Mathematics of Diffusion-Controlled Precipitation in the Presence of Homogeneously Distributed Sources and Sinks

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The growth-rate equations have been derived for diffusion-controlled precipitation while the diffusing species is continually being created and destroyed throughout the material. Three mechanisms were treated: (1) Bulk diffusion from a large spherical region to a small, concentric spherical particle; (2) diffusion in a spherical region to the wall of the sphere and subsequent instantaneous diffusion to a precipitate particle on the sphere's surface; and (3) two-dimensional diffusion in a circular region to a spherical particle located at the center of the circle. Ham's method, in which the concentration is expanded in eigenfunctions of an appropriate eigenvalue problem, was extended to take into account the presence of sinks and sources. The resulting equations were solved with the aid of a digital computer. The results show that, in the short-time approximation, the radius is proportional to the time for case (1), the radius is proportional to the cube root of the time for case (2), and the radius shows a rapid rise at very short times and then a slower, almost linear increase with time for case (3). For long times, the shape of the radius-time curves is more complex.

INTRODUCTION

THE most comprehensive treatment of the theory of diffusion-controlled precipitation in the absence of sinks and sources has been developed by Ham using an eigenfunction expansion technique.[1] As far as the authors are aware, no comparable treatment of precipitation processes in which the diffusing species is continually being created and destroyed has been given. In view of the growing interest in such problems as void growth during plastic deformation,[2–4] bubble formation in fissionable materials,[5] and the enhanced growth of bubbles in irradiated metals containing helium,[6] an analysis of the theory including the effects of sinks and sources is highly desirable at this time. It is the purpose of this paper to present this theory for a number of special cases of physical interest and to show how the theory may be used to distinguish among alternative mechanisms of precipitation.

The problems to be solved are essentially boundary value problems for a nonhomogeneous diffusion equation. The eigenfunction expansion method used by Ham can be extended to take into account the sink and source terms, and this procedure is used throughout the present paper. It is assumed that the rate of production of the diffusing species is a constant independent of position and time and that the rate of destruction is proportional to the concentration. Three special cases, corresponding to three different mechanisms of precipitation, will be treated in this paper. These are:

(1) Diffusion in a spherical region of radius L to a spherical precipitate particle of radius $R<L$ located at the center of the large sphere,

(2) diffusion in a spherical region of radius L to the surface of the sphere and subsequent instantaneous diffusion to a precipitate particle located on the surface of the sphere, and

(3) diffusion in a two-dimensional circular region of radius L to a precipitate particle of radius R located at the center of the large circle.

Throughout this paper it is assumed that the particle grows slowly enough so that its size variation with time need not be considered in setting up the boundary conditions to the diffusion equation.

EIGENFUNCTION EXPANSIONS AND THE DIFFUSION EQUATION

The general diffusion equation to be solved is

$$\partial n/\partial t = D\nabla^2 n + \kappa_1 - \kappa_2 n, \tag{1}$$

where n is the concentration of diffusing species, t is the time, D the diffusion coefficient, κ_1 the rate of production of the diffusing species, and κ_2 an annihilation constant such that $\kappa_2 n$ is the rate at which the species is destroyed. κ_1 and κ_2 are taken to be constants independent of n and t.

In the problems being considered in this paper, the boundary conditions always have the form

$$n(\mathbf{R},t)=0, \tag{2}$$

$$(\nabla n)_{\mathrm{L}}=0, \tag{3}$$

$$n(\mathbf{r},0)=0. \tag{4}$$

That is, the concentration is always zero on some surface or curve $\mathbf{R}$, the gradient is always zero on some surface or curve $\mathbf{L}$, and the concentration at zero time is everywhere zero.

The concentration can always be expanded in a set

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of orthonormal eigenfunctions $\psi_j(\mathbf{r})$,

$$n=\sum_j a_j(t)\psi_j(\mathbf{r}), \tag{5}$$

where $a_j(t)$ are the expansion coefficients and $\psi_j(\mathbf{r})$ are the solutions of the following eigenvalue problem:

$$\nabla^2\psi_j+\lambda_j^2\psi_j=0, \tag{6a}$$

$$\psi_j(\mathbf{R})=0;\quad (\nabla\psi_j)_{\mathrm{L}}=0. \tag{6b}$$

The λ_j^2 are the eigenvalues of the problem.

Substituting Eq. (5) into Eq. (1) and using Eq. (6a) gives

$$\sum_j \psi_j(da_j/dt+D\lambda_j^2a_j+\kappa_2a_j)=\kappa_1. \tag{7}$$

Now multiply by ψ_j and integrate. Since we require that the ψ_j form an orthogonal set, it follows that

$$da_j/dt+(D\lambda_j^2+\kappa_2)a_j=\beta_j, \tag{8}$$

where

$$\beta_j\equiv\kappa_1\int_{\mathbf{r}}\psi_j(\mathbf{r})d\mathbf{r}. \tag{9}$$

Integrating Eq. (8) and using the condition (4) gives

$$a_j=\beta_j\tau_j(1-e^{-t/\tau_j}), \tag{10}$$

where

$$\tau_j\equiv 1/(D\lambda_j^2+\kappa_2) \tag{11}$$

is an effective relaxation time.

Combining Eqs. (10) and (5) gives the general form

$$n=\sum_j \beta_j\tau_j(1-e^{-t/\tau_j})\psi_j(\mathbf{r}). \tag{12}$$

$\psi_j(\mathbf{r})$ is obtained by solving the eigenvalue problem (6). Once n is given explicitly as a function of $\mathbf{r}$ and t, the derivation of the rate of growth of the precipitate particle is straightforward.

The procedure leading to Eq. (12) is entirely analogous to that of Ham[1] except that it has been extended to account for the presence of κ_1 and κ_2n in the diffusion equation.

CASE 1. DIFFUSION TO A SPHERICAL PARTICLE

For spherical symmetry, the eigenvalue problem of Eq. (6) becomes

$$d^2(r\psi_j)/dr^2+\lambda_j^2(r\psi_j)=0, \tag{13}$$

$$\psi_j(R)=0, \tag{14}$$

$$(d\psi_j/dr)_{r=L}=0. \tag{15}$$

Equations (13) to (15) describe a physical situation in which a spherical particle of radius R is collecting the diffusing species from a surrounding spherical region of radius L. If the specimen contains many precipitate particles, then these equations imply that the particles are small enough so that they may be treated independently and $2L$ then becomes the mean distance between the particles.

The solution of Eq. (13) is

$$\psi_j=C_j\frac{\sin(\lambda_jr+\delta_j)}{r}, \tag{16}$$

where C_j and δ_j are to be evaluated from the normalization condition and the boundary condition (14), respectively. Equation (14) requires that $\delta_j=-\lambda_jR$, and the normalization condition requires that

$$C_j^2=\left[4\pi\int_R^L \sin^2\lambda_j(r-R)dr\right]^{-1}, \tag{17}$$

or

$$C_j^{-2}=2\pi[(L-R)-L/(1+L^2\lambda_j^2)]. \tag{18}$$

Differentiating Eq. (16) and applying the condition (15) shows that the λ_j are the roots of the equation

$$\tan\lambda_j(L-R)=L\lambda_j. \tag{19}$$

The lowest root of Eq. (19) is[1]

$$\lambda_0^2=3R/L^3[1+(9/5)R/L]. \tag{20}$$

The higher λ_j's increase so rapidly with increasing j's, that terms with $j\geq 1$ contribute a negligible amount to the series in Eq. (12) and may be neglected.

