

THE UNIVERSITY OF MICHIGAN  
COLLEGE OF ENGINEERING  
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Technical Note

CHEMICAL SINTERING OF BERTHOLLIDE COMPOUNDS

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## ABSTRACT

The role of solid-state reactions in the sintering of berthollide compounds is examined. Under some conditions, the free energy change of the chemical transformation is the determining factor for the welding together of particulate nonstoichiometric solids. A diffusional transfer of matter in the solid controls the chemical reaction and, consequently, sintering. Mathematical expressions for diffusion and sintering in the simple case of two spherical particles are presented and the results are compared with experimental data on the sintering of zinc oxide microspheres. Equations for the shrinkage of pores as a result of a chemical reaction are also presented.



## INTRODUCTION

The transformation of a particulate solid into a compact body involves different steps in terms of macroscopic thermodynamic and kinetic concepts. In recent years, almost all the emphasis has been on the study of sintering mechanisms which are motivated by a decrease of surface free energy of the system.<sup>1</sup> These mechanisms undoubtedly control the predominant step in the initial welding together of elemental and multicomponent solids with fixed composition, but in systems of variable composition a different driving force can operate during the initial stages of sintering. Thus, whenever the solid undergoes chemical transformations during sintering, the free energy change of the chemical reaction is available to assist in sintering. The contribution of this type of sintering to the total sintering of a system depends, of course, on the extent of the chemical transformation. The chemical motivation for sintering is, however, a much more powerful driving force than that resulting from a change in surface free energy. In an aggregate of particles of about  $10\mu$  in diameter, the lowering of free energy ensuing complete sintering is of the order of 1 cal/mole, while this quantity is roughly  $10^4$  times larger whenever a chemical reaction controls the welding together of the particulate mass. In the following discussion a broad formulation of chemical sintering is presented together with a brief summary of the corresponding kinetics and pertinent experimental observations.

## GENERAL CONSIDERATIONS

The use of the physicochemical equilibrium from the surrounding phase is a well-recognized method for controlling the composition of a solid berthollide phase. It is also known that the compositional control can be confined to the surface only or can penetrate to various depths in the interior according to the rate of the equilibration reaction. Whenever the solid is initially not in equilibrium with the surroundings, diffusion currents are set up through the crystal. These fluxes are controlled by the boundary values of the various chemical potentials. At sintering temperatures, the interchange of matter at the surface is rapidly established and the values of the chemical potentials at the surface are constant. The boundary values, then, are dependent on the kinetically significant step of the equilibration reaction, namely, the interchange of matter between surface and interior. In a general fashion, three different stages of the equilibration reaction are recognizable: a steady state involving an essentially constant chemical potential gradient, and two unsteady states, which set up at the beginning and near the end of the process, characterized by a variable gradient of the chemical potential. The present discussion will be restricted to the former case.

Let us consider the propagation of the equilibration reaction into the interior of a single crystal of a nonstoichiometric compound, like a metal oxide containing an excess of metal over the stoichiometric composition. As a limiting case it is possible to assume that the diffusion of the metallic component is much faster than the diffusion of the oxygen species and a surface layer of fresh compound will be formed. The growth will be controlled

by the excess of the metallic component initially present and the diffusion rate. If two spherical particles of this compound are brought in contact, an increase of their diameter with consequent welding of the two particles and the formation of a neck between them will occur as a result of the chemical reaction (Fig. 1).

Taking some typical values,  $x \approx 2 \times 10^{-2}$  mm,  $2R \approx 1$  mm, since  $x^2 = (R' + R)(R' - R) = 2RAR$ , one obtains  $\Delta R \approx 5 \times 10^{-3}$  mm. In the case of zinc oxide, which will be discussed later, this value corresponds to about  $2 \times 10^{16}$  zinc ions, which, if distributed over all the original sphere, would require an initial concentration of excess zinc of about  $3 \times 10^{19}$  ions/cc. This relatively high concentration of excess metal component is generally possible when the original substance is prepared in an atmosphere saturated with the corresponding species. This value of the excess concentration becomes considerably smaller if the density of the newly formed oxide shell is lower than the bulk density.

