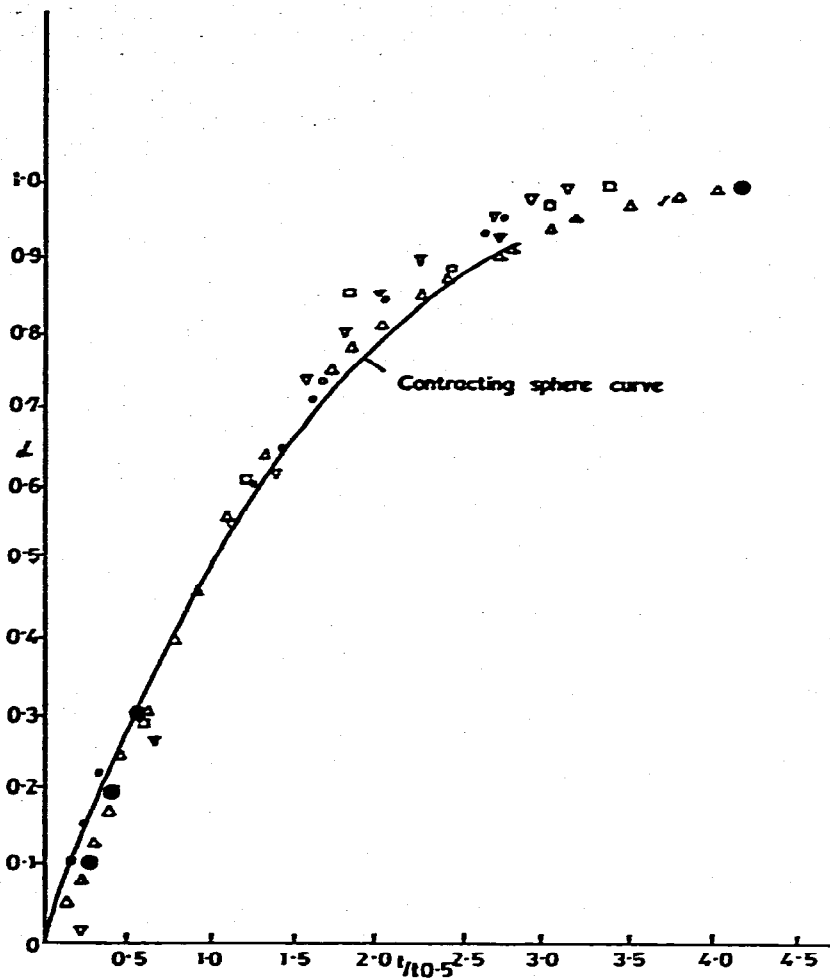


Fig. 3. Reduced time plots for oxygen bubbles in soda-lime glass. Experiments were carried out at: O, 950°C; ●, 1000°C; Δ, 1100°C; ▽, 1200°C; and □, 1300°C.

α is given by

$$\alpha = \frac{V_i - V_t}{V_i - V_f}$$

where V_i = the initial volume of the bubble;

V_t = the volume at time t ;

V_f = the final or residual volume.

The common curve that results indicates that over the temperature range investigated (950–1300°C) the behaviour is isokinetic and the theoretical line drawn on the graph indicates that it matches, very closely, the expected behaviour attributed to a contracting sphere¹², viz.:

$$1 - (1 - \alpha)^{1/3} = kt$$

where $k = \frac{v}{r}$

and v = velocity of advance of interface (assumed constant);

r = initial radius of spherical bubble (the radius is used here and not the diameter because most quoted uses of the contracting sphere equation use the radius term).