If the approximation is made that $R\ll L$, and Eqs. (18) and (20) are combined, the result is

$$C_0=1/[2(\pi R)^{\frac{1}{2}}]. \tag{21}$$

The only quantity that remains to be determined in order to make use of Eq. (12) is β_j. This can be evaluated by substituting Eq. (16) into Eq. (9):

$$\beta_j=4\pi\kappa_1C_j\int_R^L \sin\lambda_j(r-R)r\,dr. \tag{22}$$

Performing the integration and making use of Eq. (19) gives

$$\beta_j=4\pi\kappa_1C_jR/\lambda_0. \tag{23}$$

Retaining only the first term in the series, substitution of Eqs. (16), (20), (21), and (23) into Eq. (12) gives

$$n=\frac{\kappa_1\tau_0}{\lambda_0}\frac{\sin\lambda_0(r-R)}{r}(1-e^{-t/\tau_0}). \tag{24}$$

The rate of growth of the precipitate particle can be calculated from the flux of atoms across the particle surface. This is

$$dV/dt=4\pi R^2vJ_R, \tag{25}$$

where V is the particle volume, v is the volume per atom of diffusing species, and J_R is the flux entering the particle. J_R is related to the concentration gradient by

$$J_R=D(\partial n/\partial r)_R. \tag{26}$$

TABLE I. Solutions of Eq. (38): $(\alpha'\rho+1)\rho d\rho/dt'=[1-e^{-(\alpha'\rho+1)t}]$.

	$\alpha=0.01$			$\alpha=0.1$			$\alpha=0.5$			$\alpha=1$			$\alpha=2$			$\alpha=5$	
t'	ρ	$d\rho/dt'$	t'	ρ	$d\rho/dt'$	t'	ρ	$d\rho/dt'$	t'	ρ	$d\rho/dt'$	t'	ρ	$d\rho/dt'$	t'	ρ	$d\rho/dt'$
0.02	0.01993	0.9934	0.02	0.01993	0.9934	0.02	0.01993	0.9933	0.02	0.01993	0.9932	0.02	0.01993	0.9931	0.02	0.01993	0.9926
0.08	0.07895	0.9738	0.08	0.07894	0.9736	0.08	0.7892	0.9727	0.08	0.07889	0.9716	0.08	0.07882	0.9693	0.1	0.09777	0.9503
0.14	0.1368	0.9549	0.14	0.1368	0.9543	0.14	0.1366	0.9516	0.14	0.1365	0.9483	0.14	0.1362	0.9417	0.18	0.1715	0.8919
0.2	0.1935	0.9364	0.2	0.1935	0.9352	0.20	0.1931	0.9300	0.2	0.1927	0.9236	0.2	0.1918	0.9111	0.26	0.2402	0.8241
0.26	0.2492	0.9185	0.26	0.2490	0.9166	0.26	0.2482	0.9082	0.26	0.2473	0.8979	0.26	0.2455	0.8781	0.34	0.3033	0.7533
0.32	0.3038	0.9011	0.32	0.3035	0.8983	0.32	0.3021	0.8861	0.32	0.3004	0.8714	0.32	0.2971	0.8436	0.42	0.3608	0.6840
0.38	0.3573	0.8842	0.38	0.3568	0.8804	0.38	0.3546	0.8640	0.38	0.3519	0.8445	0.38	0.3467	0.8084	0.5	0.4129	0.6196
0.44	0.4099	0.8677	0.44	0.4091	0.8629	0.44	0.4058	0.8420	0.44	0.4017	0.8174	0.44	0.3941	0.7729	0.58	0.4601	0.5614
0.50	0.4615	0.8518	0.5	0.4604	0.8457	0.50	0.4550	0.8201	0.5	0.4500	0.7904	0.50	0.4394	0.7378	0.66	0.5029	0.5101
0.56	0.5121	0.8362	0.56	0.5106	0.8290	0.56	0.5042	0.7984	0.56	0.4966	0.7637	0.56	0.4827	0.7035	0.74	0.5419	0.4655
0.62	0.5618	0.8211	0.62	0.5599	0.8126	0.62	0.5514	0.7770	0.62	0.5416	0.7372	0.62	0.5239	0.6703	0.82	0.5776	0.4270
0.68	0.6106	0.8065	0.68	0.6081	0.7966	0.68	0.5974	0.7559	0.68	0.5851	0.7114	0.68	0.5631	0.6385	0.9	0.6104	0.3938
0.74	0.6586	0.7922	0.74	0.6555	0.7810	0.74	0.6422	0.7353	0.74	0.6270	0.6862	0.74	0.6005	0.6082	0.98	0.6407	0.3653
0.8	0.7057	0.7784	0.8	0.7019	0.7658	0.8	0.6857	0.7151	0.8	0.6674	0.6619	0.80	0.6361	0.5795	1.165	0.7032	0.3133
0.86	0.7520	0.7649	0.86	0.7474	0.7510	0.86	0.7280	0.6955	0.86	0.7064	0.6384	0.86	0.6701	0.5525	1.325	0.7505	0.2798
0.92	0.7975	0.7518	0.92	0.7920	0.7365	0.92	0.7691	0.6763	0.92	0.7440	0.6158	0.92	0.7025	0.5272	1.525	0.8032	0.2481
0.98	0.8422	0.7391	0.98	0.8357	0.7224	0.98	0.8092	0.6577	0.98	0.7803	0.5941	1.000	0.7434	0.4960	1.725	0.8503	0.2239
1.085	0.9187	0.7177	1.085	0.9103	0.6986	1.085	0.8766	0.6266	1.085	0.8408	0.5584	1.165	0.8205	0.4402	1.925	0.8931	0.2049
1.165	0.9755	0.7021	1.205	0.9926	0.6728	1.205	0.9497	0.5932	1.205	0.9055	0.5212	1.325	0.8872	0.3960	2.125	0.9325	0.1894
						1.285	0.9963	0.5722	1.285	0.9463	0.4984	1.485	0.9476	0.3596	2.325	0.9690	0.1766
									1.365	0.9853	0.4772	1.605	0.9893	0.3365	2.485	0.9965	0.1677
	$\alpha=7$			$\alpha=10$			$\alpha=20$			$\alpha=50$			$\alpha=70$			$\alpha=100$	
0.02	0.01993	0.9923	0.02	0.01993	0.9919	0.02	0.01991	0.9904	0.02	0.01988	0.9860	0.01	0.009975	0.9941	0.01	0.009971	0.9930
0.12	0.1163	0.9276	0.1	0.09720	0.9337	0.1	0.09609	0.9025	0.12	0.1089	0.7672	0.05	0.04856	0.9242	0.05	0.04815	0.9011
0.22	0.2045	0.8334	0.18	0.1686	0.8468	0.18	0.6131	0.7704	0.18	0.1502	0.6132	0.1	0.09120	0.7754	0.1	0.08869	0.7167
0.32	0.2826	0.7299	0.28	0.2471	0.7246	0.26	0.2194	0.6377	0.28	0.2015	0.4280	0.3	0.1953	0.3448	0.2	0.1444	0.4282
0.42	0.3506	0.6321	0.4	0.3258	0.5897	0.34	0.2657	0.5263	0.42	0.2508	0.2935	0.5	0.2492	0.2175	0.3	0.1795	0.2928
0.52	0.4095	0.5470	0.52	0.3898	0.4827	0.42	0.3042	0.4403	0.65	0.3039	0.2031	0.7	0.2869	0.1653	0.4	0.2052	0.2265
0.62	0.4605	0.4766	0.64	0.4427	0.4033	0.54	0.3513	0.3501	0.92	0.3528	0.1521	0.9	0.3168	0.1362	0.7	0.2585	0.1441
0.72	0.5052	0.4196	0.76	0.4875	0.3452	0.7	0.4008	0.2762	1.285	0.4015	0.1182	1.2	0.3540	0.1096	0.9	0.2846	0.1193
0.82	0.5448	0.3739	0.88	0.5262	0.3023	0.9	0.4502	0.2220	1.765	0.4518	0.09383	1.6	0.3933	0.08910	1.2	0.3172	0.09636
0.92	0.5803	0.3372	1.00	0.5604	0.2698	1.165	0.5029	0.1798	2.365	0.5024	0.07622	2	0.4262	0.07609	1.6	0.3519	0.07854
1.045	0.6201	0.3008	1.285	0.6293	0.2179	1.485	0.5551	0.1488	3.085	0.5522	0.06329	2.5	0.4613	0.06511	2.5	0.4119	0.05755
1.245	0.6757	0.2581	1.565	0.6855	0.1857	1.845	0.6044	0.1264	3.925	0.6010	0.05358	3.0	0.4919	0.05739	3.5	0.4629	0.04568
1.445	0.7241	0.2275	1.845	0.7342	0.1633	2.245	0.6514	0.1094	4.925	0.6505	0.04586	4	0.5437	0.04709	4.5	0.5048	0.03849
1.645	0.7672	0.2046	2.125	0.7774	0.1466	2.725	0.7003	0.09517	6.125	0.7015	0.03952	4.5	0.5663	0.04345	6.0	0.5570	0.03167
1.845	0.8063	0.1867	2.405	0.8166	0.1336	3.285	0.7501	0.08332	7.485	0.7516	0.03449	5	0.5872	0.04044	8	0.6143	0.02608
2.045	0.8421	0.1722	2.685	0.8525	0.1232	3.925	0.8001	0.07351	9.005	0.8008	0.03043	7	0.6591	0.03219	10	0.6625	0.02244
2.245	0.8754	0.1603	2.965	0.8857	0.1145	4.685	0.8526	0.06498	10.805	0.8522	0.02691	8	0.6898	0.02941	15	0.7599	0.01709
2.445	0.9064	0.1502	3.285	0.9210	0.1063	5.485	0.9011	0.05826	12.725	0.9011	0.02410	9	0.7181	0.02716	20	0.8373	0.01410
2.685	0.9412	0.1400	3.565	0.9499	0.1003	6.365	0.9503	0.05258	14.965	0.9521	0.02161	15	0.8540	0.01927	25	0.9025	0.01214
2.885	0.9684	0.1327	3.845	0.9773	0.09499	7.325	0.9983	0.04776	17.205	0.9982	0.01967	20	0.9412	0.01589	30	0.9596	0.01075
3.125	0.9994	0.1252	4.045	0.9959	0.09162												