#### DIFFUSION EQUATION FOR SPHERES

To derive an expression for the rate of sintering of two spheres (Fig. 2),  $x = f(t)$ , where  $t$  is time, the diffusion equation within a sphere must be evaluated.<sup>2</sup>

Let us consider the diffusional transport of a species of concentration  $C$  and diffusion coefficient  $D$  within a spherical, isotropic particle (Fig. 2). Assuming that the diffusion currents are divergence-less, the diffusion equation is:

$$\frac{\partial^2 C}{\partial r^2} + \frac{2\partial C}{r\partial r} = \frac{1}{D} \frac{\partial C}{\partial t} \quad (1)$$

The boundary conditions are:

$$C(r,0) = C_0$$

$$C(R,0) = C_s$$

where  $C_0$ ,  $C_s$  are the initial and the surface concentration, respectively. By integration of Eq. (1) and expansion of the resulting Fourier series, one obtains:

$$C(r,t) = C_s + \frac{4R}{\pi r} (C_0 - C_s) \sum_{n=0}^{n=\infty} \left( \frac{1}{2n+1} \right) \sin \frac{2n+1}{R} x \times \exp \left\{ -D \left( \frac{2n+1}{R} \pi \right)^2 t \right\} \quad (2)$$

The concentration gradient of the excess component in the surface layer is:

$$\left( \frac{\partial C}{\partial r} \right)_{r=R} = -\frac{4}{R} (C_0 - C_s) \sum_{n=0}^{n=\infty} \exp \left\{ -D \left( \frac{2n+1}{R} \pi \right)^2 t \right\} \quad (3)$$

Assuming steady-state diffusion through the newly formed surface layer and equating the rate of volume increase in the latter to the diffusional flux, one obtains the following expression for the rate of increase of bridge width  $x$ :

$$x^2 = 2 \left( \frac{2R}{\pi} \right)^2 \left( \frac{C_0 - C_s}{Z} \right) \sum_{n=0}^{n=\infty} \left( \frac{1}{2n+1} \right)^2 \left[ 1 - \exp \left\{ -D \left( \frac{2n+1}{R} \pi \right)^2 t \right\} \right] \quad (4)$$



Introducing the value  $x_m = x$  for  $t \rightarrow \infty$  into Eq. (4) and rearranging, one has:

$$-\ln \left[ 1 - \left( \frac{x}{x_m} \right)^2 \right] = D \left( \frac{\pi}{R} \right)^2 t + \ln \frac{\pi^2}{8} \quad (5)$$

Equation (5) can be expanded into the series:

$$D \left( \frac{\pi}{R} \right)^2 t = \left( \frac{x}{x_m} \right)^2 + \frac{1}{2} \left( \frac{x}{x_m} \right)^4 + \frac{1}{3} \left( \frac{x}{x_m} \right)^6 + \dots + \frac{1}{n} \left( \frac{x}{x_m} \right)^{2n} + \dots \quad (6)$$

Equation (6) shows that the relationship between neck width and time during sintering is a function of the extent of sintering. This is a characteristic feature of this type of sintering, differing markedly from the behavior of sintering motivated by surface free energy changes. Furthermore, from Eq. (6) the relation between two particles of radii,  $R_a$  and  $R_b$ , and their sintering rates can be derived:

$$R_a^2 \ln \left\{ \frac{\pi^2}{8} \left[ 1 - \left( \frac{x}{x_m} \right)_a^2 \right] \right\} = R_b^2 \ln \left\{ \frac{\pi^2}{8} \left[ 1 - \left( \frac{x}{x_m} \right)_b^2 \right] \right\} = \dots = \text{const.} \quad (7)$$

where  $(x_m)_a = \frac{C_o - C_s}{Z} R_a^2$  and  $Z = \frac{\sigma_s}{M_{\text{comp}}}$ ,  $\sigma_s$  = surface density of the compound formed,  $M_{\text{excess}}$ ,  $M_{\text{comp}}$  molecular weight of diffusing species and compound formed, respectively. For  $\left( \frac{x}{x_m} \right) \ll 1$ , Eq. (6) gives the following relation between the time required to obtain a certain geometrical configuration and the initial radii of the spheres:

$$\frac{(t_1)_a}{(t_2)_b} = \left( \frac{R_a}{R_b} \right)^2$$

Thus, a parabolic scaling law is obtained during the early stages of sintering.

For  $t \rightarrow \infty$

$$\frac{(x_m)_a}{(x_m)_b} = \frac{R_a}{R_b}$$

showing that there is a linear dependence between the final neck width and the initial radii of the spheres.

#### COMPARISON WITH EXPERIMENTAL DATA

The sintering of nonstoichiometric zinc oxide in the temperature range 600 to 1100°C occurs preponderantly according to the mechanism presently discussed.<sup>2,3</sup> This is demonstrated by the fact that only zinc oxide spheres which contain an excess of zinc larger than that corresponding to the equilibrium with the gas phase during sintering have been found to undergo sintering in the above temperature range. Separately equilibrated spheres could not be readily sintered up to 1100°C. Furthermore, the experimental data plotted according to Eq. (5) should yield a straight line in a graph of

$-\ln \left[ 1 - \left( \frac{x}{x_m} \right)^2 \right]$  vs. time. Some typical values of the rate of sintering of zinc oxide microspheres at three different temperatures are shown in Fig.

