Diffusion controlled colloidal growth rates for nonspherical clusters[a)]

J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Paul Meakin

Central Research and Development Department,[b)] Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

(Received 23 August 1982; accepted 5 November 1982)

Recent computer simulations[1,2] indicate that colloids which grow by a diffusion mechanism will have complex dendritic shapes for spatial dimension $d=2, 3, 4$ in contrast to the conventional spherical picture. The colloid shape may be characterized in terms of the radius of gyration R and the number of monomers aggregated N according to

$$N=\rho R^D \ , \tag{1}$$

where ρ is a dimensional constant and $D=\eta d$. In the conventional picture $\eta=1$; the computer simulations[2] indicate a more open structure with $\eta=5/6$.

The purpose of this note is to indicate the implication of the new result for colloid shape on the rate law for coagulation.

Our model for the colloid particle growth consists of monomers diffusing spherically symmetrically toward a single macroparticle. The monomers stick to the macroparticle (and do not migrate) once they touch any surface and form a complex cluster that has the property of Eq. (1).

Omitting inconsequential numerical constants, we solve for the steady state spherically symmetric flux J entering through a conceptual spherical surface surrounding the colloid at radius R. The flux is determined from the steady state concentration profile $c(r)$ of monomers according to the diffusion equation

$$\frac{1}{r^{d-1}}\frac{d}{dr}\, r^{d-1}\frac{d}{dr}\, c(r)=0 \tag{2}$$

with absorbing boundary conditions at the conceptual surface $c(R)=0$ and $c(r)\rightarrow c_0$ as $r\rightarrow\infty$. In light of the underlying mechanism, the spherically symmetric absorbing boundary condition is an idealization but this should not influence the functional form of results we obtain. From Eq. (3) one finds a concentration profile $c(r)=c_0[1-(R/r)^{d-2}]$ $d\geq 3$ and a flux $J=\mathfrak{D}c_0R^{d-2}$.

The resulting equation for the colloidal particle growth rate is identical to the conventional theory[3-5] of colloidal growth suitably modified to take into account that growth only occurs by aggregation of monomer on a single nucleating center and that the monomer is continuously replenished far from the macroparticle

$$\frac{dN}{dt}=J=\mathfrak{D}c_0R^{d-2} \tag{3}$$

where $\mathfrak{D}$ is the monomer diffusion coefficient. We obtain a particle growth rate law by combining Eqs. (3) and (1). The result when growth occurs through complex stable shapes according to Eq. (1) with $\eta<1$, is

$$R^{\alpha}(t)-R^{\alpha}(0)=\left[(\text{const.})\,\frac{\mathfrak{D}c_0}{\rho}\right]t \tag{4}$$

with

$$\alpha=2+(\eta-1)\,d=D-(d-2) \tag{5}$$

for α positive and $d\geq 3$.

The conventional spherical colloidal growth picture $\eta=1$, predicts the square radius law Eq. (6), familiar from combustion theory,[6,7] for all $d\geq 3$,

$$R^2(t)-R^2(0)=kt\ . \tag{6}$$

The computer simulation suggests $\eta=5/6$ which for three dimensions leads to a rate law of the form of Eq. (4) with $\alpha=3/2$. This is our main result and suggests a considerable variation from the square power law for the rate of coagulation in three dimensions. A similar analysis for $d=3$ has been presented by Witten.[8]

It is interesting to note that Eq. (1) implies startling dimensionality dependence for the rate law when $\eta<1$. In the case $\eta=5/6$, we find the rate law Eq. (4) for $3\leq d\leq 12$ and exponential growth $[dR^{10}(t)/dt]=\mathfrak{D}c_0R^{10}(t)$ at $d=12$.

This difference in behavior as a function of d may be understood as follows: combining Eqs. (1) and (2), one finds the ratio of the change in the number of particles in a cluster δN (in time interval δt) to the number of particles in the cluster

$$\frac{\delta N}{N}=\left(\frac{\mathfrak{D}c_0\delta t}{\rho}\right)R^{(1-\eta)d-2}\sim R^{-\alpha}\ . \tag{7}$$

In the conventional case $\eta=1$ and this ratio remains R^{-2} in all d yielding the square rate law Eq. (6). For $\eta<1$, there is a particular variation of the ratio with d. Below a critical dimension [$d=12$ in the case $\eta=5/6$], the ratio $[\delta N/N]$ decreases with increasing R, resulting in the modified rate law Eq. (4).

However, above this critical dimension, the ratio in Eq. (7) increases with increasing R, since α is negative. This signifies that the cluster size overwhelms any surrounding conceptual spherical surface outside of which a diffusive steady state flux is presumed to be established. Thus, our procedure must be modified. In this regime $(d-2)>D$, the cluster becomes transparent to diffusion and we expect that each particle in the cluster will absorb separately. This, in turn, pre-

0021-9606/83/042093-02$2.10

dicts exponential growth for $N(t)$ in all dimensions above the critical dimension which is determined from Eq. (5) according to $\alpha(d_c)=0$. We caution that the result $\eta=5/6$ has been inferred from computer simulation in $d=$ two, three, and four dimensions; there is no reason to believe it would be valid in all higher dimensions.