Evaluating the derivative from Eq. (24) gives

$$(\partial n/\partial r)_R=(\kappa_1\tau_0/R)(1-e^{-t/\tau_0}), \tag{27}$$

so that Eq. (25) becomes

$$dV/dt=4\pi RDv\kappa_1\tau_0(1-e^{-t/\tau_0}), \tag{28}$$

or

$$RdR/dt=Dv\kappa_1\tau_0(1-e^{-t/\tau_0}). \tag{29}$$

The relaxation time τ_0 is related to the particle radius R through Eqs. (11) and (20). Thus, for $R\ll 1$,

$$1/\tau_0=(3DR/L^3)+\kappa_2. \tag{30}$$

Equation (29) cannot be solved analytically, but useful numerical solutions can be obtained by defining the quantities α, R', and t' by

$$\alpha\equiv\tau_A/\tau_D, \tag{31}$$

$$t'\equiv t/\tau_A, \tag{32}$$

$$C_1\equiv\tau_A{}^2Dv\kappa_1/L^2, \tag{33}$$

$$R'=R/L. \tag{34}$$

In these equations τ_A and τ_D are defined by

$$\tau_A=1/\kappa_2;\quad \tau_D=L^2/3D. \tag{35}$$

τ_A and τ_D have the dimensions of time and may be thought of as the relaxation times of the annihilation and diffusion processes, respectively.

By using the definitions embodied in Eqs. (31) to (35), Eq. (29) becomes

$$(\alpha R'+1)R'dR'/dt'=C_1[1-e^{-(\alpha R'+1)t'}]. \tag{36}$$

Now transform R' according to the definition

$$\rho\equiv R'C_1^{-\frac{1}{2}}. \tag{37}$$

Then Eq. (36) becomes

$$(\alpha'\rho+1)\rho d\rho/dt'=1-e^{-(\alpha'\rho+1)t'}, \tag{38}$$

where

$$\alpha'=C_1^{\frac{1}{2}}\tau_A/\tau_D.$$

Equation (38) was solved for ρ and $d\rho/dt'$ by a Runge-Kutta integration program on a digital computer for the initial conditions $\rho=0$ and $d\rho/dt'=1$ at $t'=0$. [Note that for $t'\ll 1/(\alpha'\rho+1)$, Eq. (38) gives $\rho^2\approx t'^2$ +constant, so that if the radius is zero at $t=0$ it is proportional to the time for small t.] The results are shown in Table I and are displayed graphically in Fig. 1, where ρ, the reduced radius, is plotted against t', the reduced time, for a range of values of α.

A special case of Eq. (36), of great interest because of its application to the formation of voids in metals,[7] is given by the condition ($\alpha R' \ll 1$). This means that the annihilation constant κ_2 is much greater than $3DR/L^3$. In this case, Eq. (36) reduces to

$$R'dR'/dt' = C_1(1-e^{-t'}). \tag{39}$$

Integration of Eq. (37) gives

$$\tfrac{1}{2}R'^2 = C_1(t' + e^{-t'} - 1). \tag{40}$$

In the short-time approximation, when $t' \ll 1$, Eq. (40) simplifies to

$$R' = C_1^{\frac{1}{2}} t', \tag{41}$$

so that in this special case the radius is proportional to the time.

CASE 2. DIFFUSION TO THE WALL OF A SPHERE

In this section, the physical situation being considered is one in which the diffusing species is being created and destroyed throughout a spherical region of radius L. This species diffuses to the surface of the spherical region and then migrates instantaneously to a spherical precipitate particle located on this surface. The eigenvalue equation is the same as for case 1,

$$d^2(r\psi_j)/dr^2 + \lambda_j^2(r\psi_j) = 0; \tag{42}$$

but the boundary conditions in this case are

$$\psi_j(L) = 0, \tag{43}$$

$$(d\psi_j/dr)_0 = 0. \tag{44}$$

The eigenfunctions of Eq. (42) are again given by

$$\psi_j = C_j \frac{\sin(\lambda_j r + \delta)}{r}, \tag{45}$$

but C_j and δ have values that are different from those for case 1, because the boundary conditions are different. From (43), it is found that $\delta = -\lambda_j L$ so that Eq. (45) becomes

$$\psi_j = C_j \frac{\sin\lambda_j(r-L)}{r} = -C_j \frac{\sin\lambda_j(L-r)}{r}. \tag{46}$$

The normalization condition is

$$C_j^2 = \left[4\pi \int_0^L \sin^2\lambda(r-L)dr\right]^{-1}, \tag{47}$$

which gives

$$C_j^{-2} = \frac{4\pi}{\lambda_j}\left(\frac{\lambda_j L}{2} - \frac{\sin 2\lambda_j L}{4}\right). \tag{48}$$

The λ_j are determined by the boundary condition

[7] P. R. Oliver and L. A. Girifalco (to be published).