DISCUSSION

The results shown here present a different treatment from those usually given for contracting bubbles of gas in a glass melt, but the experimental data are very similar and it is shown here that other data collected from published work are amenable to the same treatment. This can be illustrated by an inspection of the curves for oxygen bubbles shown by Greene and Kitano². These indicate a reasonably

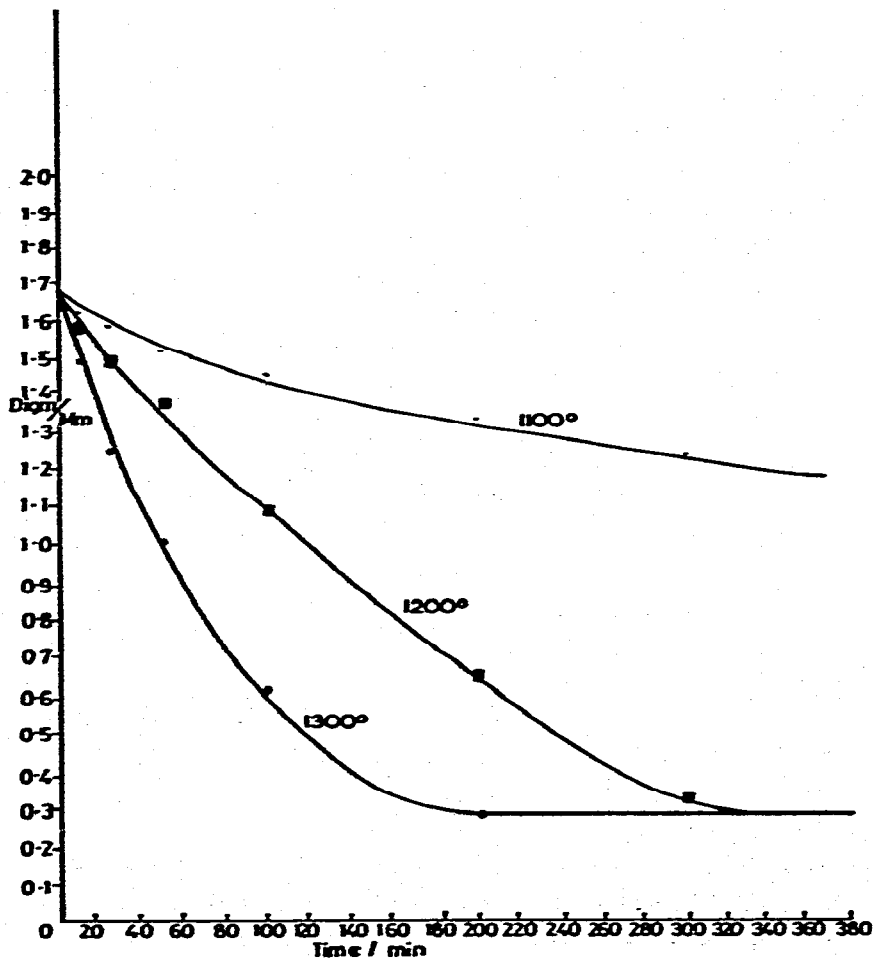


Fig. 4. Data from Greene and Kitano's work² on oxygen bubbles in soda-lime glass. Replotted as diameter of bubble against time. Experiments at: ●, 1100°C; ■, 1200°C; ○, 1300°C.

linear plot of bubble diameter against time although a dependence upon the square root of time is used. This is because the data are always presented as a plot of bubble diameter against the square root of time and the actual experimental data of bubble diameter against time is rarely quoted. On the basis of the square root of time plots, Green and Kitano state that, after a period of slow absorption ... the diameter decreases linearly with the square root of time'. The actual experimental plots obtained by Greene and Kitano and referred to in the above quotation can be recalculated and plotted as bubble diameter against time and are shown in Figs. 4 and 5. These show quite clearly that the initial rate of decrease of diameter is no smaller than the subsequent decrease and in some cases it is marginally faster.

The problem of the kinetic decomposition of a solid is one of a changing interface and has some similarities with the changing dimensions of a bubble in molten glass.