3. From these data it is possible to derive an activation energy for diffusion of excess zinc ions of about 18.0 kcal/mole. This value is of the same order of magnitude as the value of 12.6 kcal/mole obtained by means of measurements of electrical conductivity in zinc oxide.<sup>4</sup> From Eq. (5) an estimate of the value of the diffusion coefficient of the excess zinc can be obtained.

At 900°C, after 8 hours, for spheres with a radius of about 0.5 mm,  $-\ln \left[ 1 - \left( \frac{x}{x_m} \right)^2 \right] = 0.5$ , which gives  $D \cong 1 \times 10^{-7} \text{ cm}^2/\text{sec}$ . This value is of the same order of magnitude as that determined by extrapolating diffusion data obtained from electrical measurements in zinc oxide.<sup>4</sup>

Finally, there is direct, visual evidence that a sintering reaction takes place between zinc oxide spheres under the experimental conditions previously outlined. An examination of the configuration of the bridge between sintering spheres showed a sharp profile with a discontinuous change of curvature from one sphere to the other. This contrasts with the more or less smoothed-out change in the neck curvature which results from a decrease of surface free energy.

In order to compare the sintering mechanism just discussed with a sintering operation not controlled by a chemical process, we shall present some data on the welding together of vanadium pentoxide microspheres. These data were obtained under initial conditions of compositional equilibrium of the solid phase with the surrounding atmosphere. Thus, the chemical composition of the oxide did not vary significantly in the course of sintering.

Typical sintering data obtained on air annealed and equilibrated spheres are summarized in Fig. 4 where the logarithm of the half-width of the neck connecting the spheres is plotted against the logarithm of time for different temperature and constant sphere radius (0.73 mm). All runs were performed in air except for one run conducted in one atmosphere of steam. The average inverse slope, computed from the straight lines drawn through the experimental points of Fig. 4 is  $\sim 4$ .

The data clearly show that the relationship between the neck width and time is constant throughout the whole range of sintering investigated, thus fulfilling the fundamental requirement of a sintering mechanism motivated by surface free energy decrease. The reported relationship,  $x^4 \propto \text{time}$ , can be tentatively taken as an indication that sintering of vanadium pentoxide is controlled by a diffusional process, involving migration of vacancies along the surface and grain boundaries, which act as vacancy sink.<sup>5</sup> In view of the polycrystalline nature of the vanadium pentoxide used, grain-boundary processes are likely to be kinetically pronounced. The relatively low value of the activation energy ( $\sim 35$  kcal/mole) supports the view of diffusion along grain boundaries, but it is not possible, on the basis of the above data only, to draw a definite conclusion on the mechanism of sintering of vanadium pentoxide. In particular, data on the type of scaling law obeyed are required. The presence of water vapor in the surrounding atmosphere during sintering did not noticeably alter the rate of the process. This fact implies that no large composition changes were produced by the presence of water vapor, possibly due to a large positive free energy change ( $> 54$  kcal/mole) for the reaction:

$$\text{H}_2\text{O} + \text{V}_2\text{O}_5 \rightarrow \text{O adsorbed on V}_2\text{O}_5 + \text{H}_2.$$

#### SHRINKAGE REACTIONS IN PORES

During sintering of a particulate solid, pore shrinkage occurs almost concurrently with the welding together of individual particles. If the gas-phase composition prevailing inside the pores differs from the composition corresponding to equilibrium with the bulk of a berthollide crystal, pore

shrinkage will set in. The shrinkage is controlled by a chemical driving force in a fashion similar to the previous case of bridge formation between chemically sintering spheres. Although no experimental data on the rate of pore shrinkage in nonstoichiometric compounds have been published as yet, it is of interest to discuss briefly general mathematical expressions applicable to such a process.

Let us consider a simple case of a narrow, cylindrical pore imbedded in an isotropic solid mass and a diffusion flux perpendicular to the pore surface (Fig. 5). Since the partial pressure of the gas surrounding the solid is higher on the outside surface near the pore mouth, shrinkage of the pore by a chemical reaction with the gas phase will occur preferentially in the inside of the pore instead of at the pore ends. We shall consider only a portion of the pore which is deep inside the crystal and unaffected by the conditions prevailing at the mouths.