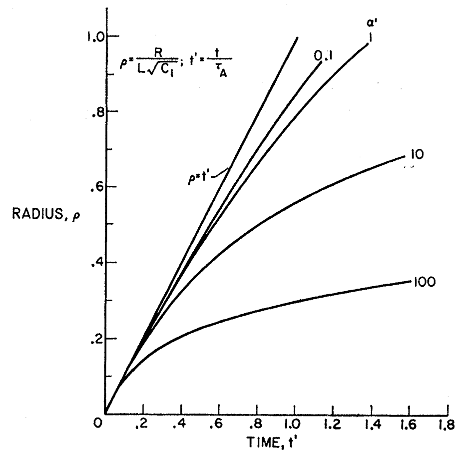

FIG. 1. Reduced radius versus reduced time for spherical mechanism calculated from Eq. (38).

(44). Differentiating (45) gives

$$\frac{d\psi_j}{dr} = A_j\left(\frac{\lambda_j \cos\lambda_j(r-L)}{r} - \frac{\sin\lambda_j(r-L)}{2}\right). \tag{49}$$

This derivative is not defined at $r=0$. In order to make use of the boundary condition, it is necessary to take the limit of (47) as r goes to zero. The result is that

$$\sin\lambda_j L = 0, \tag{50}$$

so that the λ_j are given by

$$\lambda_j = j\pi/L. \tag{51}$$

Equation (50) simplifies the expression for C_j, since it requires that the second term in (48) be zero. Therefore,

$$C_j^{-2} = 2\pi L. \tag{52}$$

Combining Eqs. (52), (42), and (46) gives the final result for ψ_j:

$$\psi_j = (2\pi L)^{-\frac{1}{2}} \frac{\sin[(j\pi/L)(r-L)]}{r}. \tag{53}$$

The constants β_j are evaluated from Eq. (9) just as in case 1:

$$\beta_j = 4\pi(2\pi L)^{-\frac{1}{2}}\kappa_1 \int_0^L r \sin\left(\frac{j\pi}{L}(r-L)\right)dr. \tag{54}$$

Performing the integration gives

$$\beta_j = -2\sqrt{2}\kappa_1 L^{\frac{3}{2}}/j\sqrt{\pi}. \tag{55}$$

The relaxation times τ_j are given by substituting Eq. (44) into Eq. (11):

$$1/\tau_j = Dj^2\pi^2/L^2 + \kappa_2. \tag{56}$$

The concentration as a function of position and time is obtained by substituting Eq. (53), (55), and (56)

TABLE II. Values of $S_1(\alpha)=\sum_{j=1}^{\infty}\frac{1}{1+\alpha j^2}$ and $S_3(\alpha)=\sum_{j=1}^{\infty}\frac{1}{(1+\alpha j^2)^2}$.

α	$S_1(\alpha)$	$S_3(\alpha)$	α	$S_1(\alpha)$	$S_3(\alpha)$
0.01	15.2063	7.3539	4	0.3563	0.04465
0.05	6.5241	3.0124	4.5	0.3212	0.03677
0.10	4.4668	1.9836	5	0.2924	0.03081
0.20	3.0121	1.2562	6.0	0.2481	0.02254
0.30	2.3676	0.93431	7	0.2155	0.01721
0.40	1.9837	0.74314	8	0.1904	0.01357
0.50	1.7219	0.61376	9	0.1706	0.01097
0.60	1.5289	0.51949	10	0.1546	9.054×10^{-3}
0.70	1.3793	0.44749	15	0.1051	4.262×10^{-3}
0.80	1.2592	0.39066	20	0.07964	2.469×10^{-3}
0.90	1.1600	0.34470	25	0.06411	1.609×10^{-3}
1	1.0765	0.30684	30	0.05365	1.131×10^{-3}
1.2	0.9431	0.24834	40	0.04045	6.458×10^{-4}
1.4	0.8406	0.20555	50	0.03247	4.171×10^{-4}
1.6	0.7591	0.17317	60	0.02711	2.915×10^{-4}
1.8	0.6926	0.14800	70	0.02328	2.151×10^{-4}
2	0.6371	0.12801	80	0.02039	1.652×10^{-4}
2.5	0.5315	0.09286	90	0.01814	1.309×10^{-4}
3	0.4563	0.07050	100	0.01634	1.062×10^{-4}
3.5	0.4001	0.05537			

into Eq. (12):

$$n=-\frac{2L\kappa_1}{\pi}\sum_j\frac{1}{j}\left(\frac{Dj^2\pi^2}{L^2}+\kappa_2\right)^{-1}\times\left\{1-\exp\left[-\left(\frac{Dj^2\pi^2}{L^2}+\kappa_2\right)t\right]\right\}\sin\left(\frac{j\pi}{L}(r-L)\right). \quad (57)$$

The total number of atoms entering the surface of the sphere is given by the flux at $r=L$, and all of these atoms reach the precipitate particle so that the rate of growth of the volume of the particle is

$$dV/dt=4\pi L^2vJ_L=-4\pi L^2vD(\partial n/\partial r)_L, \quad (58)$$

J_L being the flux at $r=L$. From Eq. (57), the derivative is

$$\left(\frac{\partial n}{\partial r}\right)_L=-2\kappa_1\sum_j\left(\frac{Dj^2\pi^2}{L^2}+\kappa_2\right)^{-1}\times\left\{1-\exp\left[-\left(\frac{Dj^2\pi^2}{L^2}+\kappa_2\right)t\right]\right\}. \quad (59)$$

The value of the sum in Eq. (59) depends on the relative magnitudes of the rate of diffusion and the rate of annihilation. In the general case, a graphical procedure is most convenient for investigating the form of the dependence of the particle growth rate on time. For this purpose define two relaxation times, one for the diffusion process and one for the annihilation process, just as in case 1:

$$\tau_D\equiv L^2/D\pi^2, \quad (60)$$

$$\tau_A\equiv 1/\kappa_2. \quad (61)$$

Then Eq. (59) becomes

$$\left(\frac{\partial n}{\partial r}\right)_L=-2\kappa_1\sum_j\left(\frac{\tau_D\tau_A}{\tau_Aj^2+\tau_D}\right)\times\left\{1-\exp\left[-\left(\frac{\tau_Aj^2+\tau_D}{\tau_A\tau_D}\right)t\right]\right\}. \quad (62)$$

