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 $R^{3/2}(t) \sim t$.

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

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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

after insertion of the magnet. Measurements immediately before and after application of the magnetic field were linearly extrapolated to a time selected for comparison with the magnetic measurement. Gravimetric and magnetic results were similar and would not yield the observed magnetic effects.

Here, we combined TMGA and EGA to further confirm the validity of the gravimetric method. We repeated measurements on CoO → Co which had shown magnetic effects[3] and simultaneously included measurements of H_2O by EGA. Emitted H_2O was recorded as dew point, converted to vapor pressure and, with known H_2 flow rate, recalculated as mg H_2O/ℓ of gas. Both TMGA and EGA data were read from continuous chart recordings at 30 s intervals and presented as % Co for direct comparison. Figure 1 shows composition vs time for simultaneous TMGA-EGA. The same shaped symbols were used for an individual reduction, closed symbols (TMGA), and open ones (EGA). Figure 1 shows that a strong magnetic field has an effect on these reductions. In every case, whether using TMGA or EGA, the reaction rate is enhanced by the 4.6 kOe field. This supports our earlier conclusion that magnetic fields influence reductions of some metal oxides and that TMGA is not seriously in error.[2-5] Although TMGA and EGA results differed for a given run, reductions under the magnetic field always occurred faster than those without; discrepancies occur only in fine structure and do not alter our conclusion.

Several additional runs were conducted to those shown in Fig. 1. Some of these were run with 20% H_2 in N_2 at 400 °C; others were run under the same conditions as in Fig. 1. The application of a strong magnetic field always resulted in a faster reduction rate.

Rowe et al.[3] observed magnetic effects in the two-step reduction of Co_3O_4 → CoO → Co, whereas Gallagher et al.[6] found none. An intermediate step makes it more difficult to ascertain small rate changes in one of the steps. Rowe et al. saw no magnetic effect in the first step, but the second step appeared faster under an external magnetic field. Gallagher et al.'s constantly rising temperature would cause reaction rates to increase substantially with time. By the second step, the rate may be fast enough that small differences in rate found by Rowe et al. were washed out, especially since the rate of the first step does not depend on the magnetic field. This difference in heating program may explain the discrepancies between the two groups. Increasing temperature runs are not as sensitive for observation of the small magnetic effects exhibited in Fig. 1.

We continue to conclude that a strong magnetic field affects reduction rates of some metal oxides, in particular the reactions CoO → Co, Fe_3O_4 → Fe, and FeO → Fe. Other reactions NiO → Ni, Co_3O_4 → CoO, and Fe_2O_3 → Fe_3O_4 do not seem to be affected by a strong external field.
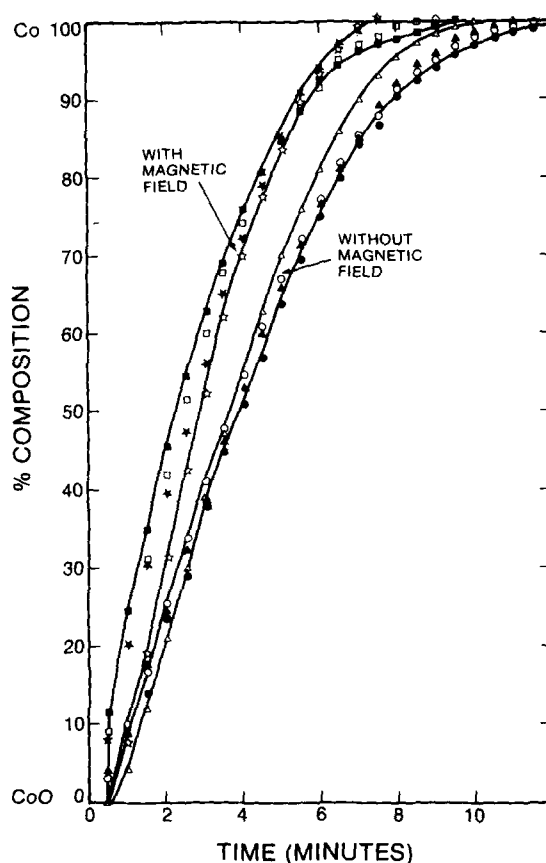

FIG. 1. Composition vs time curves using simultaneous TMGA-EGA at 300 °C. The closed symbols represent data from TMGA and the open ones from EGA. In all cases the presence of the 4.6 kOe magnetic field enhances the reaction rate of CoO to Co. The lines are added to simply enclose the data and help delineate between the presence or absence of a strong magnetic field.

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