For  $r > r_0$  the diffusion equation is:

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} = \frac{1}{D} \frac{\partial C}{\partial t} \quad (8)$$

where  $D$  is assumed to be independent of  $r$ . The following conditions are set up:

$$\begin{aligned} C(r,0) &= C_0, \quad C(r_0,0) = C_s, \quad C(r_a,t) \cong C_0, \quad C(r_1,t) = \\ C'_s, \quad \left(\frac{\partial C}{\partial r}\right)_{r_a} &= 0, \quad \left(\frac{\partial^2 C}{\partial r^2}\right)_{r_0} \cong 0. \end{aligned} \quad (9)$$

Since the gas composition in the pore is a function of the pore diameter, it will generally be  $C_s \neq C'_s$ . For simplicity, let us assume  $C'_s \approx C_s$ . The

corresponding diffusion profile is shown in Fig. 6. Let  $C = TU$  (9); Eq. (8)

rearranges into:

$$\frac{d^2U}{dr^2} + \frac{1}{r} \frac{dU}{dr} + \alpha^2 U = 0 \quad (10)$$

where

$$T = A \exp \{D\lambda t\} \quad (11)$$

and  $A = \text{const}$ ,  $\lambda = \frac{1}{U} \left( \frac{d^2U}{dr^2} + \frac{1}{r} \frac{dU}{dr} \right) = -\alpha^2$ . Since  $T$  decreases as time increases,  $\lambda$  must have a negative value. Equation (10) is a zero-order Bessel function with  $U = B_1 J_0(\alpha r) + B_2 Y_0(\alpha r)$ ,  $B_1, B_2 = \text{constants}$ . For small enough pores, the radius can be reduced to zero and  $U = B_1 J_0(\alpha r)$  and, from Eq. (9):

$$C(r,t) = A [\exp \{-D\alpha^2 t\}] J_0(\alpha r) \quad (12)$$

The value of  $\alpha$  can be determined by means of the condition  $\left( \frac{\partial^2 C}{\partial r^2} \right)_{r_0} \cong 0$  and Eq. (12). The following condition results:

$$A \exp \{-D \alpha^2 t\} \alpha^2 J_0''(\alpha r_0) = 0 \quad (13)$$

whose solutions are represented by any value  $\alpha_n$  satisfying the condition:

$$J_0''(\alpha_n r_0) = 0 \quad (14)$$

$n = \text{integral number from 1 on.}$

Substituting Eq. (14) into (12), the following expression for the concentration of the diffusing species obtains:

$$C(r,t) = \sum_{n=1}^{n=\infty} A_n \exp \{-D \alpha_n^2 t\} J_0(\alpha_n r) \quad (15)$$

The value of  $A_n$  can be calculated by setting the condition  $C_o(r,0) = C_o$  in Eq. (15):

$$C_o = \sum_{n=1}^{n=\infty} A_n J_o(\alpha_n r)$$

Equation (15) can be solved to give values of  $C$  as a function of  $t$  and  $r$ , for  $r > r_o$ . These values can be used to compute the decrease of pore radius as a function of time. The decrease is given by:

$$r_o - r = \frac{D}{\rho N} \int_0^t \left( \frac{\partial C}{\partial r} \right)_{r_o} dt$$

where  $N$  and  $\rho$  are the molecular weight and density of reaction product, respectively.

## CONCLUSIONS

The welding together of individual particles of nonstoichiometric solids and the shrinkage of their pores can be assisted by the chemical equilibration process which sets in whenever sintering conditions are different from those prevailing during the preparation of the aggregate. This type of sintering is controlled by the free energy change of a chemical reaction. The extent of this sintering is dependent on the initial deviation of the system from the composition corresponding to sintering conditions. Thermodynamically, however, chemical sintering is a preferred process over sintering controlled by the decrease of surface free energy of the particulate body. In contrast with the latter type of sintering, chemical sintering may be reverted at will

by modifying the thermodynamic conditions of the surrounding phase which may also consist of a solid phase. In general, any solid-state reaction can be used to promote sintering. From a practical standpoint, whenever the purity of the final compact is not important, this method offers interesting possibilities for improved conditions (lower temperatures) and better control of sintering than the method based on surface free energy changes. There is already evidence showing the striking effects produced on the sintering of a solid mass by the addition of small amounts of chemically interacting solids. Similarly related effects are probably responsible for large compositional differences between surface and bulk in alloys during surface processes.<sup>6</sup> The role of chemical interactions in heterogeneous systems involving a solid phase, together with the characteristic reactivity of interphases is, thus, of paramount importance in a variety of fundamental and applied processes.