The kinetics of a solid state decomposition are largely governed by the geometry of the reaction interface and by the diffusion of material up to and away from the

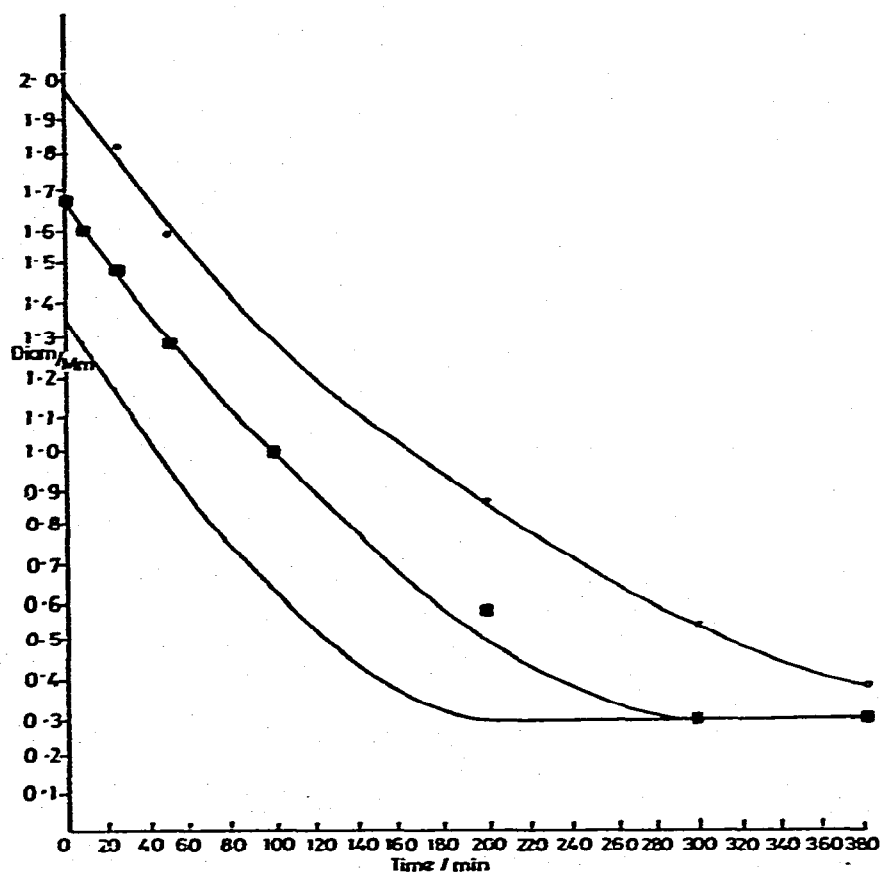


Fig. 5. Data from Greene and Kitano's work² on oxygen bubbles in barium aluminium alkali silicate glass. Replotted as diameter of bubble against time. Three bubbles at 1200°C.

interface. An almost similar treatment could be made regarding the changing dimensions of a bubble in molten glass. It is worthwhile therefore, to look at the equations put forward for solid state decompositions and how far they may be used in the case of a bubble in molten glass. The problem is very largely one of recognising the appropriate kinetic equation to use. This has been described by Sharp et al.^{1,2} using the concept of reduced time.

The kinetic relationship is first expressed in the form

$$F(\alpha) = kt$$

where α is the fraction of the process that has taken place, and has a limiting value when completed of unity, and t is the time.

The time scale is altered so that the function $F(\alpha)$ becomes

$$F(\alpha) = A(t/t_{0.5})$$

where $t_{0.5}$ is the time of 50% completion of the process and A is a calculable constant depending on the form of $F(\alpha)$. This reduced time ($t/t_{0.5}$) is a dimensionless quantity.