Since the eigenvalues given by Eq. (44) can be either positive or negative, the index j runs from $-\infty$ to $+\infty$. However, the terms in the sum involve only j^2. Therefore, Eq. (62) can be written as

$$\left(\frac{\partial n}{\partial r}\right)_L=-2\kappa_1\tau_A(1-e^{-t/\tau_A})-4\kappa_1\sum_{j=1}^{\infty}\left(\frac{\tau_D\tau_A}{\tau_Aj^2+\tau_D}\right)\times\left\{1-\exp\left[-\left(\frac{\tau_Aj^2+\tau_D}{\tau_A\tau_D}\right)t\right]\right\}, \quad (63)$$

or

$$\left(\frac{\partial n}{\partial r}\right)_L=-2\kappa_1\tau_A(1-e^{-t/\tau_A})-4\kappa_1\tau_A\sum_{j=1}^{\infty}\frac{1}{1+j^2(\tau_A/\tau_D)}\times\left\{1-\exp\left[-\left(\frac{\tau_A}{\tau_D}j^2+1\right)\frac{t}{\tau_A}\right]\right\}. \quad (64)$$

Combining Eqs. (58) and (64)

$$dV/dt=8\pi L^2vD\kappa_1\tau_A[(1-e^{-t/\tau_A})+2S(\tau_A/\tau_D,t/\tau_A)], \quad (65)$$

where

$$S\left(\frac{\tau_A}{\tau_D},\frac{t}{\tau_A}\right)=\sum_{j=1}^{\infty}\frac{1}{1+j^2(\tau_A/\tau_D)}\times\left\{1-\exp\left[-\left(\frac{\tau_A}{\tau_D}j^2+1\right)\frac{t}{\tau_A}\right]\right\}. \quad (66)$$

Integrating Eq. (65), with the condition $V=0$ at $t=0$, gives

$$V=C_2\tau_A\{t'[1+2S_1(\alpha)]+e^{-t'}[1+2S_2(\alpha,t')]-[1+2S_3(\alpha)]\}, \quad (67)$$

where C_2, t', $S_1(\alpha)$, $S_2(\alpha,t')$, and $S_3(\alpha)$ are defined by

$$C_2=8\pi L^2vD\kappa_1\tau_A, \quad (68)$$

$$\alpha=\tau_A/\tau_D, \quad (69)$$

$$t'=t/\tau_A, \quad (70)$$

$$S_1(\alpha)=\sum_{j=1}^{\infty}\frac{1}{1+\alpha j^2}, \quad (71)$$

$$S_2(\alpha,t')=\sum_{j=1}^{\infty}\frac{\exp(-\alpha j^2t')}{(1+\alpha j^2)^2}, \quad (72)$$

$$S_3(\alpha)=\sum_{j=1}^{\infty}\frac{1}{(1+\alpha j^2)^2}. \quad (73)$$

TABLE III. Values of $S_2(\alpha,t)=\sum_{j=1}^{\infty}\frac{\exp(-\alpha_j^2t')}{(1+\alpha_j^2)^2}$.

α	t′ 0.01	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1	1.2
0.01	7.2861	7.0685	6.84489	6.4971	6.2139	5.9746	5.7666	5.5824	5.4171	5.2672	5.1302	5.0040	4.7786
.05	2.9821	2.8847	2.7865	2.6292	2.5026	2.3955	2.3025	2.2201	2.1462	2.0792	2.0179	1.9615	1.8607
.1	1.9622	1.8934	1.8239	1.7127	1.6231	1.5477	1.4817	1.4234	1.3712	1.3238	1.2804	1.2405	1.1692
.2	1.2411	1.1924	1.1433	1.0647	1.0013	.9478	.9013	.8601	.8232	.7897	.7590	.7308	.6804
.3	.9219	.8822	.8421	.7779	.7263	.6826	.6447	.6111	.5810	.5537	.5287	.5057	.4647
.4	.7324	.6981	.6634	.6079	.5632	.5255	.4928	.4638	.4379	.4144	.3929	.3732	.3380
.5	.6042	.5735	.5426	.4931	.4533	.4198	.3907	.3650	.3421	.3213	.3023	.2850	.2541
.6	.5108	.4829	.4547	.4098	.3738	.3434	.3172	.2940	.2733	.2547	.2378	.2223	.1950
.7	.4395	.4137	.3878	.3465	.3135	.2857	.2617	.2407	.2220	.2051	.1899	.1761	.1518
.8	.3832	.3592	.3352	.2969	.2663	.2407	.2187	.1995	.1824	.1672	.1534	.1410	.1194
.9	.3377	.3152	.2927	.2570	.2286	.2049	.1847	.1670	.1514	.1375	.1251	.1139	9.470×10^{-2}
1	.3002	.2791	.2579	.2245	.1980	.1579	.1572	.1409	.1266	.1140	.1027	9.270×10^{-2}	7.563×10^{-2}
1.2	.2424	.2234	.2045	.1748	.1514	.1323	.1161	.1022	9.023×10^{-2}	7.975×10^{-2}	7.056×10^{-2}	6.248×10^{-2}	4.905×10^{-2}
1.4	.2001	.1829	.1658	.1392	.1185	.1016	8.762×10^{-2}	7.575×10^{-2}	6.561×10^{-2}	5.691×10^{-2}	4.939×10^{-2}	4.290×10^{-2}	3.238×10^{-2}
1.6	.1682	.1524	.1368	.1127	9.427×10^{-2}	7.943×10^{-2}	6.722×10^{-2}	5.703×10^{-2}	4.847×10^{-2}	4.124×10^{-2}	3.511×10^{-2}	2.990×10^{-2}	2.170×10^{-2}
1.8	.1434	.1288	.1145	9.265×10^{-2}	7.607×10^{-2}	6.293×10^{-2}	5.227×10^{-2}	4.351×10^{-2}	3.628×10^{-2}	3.027×10^{-2}	2.526×10^{-2}	2.110×10^{-2}	1.471×10^{-2}
2	.1237	.1102	9.702×10^{-2}	7.705×10^{-2}	6.211×10^{-2}	5.043×10^{-2}	4.110×10^{-2}	3.357×10^{-2}	2.745×10^{-2}	2.245×10^{-2}	1.838×10^{-2}	1.504×10^{-2}	1.008×10^{-2}
2.5	8.915×10^{-2}	7.773×10^{-2}	6.682×10^{-2}	5.065×10^{-2}	3.897×10^{-2}	3.018×10^{-2}	2.344×10^{-2}	1.824×10^{-2}	1.419×10^{-2}	1.105×10^{-2}	8.61×10^{-3}	6.70×10^{-3}	4.06×10^{-3}
3	6.726×10^{-2}	5.741×10^{-2}	4.817×10^{-2}	3.484×10^{-2}	2.557×10^{-2}	1.887×10^{-2}	1.396×10^{-2}	1.034×10^{-2}	7.65×10^{-3}	5.67×10^{-3}	4.20×10^{-3}	3.11×10^{-3}	1.71×10^{-3}
3.5	5.249×10^{-2}	4.388×10^{-2}	3.593×10^{-2}	2.479×10^{-2}	1.735×10^{-2}	1.219×10^{-2}	8.59×10^{-3}	6.05×10^{-3}	4.26×10^{-3}	3.00×10^{-3}	2.12×10^{-3}	1.49×10^{-3}	7.41×10^{-4}
4	4.207×10^{-2}	3.444×10^{-2}	2.753×10^{-2}	1.811×10^{-2}	1.208×10^{-2}	8.08×10^{-3}	5.41×10^{-3}	3.63×10^{-3}	2.43×10^{-3}	1.63×10^{-3}	1.09×10^{-3}	7.33×10^{-4}	3.29×10^{-4}
4.5	3.443×10^{-2}	2.761×10^{-2}	2.155×10^{-2}	1.352×10^{-2}	8.58×10^{-3}	5.47×10^{-3}	3.48×10^{-3}	2.22×10^{-3}	1.42×10^{-3}	9.03×10^{-4}	5.76×10^{-4}	3.67×10^{-4}	1.49×10^{-4}
5	2.867×10^{-2}	2.252×10^{-2}	1.716×10^{-2}	1.026×10^{-2}	6.20×10^{-3}	3.76×10^{-3}	2.28×10^{-3}	1.38×10^{-3}	8.39×10^{-4}	5.09×10^{-4}	3.09×10^{-4}	1.87×10^{-4}	
6	2.072×10^{-2}	1.562×10^{-2}	1.135×10^{-2}	6.16×10^{-3}	3.37×10^{-3}	1.85×10^{-3}	1.02×10^{-3}	5.58×10^{-4}	3.06×10^{-4}	1.68×10^{-4}			
7	1.563×10^{-2}	1.131×10^{-2}	7.83×10^{-3}	3.86×10^{-3}	1.91×10^{-3}	9.50×10^{-4}	4.72×10^{-4}	2.34×10^{-4}	1.16×10^{-4}				
8	1.218×10^{-2}	8.47×10^{-3}	5.58×10^{-3}	2.49×10^{-3}	1.12×10^{-3}	5.03×10^{-4}	2.26×10^{-4}	1.02×10^{-4}					
9	9.73×10^{-3}	6.50×10^{-3}	4.09×10^{-3}	1.65×10^{-3}	6.72×10^{-4}	2.73×10^{-4}	1.11×10^{-4}						
10	7.94×10^{-3}	5.09×10^{-3}	3.05×10^{-3}	1.12×10^{-3}	4.11×10^{-4}	1.51×10^{-4}							
15	3.53×10^{-3}	1.86×10^{-3}	8.72×10^{-4}	1.94×10^{-4}									
20	1.93×10^{-3}	8.37×10^{-4}	3.07×10^{-4}										
25	1.19×10^{-3}	4.24×10^{-4}	1.21×10^{-4}										
30	7.92×10^{-4}	2.32×10^{-4}											
40	4.07×10^{-4}												
50	2.37×10^{-4}												
60	1.49×10^{-4}												