#### ACKNOWLEDGMENT

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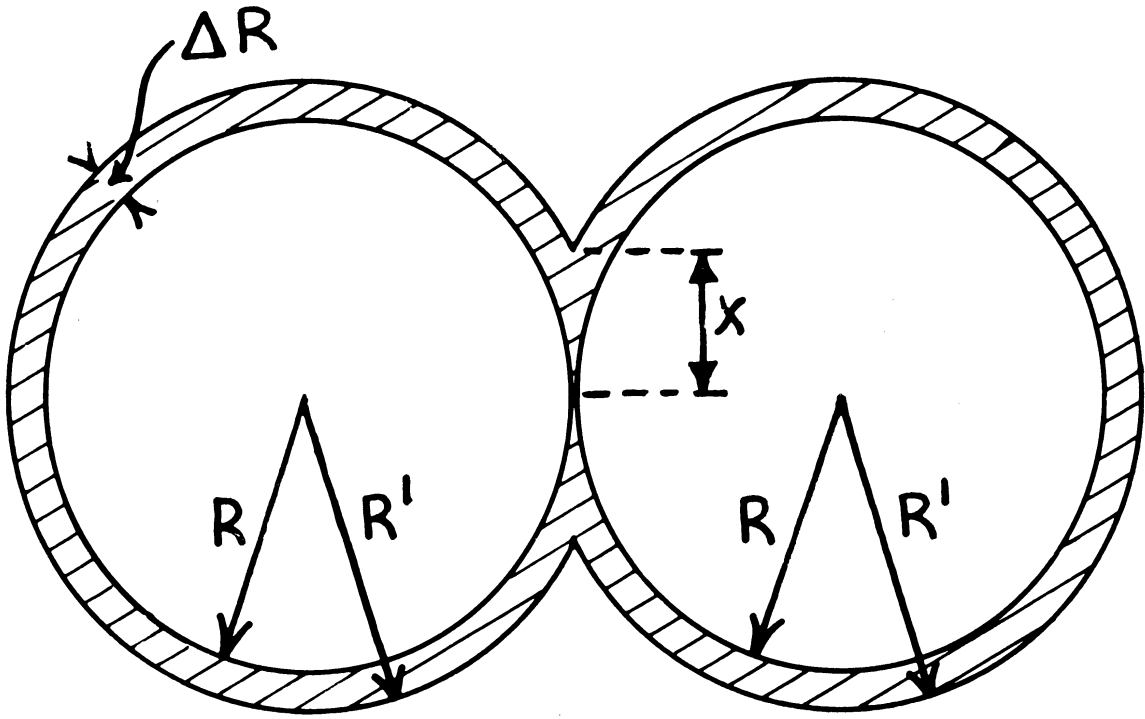


Fig. 1. Schematic model for sintering of two spheres as a result of a chemical reaction at the sphere surface.

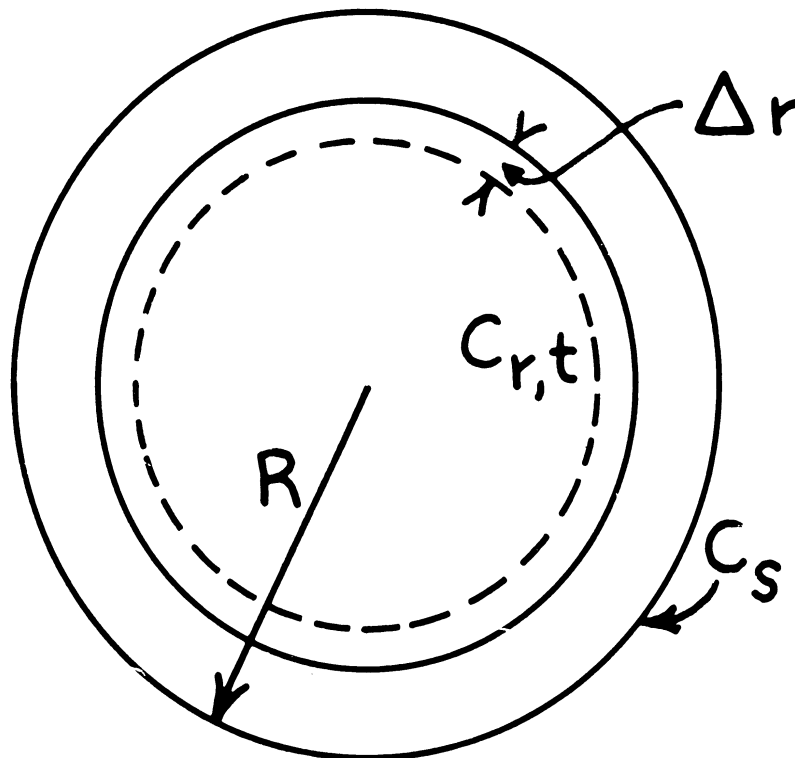


Fig. 2. Model used for the derivation of the diffusion equation.