The interface is changing and, on the assumption that the process is phase boundary controlled and the shape of the bubble is spherical, then the contracting sphere mechanism might be expected to apply. If the radius of the bubble was initially r and the constant velocity of contraction was v then from this model

$$\begin{aligned} R(\alpha) &= 1 - (1 - \alpha)^{1/3} \\ &= \left(\frac{v}{\epsilon}\right)^t \\ &= 0.2063 t/t_{0.5} \end{aligned}$$

On this basis of representation a first order decay law takes the form

$$\begin{aligned} F(\alpha) &= \ln(1 - \alpha) \\ &= kt \\ &= -0.693(t/t_{0.5}) \end{aligned}$$

If diffusion processes played an important part in determining the kinetics of the bubble contraction then this would be reflected in the form of the kinetic expression. There are several expressions to choose from but the Jander equation recognises the combined presence of diffusion and changing interface for contracting spherical surfaces and takes the form

$$\begin{aligned} D(\alpha) &= [1 - (1 - \alpha)^{1/3}]^2 \\ &= \left(\frac{K}{r^2}\right)^t \\ &= 0.0425 t/t_{0.5} \end{aligned}$$

To use Sharp's technique for establishing the kinetics one has first to show that behaviour is isokinetic. This is established by inspection of Fig. 3 where all the experimental points lie close to a common curve. The theoretical data from the various expressions can also be represented on the same graph and the experimental points in Fig. 3 are seen to cluster around the line representing the contracting sphere model. This is not an exceptional case, for reduced time plots for stationary oxygen bubbles in a soda-lime glass and in a barium aluminium alkali silicate melt obtained from the experimental curves of Greene and Kitano have also been constructed.

Similar plots have been made for contracting bubbles containing helium and neon from data published by Frischat and Oel^{6,7} and these are shown in Fig. 6. These data followed the contracting sphere mechanism but the data of Greene and Kitano, shown in Figs. 7 and 8, follows closely that expected for a first order decay mechanism.

It must be emphasised that the experimental data reported in this study obeyed the contracting sphere equation, which indicates a rate process, which is a phase boundary controlled process and not a diffusion controlled process. Furthermore, the difference between the contracting sphere relationship and the first order decay