α	t′ 1.4	1.6	1.8	2	2.5	3	3.5	4	4.5	5	6	7	8
0.01	4.5819	4.4079	4.2521	4.1115	3.8114	3.5660	3.3600	3.1834	3.0298	2.8945	2.6657	2.4784	2.3213
.05	1.7727	1.6949	1.6252	1.5623	1.4281	1.3184	1.2262	1.1473	1.0786	1.0180	.9157	.8320	.7617
.1	1.1070	1.0520	1.0028	.9583	.8634	.7858	.7206	.6648	.6162	.5734	.5011	.4419	.3924
.2	.6365	.5976	.5628	.5314	.4644	.4097	.3639	.3247	.2908	.2611	.2117	.1724	.1407
.3	.4290	.3974	.3692	.3438	.2899	.2462	.2102	.1799	.1543	.1325	9.796×10^{-2}	7.251×10^{-2}	5.369×10^{-2}
.4	.3075	.2806	.2567	.2353	.1904	.1549	.1263	.1033	8.445×10^{-2}	6.910×10^{-2}	4.629×10^{-2}	3.003×10^{-2}	2.080×10^{-2}
.5	.2275	.2043	.1837	.1655	.1281	9.944×10^{-2}	7.733×10^{-2}	6.019×10^{-2}	4.686×10^{-2}	3.649×10^{-2}	2.213×10^{-2}	1.342×10^{-2}	8.14×10^{-3}
.6	.1717	.1514	.1338	.1184	8.737×10^{-2}	6.463×10^{-2}	4.785×10^{-2}	3.544×10^{-2}	2.625×10^{-2}	1.945×10^{-2}	1.067×10^{-2}	5.86×10^{-3}	3.21×10^{-3}
.7	.1312	.1137	9.860×10^{-2}	8.558×10^{-2}	6.019×10^{-2}	4.239×10^{-2}	2.986×10^{-2}	2.104×10^{-2}	1.483×10^{-2}	1.045×10^{-2}	5.19×10^{-3}	2.58×10^{-3}	1.30×10^{-3}
.8	.1013	8.615×10^{-2}	7.330×10^{-2}	6.241×10^{-2}	4.179×10^{-2}	2.800×10^{-2}	1.877×10^{-2}	1.258×10^{-2}	8.43×10^{-3}	5.65×10^{-3}	2.54×10^{-3}	1.14×10^{-3}	5.13×10^{-4}
.9	7.888×10^{-2}	6.578×10^{-2}	5.489×10^{-2}	4.582×10^{-2}	2.920×10^{-2}	1.861×10^{-2}	1.187×10^{-2}	7.57×10^{-3}	4.83×10^{-3}	3.08×10^{-3}	1.25×10^{-3}	5.09×10^{-4}	2.07×10^{-4}
1	6.180×10^{-2}	5.054×10^{-2}	4.135×10^{-2}	3.385×10^{-2}	2.052×10^{-2}	1.245×10^{-2}	7.55×10^{-3}	4.58×10^{-3}	2.78×10^{-3}	1.68×10^{-3}	6.20×10^{-4}	2.28×10^{-4}	
1.2	3.854×10^{-2}	3.030×10^{-2}	2.383×10^{-2}	1.875×10^{-2}	1.029×10^{-2}	5.65×10^{-3}	3.10×10^{-3}	1.70×10^{-3}	9.33×10^{-4}	5.12×10^{-4}	1.54×10^{-4}		
1.4	2.446×10^{-2}	1.849×10^{-2}	1.397×10^{-2}	1.056×10^{-2}	5.24×10^{-3}	2.60×10^{-3}	1.29×10^{-3}	6.42×10^{-4}	3.19×10^{-4}	1.58×10^{-4}			
1.6	1.575×10^{-2}	1.144×10^{-2}	8.30×10^{-3}	6.03×10^{-3}	2.71×10^{-3}	1.22×10^{-3}	5.47×10^{-4}	2.46×10^{-4}	1.10×10^{-4}				
1.8	1.026×10^{-2}	7.16×10^{-3}	5.00×10^{-3}	3.49×10^{-3}	1.42×10^{-3}	5.76×10^{-4}	2.34×10^{-4}						
2	6.76×10^{-3}	4.53×10^{-3}	3.04×10^{-3}	2.04×10^{-3}	7.49×10^{-4}	2.75×10^{-4}	1.01×10^{-4}						
2.5	2.47×10^{-3}	1.50×10^{-3}	9.07×10^{-4}	5.50×10^{-4}	1.58×10^{-4}								
3	9.37×10^{-4}	5.14×10^{-4}	2.82×10^{-4}	1.55×10^{-4}									
3.5	3.68×10^{-4}	1.83×10^{-4}											
4	1.48×10^{-4}												