In summary, our point is that deviation in colloid shape from the classical $N\sim R^d$ relation will lead to significant departure from the classical rate law $R^2(t)\sim t$ when coagulation is diffusion controlled. Results for general relation $N\sim R^D$ may easily be worked out. In particular, the case $D=(5/6)d$ suggested by recent simulations predicts, in three dimensions, a rate law $R^{3/2}(t)\sim t$.

[a] Supported in part by the National Science Foundation.
[b] Contribution No. 3112.

[1] T. A. Whitten and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[2] P. Meakin, Phys. Rev. A **27**, 604 (1983).
[3] J. Th. G. Overbeek, in *Colloid Science*, edited by H. R. Kruyt (Elsevier, Amsterdam, 1952), Chap. 7, p. 278 ff.
[4] V. G. Levich, *Physiochemical Hydrodynamics* (Prentice Hall, Englewood Cliffs, N.J., 1962), Chap. 5, p. 207.
[5] S. K. Friedlander, *Smoke, Dust, and Haze* (Wiley, New York, 1977), p. 254.
[6] F. A. Williams, *Combustion Theory* (Addison–Wesley, Reading, Mass., 1965), pp. 47–50.
[7] I. Glassman, *Combustion* (Academic, New York, 1977), p. 184.
[8] T. A. Witten, Proceedings "MACRO '82" IUPAC, Amherst, Mass., June 1982, p. 88.

Effects of a strong external magnetic field on the reduction of cobalt and iron oxides: Confirmation

D. Aylmer and M. W. Rowe

Department of Chemistry, Texas A&M University, College Station, Texas 77843

(Received 22 December 1981; accepted 4 October 1982)

Rowe *et al.*[1–5] studied metal oxide reduction rates with H_2, with and without a 4.6 kOe magnetic field. They found significant rate differences due to the strong field for $Fe_3O_4\rightarrow Fe$, $FeO\rightarrow Fe$, $Co_3O_4\rightarrow CoO\rightarrow Co$, and $CoO\rightarrow Co$. Weight loss, without an external field, and increase in saturation magnetization, apparent weight, with the strong magnetic field, was measured.

Gallagher *et al.*[6] used evolved gas analysis (EGA) to follow the reduction of NiO, Fe_2O_3, and Co_3O_4 by H_2 in the earth's magnetic field and in much stronger external fields. They, however, did not confirm Rowe *et al.*[2–5] or Skorski,[7] where significant effects were noted due to strong magnetic fields.

This report presents new results obtained by simultaneous EGA and thermomagnetic–gravimetric analysis (TMGA) pointing out differences in the procedure used by Gallagher *et al.* and Rowe *et al.*, and confirming magnetic effects previously reported.[2–5,7]

We made our measurements on a Cahn RG-2000 recording electrobalance equipped with a movable 4.6 kOe permanent magnet with Faraday poles which can act on the sample or be removed. Reduction of metal oxides with H_2 at elevated temperatures with no external field were monitored by standard gravimetry. With a magnetic field, the balance records the saturation magnetization of the sample. As oxide is reduced to ferromagnetic metal, saturation magnetization causes a large increase in apparent weight. Data are then directly compared. Apparent weight is a measure of the saturation magnetization assuming that saturation magnetization is directly proportional only to the amount of magnetic metal present at a given time. The change in saturation magnetization greatly overwhelms the weight change associated with oxygen loss from the sample. Our reductions were conducted isothermally; Gallagher *et al.*[6] used linearly increasing temperature throughout the reaction. To demonstrate the reliability of the gravimetric technique, we added a Panametrics Model 700 hygrometer to the exhaust of our electrobalance system to simultaneously monitor the evolved water.

TMGA, used by Rowe *et al.* is convenient for studying the influence of a magnetic field on reduction of metal oxides. Here, oxides were relatively nonmagnetic (except Fe_3O_4) and the product metals Co, Fe, and Ni were ferromagnetic. No complexity arises following weight decrease due to oxygen loss without a magnetic field. However, when the strong magnetic field is applied, the rate is monitored by saturation magnetization, which appears as an apparent weight. An implied assumption is that the amount of ferromagnetic metal produced is directly proportional to the saturation magnetization measurement. However, complications, e.g., superparamagnetic products,[8] could render that assumption invalid. Earlier experiments indicated that magnetic "interferences" were not seriously invalidating our measurements. One was a reduction in which the magnet is moved out and in repeatedly, taking only enough time to measure the weight and saturation magnetization at each step.[4] Magnetically affected portions were analyzed separately from those without the external field, and being a single reduction, the same curve of % composition vs time is expected for both. Curves obtained would not yield the differences observed between the magnetic and nonmagnetic runs. We also conducted reductions without an external field, except that the magnet was moved into place momentarily once during the reduction.[5] We calculated % composition before, during, and