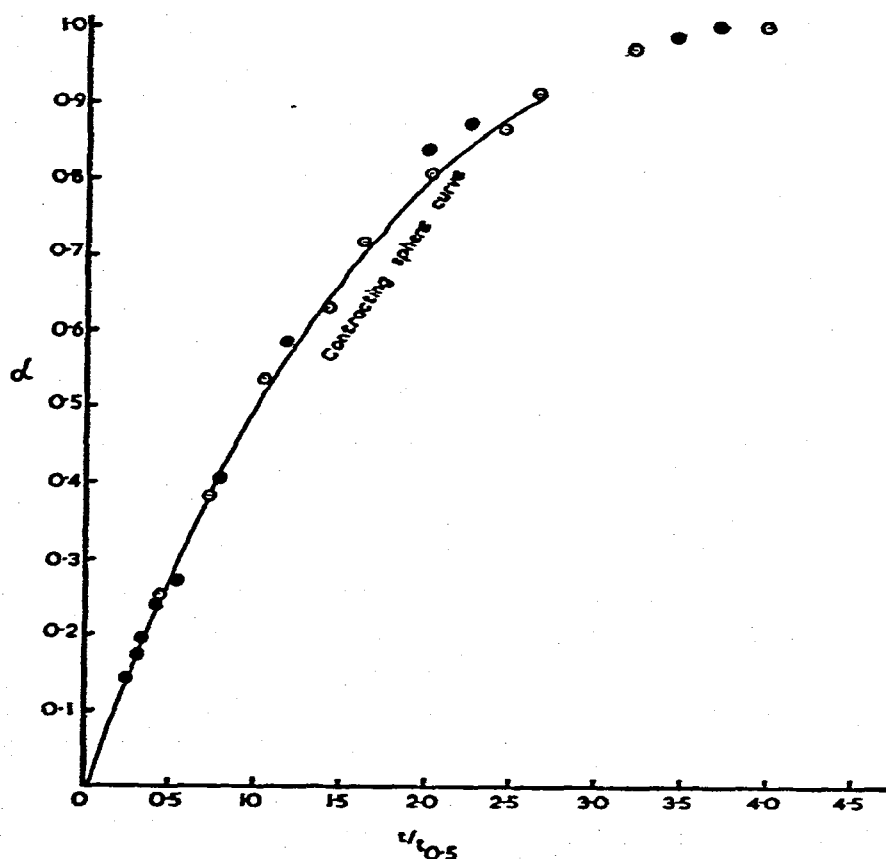


Fig. 6. Data from Frischat and Oel's work^{6,7} on helium and neon bubbles in molten glass. Plotted as a reduced time plot. O, Helium bubbles at 1002°C; ●, neon bubbles at 1143°C.

process is very small for values up to 0.65. Both Greene and Kitano and Frischat and Oel were studying stationary bubbles as opposed to the moving bubbles studied here. However, Frischat and Oel degassed their glasses prior to the experiments whereas Greene and Kitano did not. It is therefore possible that Greene and Kitano's experiments were carried out in a glass already containing dissolved oxygen, whereas the degassing process would have removed the gases in the experiments of Frischat and Oel. It can be tentatively suggested that the work of Greene and Kitano shows a first order decay relationship because the bubble contraction is becoming influenced by diffusion but the non-agreement with the Jander equation would indicate that the process is not rate-controlled by a diffusion process.

The implication of gas bubble contraction obeying the contracting sphere model is simply that the rate of contraction is determined by phase boundary conditions and not by diffusion processes.

The activation energy for this process can be established from these experiments to be 202 kJ mol^{-1} . The activation energy calculated by Greene and Kitano is 255 kJ mol^{-1} . However, they appear to have based their calculations on the rate of