α	t′ 9	10	15	20	25	30	40	50	60	70	80	90	100
0.01	2.1870	2.0704	1.6546	1.3922	1.2072	1.0677	.8680	.7293	.6257	.5446	.4788	.4241	.3777
.05	.7017	.6495	.4636	.3465	.2646	.2041	.1230	7.449×10^{-2}	4.516×10^{-2}	2.739×10^{-2}	1.661×10^{-2}	1.008×10^{-2}	6.11×10^{-3}
.1	.3500	.3134	.1857	.1120	6.786×10^{-2}	4.115×10^{-2}	1.514×10^{-2}	5.57×10^{-3}	2.05×10^{-3}	7.54×10^{-4}	2.77×10^{-4}	1.02×10^{-4}	
.2	.1150	9.409×10^{-2}	3.458×10^{-2}	1.272×10^{-2}	4.68×10^{-3}	1.72×10^{-3}	2.33×10^{-4}						
.3	3.977×10^{-2}	2.946×10^{-2}	6.57×10^{-3}	1.47×10^{-3}	3.27×10^{-4}								
.4	1.394×10^{-2}	9.34×10^{-3}	1.26×10^{-3}	1.71×10^{-4}									
.5	4.94×10^{-3}	2.99×10^{-3}	2.46×10^{-4}										
.6	1.76×10^{-3}	9.68×10^{-4}											
.7	6.35×10^{-4}	3.16×10^{-4}											
.8	2.30×10^{-4}	1.04×10^{-4}											

In order to use Eq. (67) it is necessary to evaluate the sums S_1, S_2, and S_3. This has been done for a range of values of α and t' with the aid of a digital computer. The number of terms included in the sums ranged from 64 000 to 2600, depending on the rapidity of convergence of the sums for given values of α and t'. The results are listed in Table II and III.

Figure 2 shows plots of R' against t' for different values of α calculated from Eq. (67), where R' is defined by

$$R'=R(4\pi/3C_2\tau_A)^{\frac{1}{3}}. \quad (74)$$

For $t'\ll1$, expansion of the exponentials in Eq. (67) shows that V is proportional to t'. Therefore, in the short-time approximation, the radius is proportional to the cube root of the time.

CASE 3. DIFFUSION IN A TWO-DIMENSIONAL REGION

In this case, the diffusing species moves in a two-dimensional circular region of radius L and precipitates onto a particle of radius R located at the center of the region. For this case, the eigenvalue problem of Eq. (6) becomes

$$\frac{d^2\psi_j}{dr^2}+\frac{1}{r}\frac{d\psi_j}{dr}+\lambda_j^2\psi_j=0, \quad (75)$$

$$\psi_j(R)=0, \quad (76)$$

$$(d\psi_j/dr)_{r=L}=0. \quad (77)$$

Equation (75) is the zero-order Bessel equation with the solutions

$$\psi_j=A_jJ_0(\lambda_jr)+B_jY_0(\lambda_jr), \quad (78)$$

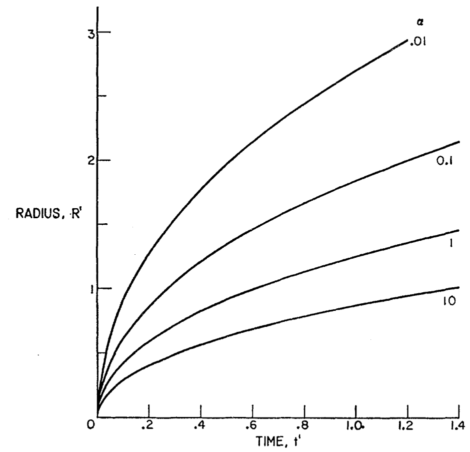

FIG. 2. Reduced radius versus reduced time for wall mechanism calculated from Eq. (67).

where A_j and B_j are constants and J_0 and Y_0 are zero-order Bessel functions of the first and second kind, respectively.

Differentiating Eq. (79) gives

$$\frac{d\psi_j}{dr}=A_j\frac{dJ_0(\lambda_j r)}{dr}+B_j\frac{dY_0(\lambda_j r)}{dr}. \tag{79}$$

From the properties of Bessel functions,

$$dJ_0(\lambda_j r)/dr=-\lambda_j J_1(\lambda_j r), \tag{80}$$

$$dY_0(\lambda_j r)/dr=-\lambda_j Y_1(\lambda_j r), \tag{81}$$

where J_1 and Y_1 are the first-order Bessel functions of the first and second kind, respectively. Using Eqs. (78) and (81), the boundary conditions, Eqs. (76) and (77) give

$$A_jJ_0(\lambda_jR)+B_jY_0(\lambda_jR)=0, \tag{82}$$

$$A_jJ_1(\lambda_jL)+B_jY_1(\lambda_jL)=0. \tag{83}$$

Solving Eqs. (82) and (83) for A_j/B_j, we have

$$A_j/B_j=-Y_0(\lambda_jR)/J_0(\lambda_jR)=-Y_1(\lambda_jL)/J_1(\lambda_jL). \tag{84}$$

Combining Eqs. (78) and (84) gives ψ_j in terms of only one constant, A_j:

$$\psi_j=A_j\{J_0(\lambda_jr)-[J_0(\lambda_jR)/Y_0(\lambda_jR)]Y_0(\lambda_jr)\}. \tag{85}$$

The constant A_j can be evaluated from the requirement that ψ_j be normalized. The result is

$$A_j^{-2}=\pi L^2\left[J_0(\lambda_jL)-\frac{J_0(\lambda_jR)}{Y_0(\lambda_jR)}Y_0(\lambda_jL)\right]^2 -\pi R^2\left[J_1(\lambda_jR)-\frac{J_0(\lambda_jR)}{Y_0(\lambda_jR)}Y_1(\lambda_jR)\right]^2. \tag{86}$$

The concentration n for this two-dimensional problem is obtained by substituting Eq. (85) into Eq. (12):

$$n=\sum_j A_j\beta_j\tau_j(1-e^{-t/\tau_j})\left[J_0(\lambda_jr)-\frac{J_0(\lambda_jR)}{Y_0(\lambda_jR)}Y_0(\lambda_jr)\right]. \tag{87}$$

The only quantity that remains to be evaluated is β_j. This can be done by substituting Eq. (85) into Eq. (9) and evaluating the integral by making use of the properties of Bessel functions. The result is

$$\beta_j=-\frac{2\pi\kappa_1}{\lambda_j}RA_j\left[J_1(\lambda_jR)-\frac{J_0(\lambda_jR)}{Y_0(\lambda_jR)}Y_1(\lambda_jR)\right]. \tag{88}$$

The rate of growth of a precipitate particle in the presence of a concentration profile given by Eq. (87) will depend on whether the particle is considered to be two or three dimensional. In this work, it will be assumed that the particle is a sphere which is bisected by the circular two-dimensional region. The diffusing species enters the sphere only through the perimeter of the great circle lying in the plane. Once the diffusing atom moves across this perimeter, however, internal surface diffusion takes place instantaneously so that the particle maintains its spherical shape. For this model, the rate of particle growth is given by

$$4\pi R^2=Dv2\pi R(\partial n/\partial r)_{r=R} \tag{89}$$

or

$$\frac{dR}{dt}=Dv/2R(\partial n/\partial r)_{r=R}. \tag{90}$$

Differentiating Eq. (87) with respect to r, evaluating the derivative at $r=R$, and substituting the result

TABLE IV. Eigenvalues for two-dimensional case, Eq. (92). λ_0R against L/R.