# SINTERING OF ZnO SPHERES

RADIUS; 0.457 mm

ATMOSPHERE; AIR

○ 700 °C, ● 800 °C,

⊙ 900 °C

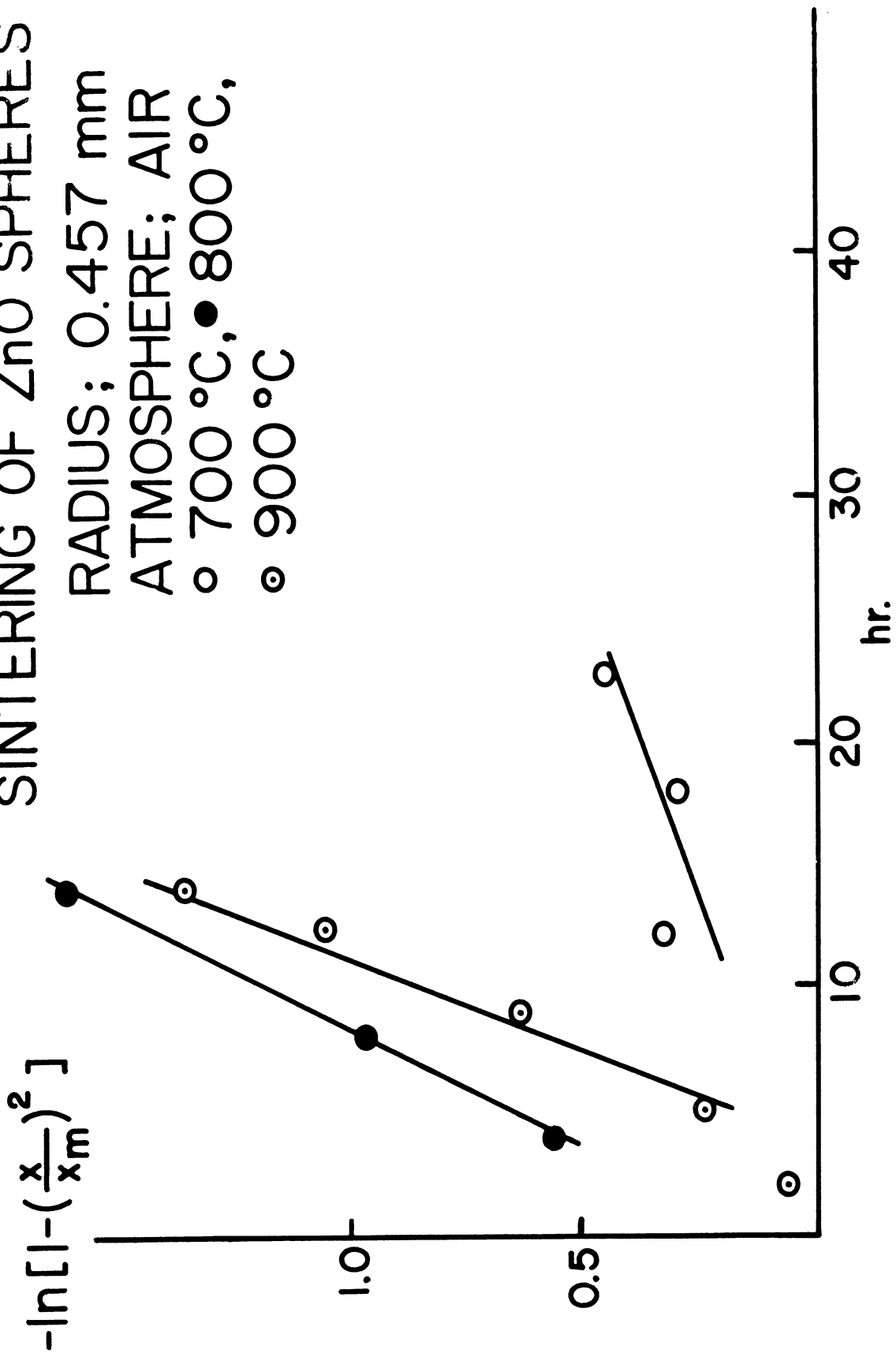


Fig. 3. Experimental data on the sintering of zinc oxide microspheres, plotted according to Eq. (5). From Ref. 1.