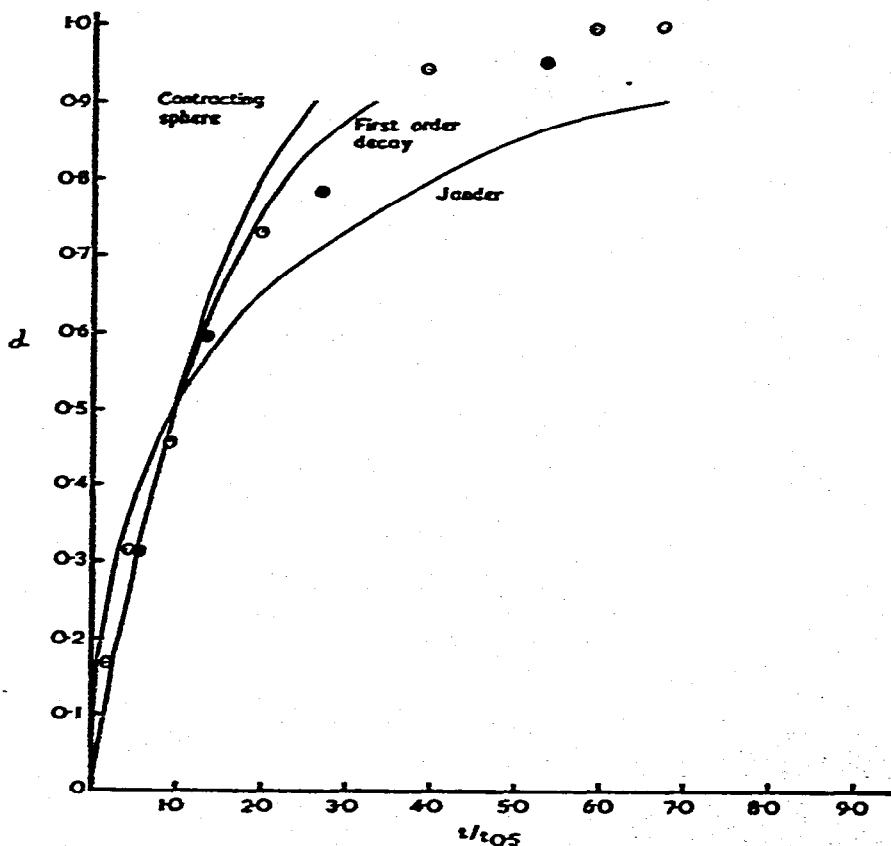


Fig. 7. Data from Greene and Kitano's work² on oxygen bubbles in soda-lime glass. Plotted as a reduced time plot. O, Experiment at 1300°C; ●, experiment at 1200°C.

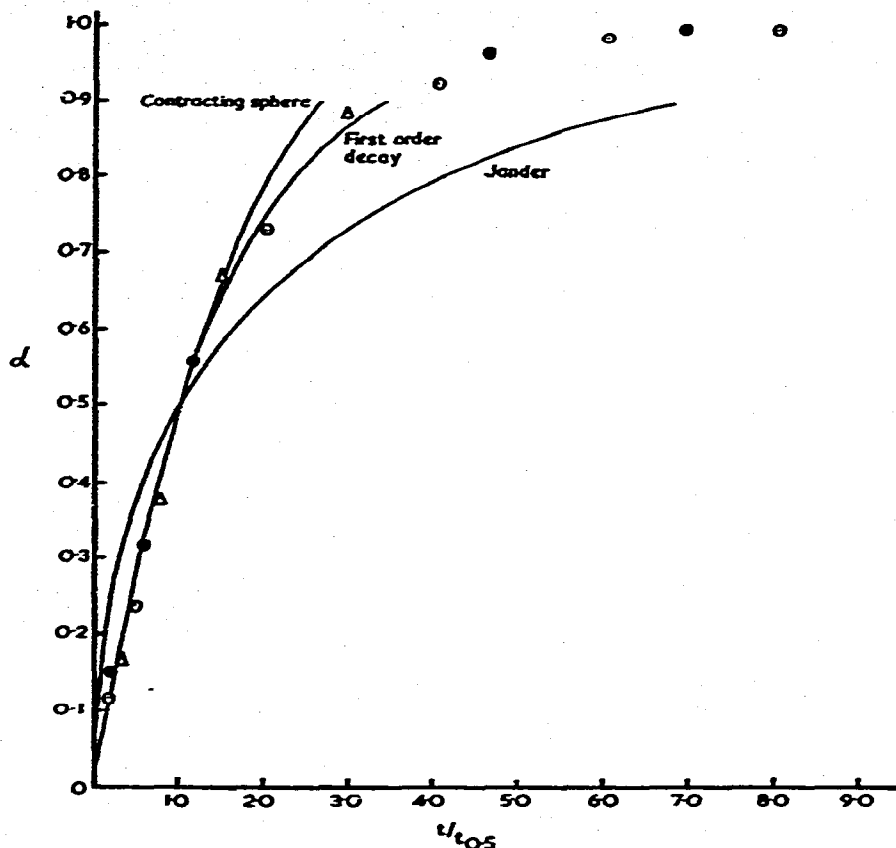


Fig. 8. Data from Greene and Kitano's work² on barium aluminium alkali Silicate glass at 1200°C. Plotted as a reduced time plot.

change of diameter whereas the activation energy calculated here is based on the rate of change of material involved, i.e., rate of volume change in the bubble.

CONCLUSIONS

It has been shown that in the case studied for a freely moving oxygen bubble in the temperature range 950–1300°C the mechanism is isokinetic and reduced time plots indicate that the contracting sphere equation provides a very good description of the experimental data. This implies that the rate of bubble contraction is a phase boundary controlled process and not a diffusion process. The activation energy of bubble contraction can be calculated to be 202 kJ mol⁻¹.

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