λ_0R	L/R	λ_0R	L/R	λ_0R	L/R	λ_0R	L/R	λ_0R	L/R
0.03	28.854	0.075	13.554	0.16	7.530	0.47	3.570	0.78	2.646
0.035	25.342	0.076	13.411	0.17	7.198	0.48	3.523	0.79	2.628
0.04	22.665	0.077	13.272	0.18	6.900	0.49	3.478	1.0	2.319
0.047	19.827	0.078	13.136	0.19	6.631	0.50	3.434	2.0	1.704
0.048	19.486	0.079	13.003	0.20	6.387	0.51	3.393	3.0	1.483
0.049	19.157	0.08	12.873	0.21	6.165	0.52	3.352	4.0	1.368
0.05	18.841	0.081	12.746	0.22	5.962	0.53	3.313	5.0	1.298
0.051	18.537	0.082	12.622	0.23	5.775	0.54	3.276	6.0	1.250
0.052	18.244	0.083	12.501	0.24	5.603	0.55	3.240	7.0	1.216
0.053	17.961	0.084	12.383	0.25	5.444	0.56	3.204	8.0	1.190
0.054	17.688	0.085	12.267	0.26	5.296	0.57	3.170	9.0	1.169
0.055	17.424	0.086	12.154	0.27	5.158	0.58	3.138	10.0	1.152
0.056	17.169	0.087	12.043	0.28	5.029	0.59	3.106	11.0	1.139
0.057	16.923	0.088	11.934	0.29	4.909	0.60	3.075	12.0	1.128
0.058	16.684	0.089	11.828	0.30	4.796	0.61	3.045	13.0	1.118
0.059	16.454	0.090	11.724	0.31	4.689	0.62	3.016	14.0	1.110
0.060	16.230	0.091	11.622	0.32	4.589	0.63	2.988	15.0	1.103
0.061	16.013	0.092	11.523	0.33	4.495	0.64	2.960	16.0	1.096
0.062	15.803	0.093	11.425	0.34	4.406	0.65	2.934	17.0	1.091
0.063	15.600	0.094	11.329	0.35	4.321	0.66	2.908	18.0	1.086
0.064	15.402	0.095	11.235	0.36	4.241	0.67	2.883	19.0	1.081
0.065	15.210	0.096	11.143	0.37	4.165	0.68	2.858	20.0	1.077
0.066	15.023	0.097	11.053	0.38	4.092	0.69	2.835		
0.067	14.841	0.098	10.964	0.39	4.023	0.70	2.811		
0.068	14.665	0.099	10.877	0.40	3.957	0.71	2.789		
0.069	14.493	0.1	10.792	0.41	3.894	0.72	2.767		
0.070	14.326	0.11	10.019	0.42	3.834	0.73	2.746		
0.071	14.164	0.12	9.367	0.43	3.777	0.74	2.725		
0.072	14.005	0.13	8.809	0.44	3.722	0.75	2.704		
0.073	13.851	0.14	8.236	0.45	3.669	0.76	2.684		
0.074	13.701	0.15	7.903	0.46	3.618	0.77	2.665		

along with Eq. (88) into Eq. (90) gives

$$\frac{dR}{dt}=Dv\kappa_1\pi\sum_j\tau_jA_j^2(1-e^{-t/\tau_j})\times\left[J_1(\lambda_jR)-\frac{J_0(\lambda_jR)}{Y_0(\lambda_jR)}Y_1(\lambda_jR)\right]^2. \quad (91)$$

The only problem that remains to be solved in order to make Eq. (91) useful is the determination of the eigenvalues λ_j. This was done with the aid of a digital computer by numerically integrating Eq. (75) for given values of λ_jR and computing the corresponding values of the ratio L/R that satisfied the boundary conditions (76) and (77). In this way the first six eigenvalues $\lambda_0, \cdots, \lambda_5$ were obtained as functions of L/R. Inserting these eigenvalues into Eq. (91) and making some approximate calculations showed that the first term in the series is the dominant one, the higher terms contributing only 10^{-2} to 10^{-3} of the first term. It is, therefore, a good approximation to write Eq. (91) as

$$\frac{dR}{dt}=Dv\kappa_1\pi\tau_0A_0^2(1-e^{-t/\tau_0})\times\left[J_1(\lambda_0R)-\frac{J_0(\lambda_0R)}{Y_0(\lambda_0R)}Y_1(\lambda_0R)\right]^2, \quad (92)$$

and only the first eigenvalues λ_0 are needed in order to use this equation. Table IV lists λ_0R as a function of L/R.

It is convenient to define a function $F(R)$ by

$$F(R)=\pi A_0^2\{J_1(\lambda_0R)-[J_0(\lambda_0R)/Y_0(\lambda_0R)]Y_1(\lambda_0R)\}^2, \quad (93)$$

so that Eq. (92) becomes

$$dR/dt=Dv\kappa_1\tau_0(1-e^{-t/\tau_0})F(R). \quad (94)$$

This equation is difficult to handle even numerically, since τ_0 is a function of R through its dependence on λ_0. However, a solution is easily obtained in the short-time approximation $t/\tau_0\ll 1$. In this case, the exponential can be expanded, and integration of Eq. (94) gives

$$Dv\kappa_1\int_0^t\tau_0\left(\frac{t}{\tau_0}-\frac{1}{2}\frac{t^2}{\tau_0^2}\right)dt=\int_0^R\frac{dR}{F(R)}. \quad (95)$$

If we retain only the first term in the expansion, then

$$\tfrac{1}{2}Dv\kappa_1t^2=\int_0^R\frac{dR}{F(R)}. \quad (96)$$

The function $F(R)$ can be computed as a function of R from the eigenvalues in Table IV and tables of Bessel functions. The time can then be obtained as a function of R by numerical or graphical integration of Eq. (96). To illustrate the form of the R against t curve, the calculation was performed for the special case of $L=10^{-3}$ cm. The results are plotted in Fig. 3.

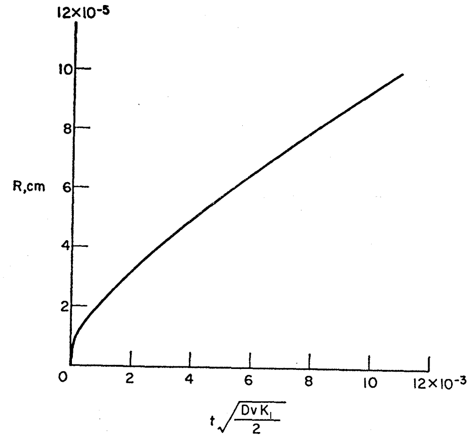

FIG. 3. Radius versus time for two-dimensional mechanism calculated from Eq. (96).

DISCUSSION AND CONCLUSION

Because of the complexity of the problem, analytic solutions of the diffusion-controlled precipitation kinetics in the presence of sources and sinks are not available. However, these solutions can be obtained by numerical methods and can be put in a convenient form.

The most striking differences among the three cases considered in this paper arise in the form of the radius-time curves in the short-time approximation. For case 1 (spherical mechanism), the radius is proportional to time for short times. For case 2 (wall mechanism), the radius is proportional to the cube root of the time. For case 3 (two-dimensional mechanism), the radius shows a very rapid rise at extemely short times and then a slower, almost linear increase with time.

The growth rate of the precipitate particle depends on the diffusion coefficient, the rate of production, and the rate of annihilation of the diffusing species. By the proper analysis of radius against time data according to the methods outlined in this paper, it should be possible to acquire the pertinent information concerning the mechanism of precipitation in systems containing sources and sinks.

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