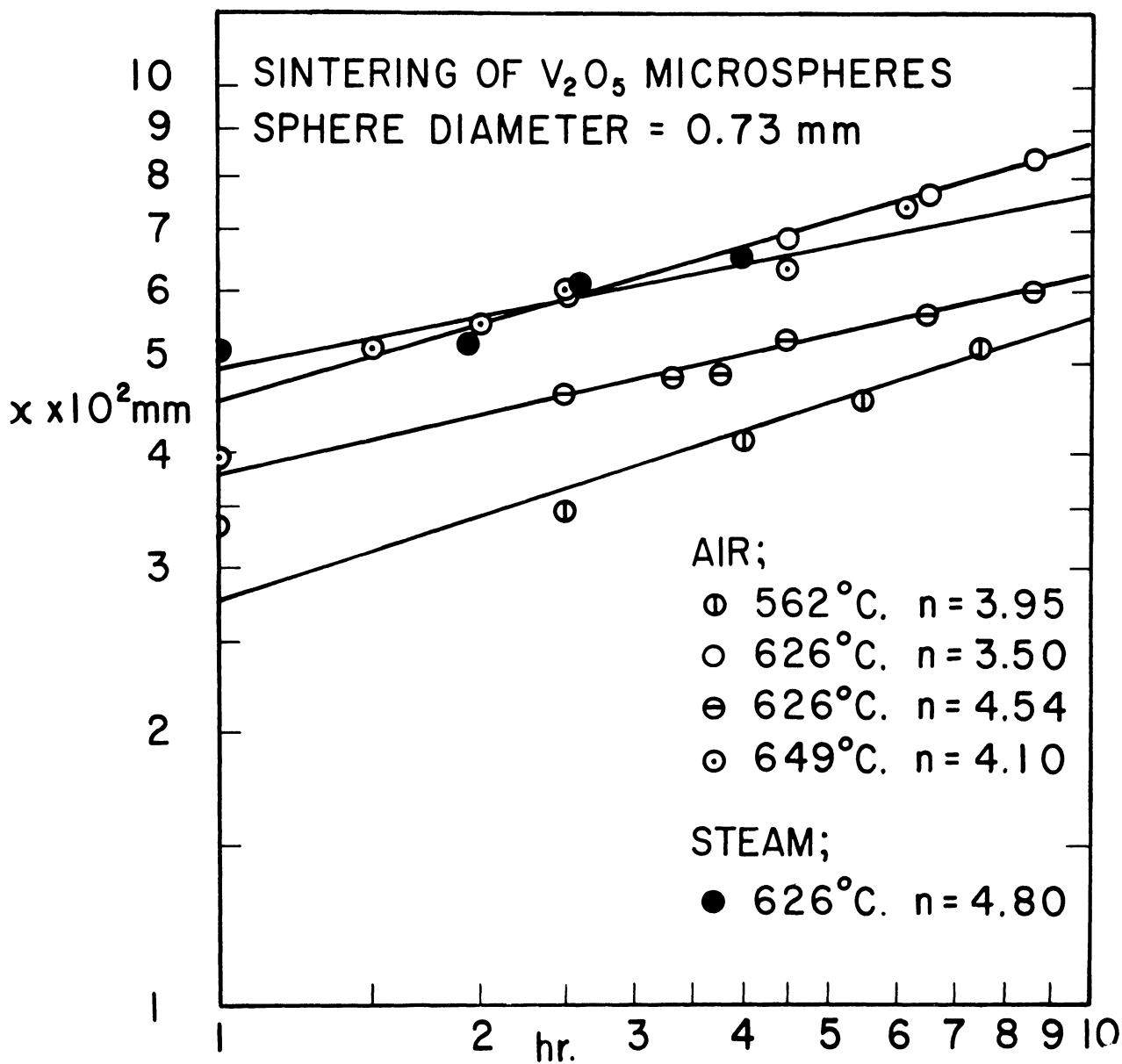


Fig. 4. Growth rate of bridges,  $x$ , between sintering vanadium pentoxide microspheres.

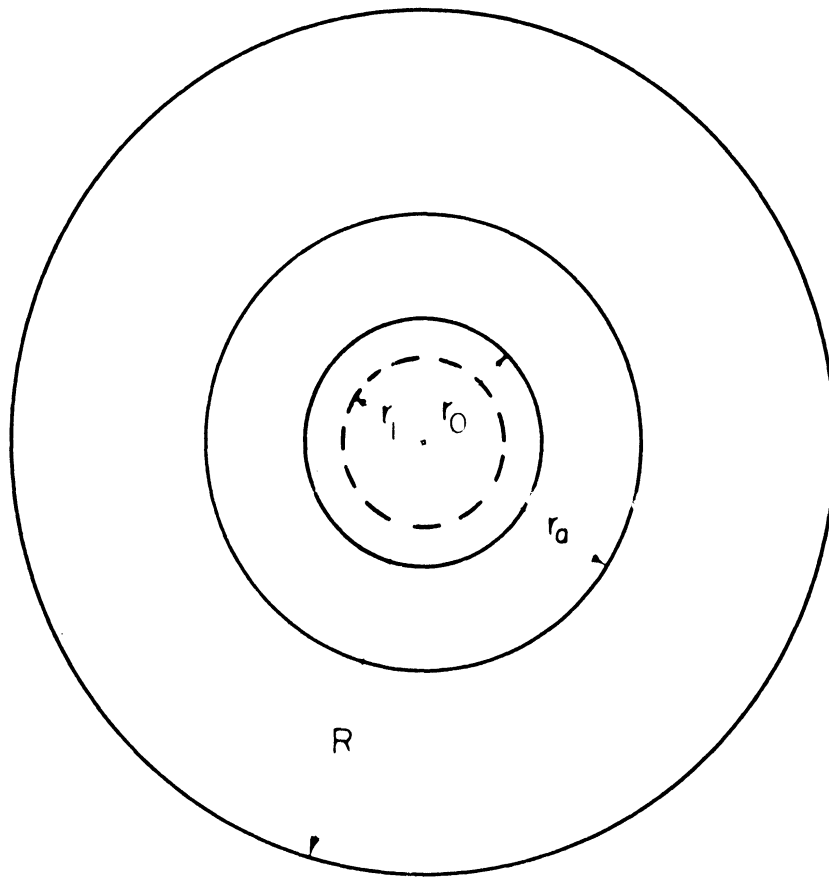


Fig. 5. Model used to evaluate pore shrinkage due to a chemical reaction.

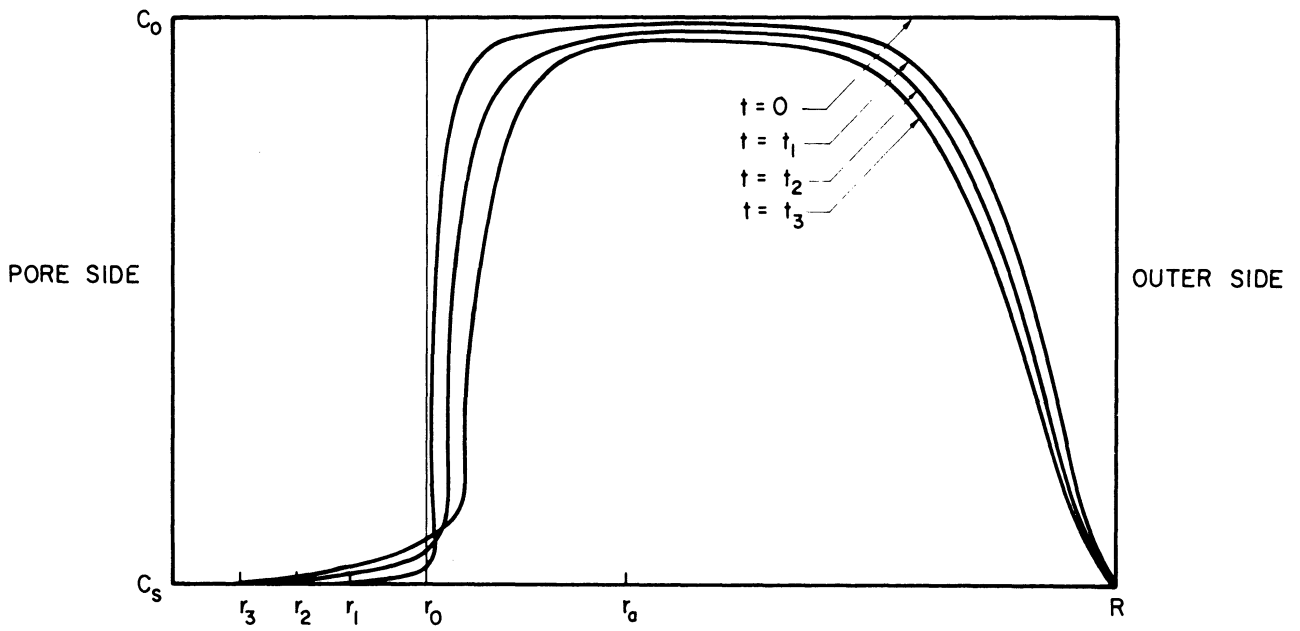


Fig. 6. Diffusion profile for pores.

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