

Abstract: Combustion Behavior of Ultra-pure, Dense Carbon Spheres at Atmospheric Pressure:

Part I: A New Experimental Technique for Determining the Depth of Reaction During Internal Burning

A technique has been developed for the continuous determination of the depth of internal reaction during the burning of carbon spheres in air. Reaction at internal surfaces can take place when the supply of oxygen to the superficial surface by boundary layer diffusion (where relevant) exceeds the rate of consumption at the superficial surface, and the balance then diffuses into the interior. Reaction of the indiffusing oxygen at internal surfaces results in a progressive drop in oxygen concentration with increasing depth so, given a thick enough slab of carbon, a point can always be found at which the oxygen concentration is effectively zero (though never theoretically so). This point represents the penetration depth of the reaction. If this depth is known it is then possible to calculate kinetic constants of reactivity from experimental results and to draw valid conclusions about the reaction mechanism. This may require the simultaneous measurement of internal surface (e.g., by B.E.T.) but B.E.T. measurements by themselves, though sometimes used in the past, are insufficient (except where it is known that reaction penetrates to the sample center) because the method does not distinguish between reacted and unreacted surface. B.E.T. and/or porosimeter measurements can be used in conjunction with progressive grinding to determine density changes from the surface down when reaction has finished or been stopped, but the technique though valuable is tedious, time-consuming, and somewhat erratic unless successive runs can be exactly reproduced.

The technique developed and described here also depends on density variations, and utilizes simultaneously two well-established techniques: continuous weighing and continuous size measurement of the sample. Spheres of carbon are used because of the spherical symmetry and geometrical precision of the sample, which are also found to be maintained to 80 or 90% burn-off in very low flow velocities. Since the weight is known then a radius can be calculated assuming no change of density that is then compared with the measured radius. If the two are equal then there was no change of density and hence no internal burning. If the two are not equal then the calculated radius is always less than the measured radius and the difference is a function of the density change which is a function of the penetration depth of the reaction.

Experimentally, carbon spheres of ultra high purity are suspended from a continuous recording balance inside an electrically heated tube furnace up which flows oxygen-vitiated or enriched air at low velocities. The sphere is illuminated by light shining down the tube, and appropriate optics either displays this, enlarged, on a gridded screen, or projects it into a camera. Temperatures of gas, furnace wall, and sample are also recorded.

The results are displayed on a plot of calculated radius against measured radius during combustion down to 80 or 90% burn-out. For temperature above 1100°C there is no internal reaction so the radii are about equal, and the points lie on a 45° line going through the origin. This has been identified as the region of boundary layer diffusion control (Zone III). For temperatures up to 100°C below this there is some internal reaction confined to a thin surface layer and the points again lie on a 45° line but displaced from the origin intercept, the extent of displacement being roughly proportional to the penetration depth. At the other extreme, below 700°C, reaction was found to be exclusively internal with 85% burn-out at constant radius, so the radius plot showed a vertical line. At higher temperatures the radius plot showed a sequence of curiously curved lines whose significance was established by constructing a plot of penetration depth against radius.

The depth of penetration as this varied with external radius showed two marked extremes. In Zone III (boundary layer diffusion control) penetration was zero as the radius decreased giving a horizontal line running along the abscissa. In Zone I, the penetration depth was 100% with mostly no variation in external radius so this was represented by a single point on the ordinate axis at 100% penetration. In Zone II there was initially some partial penetration of reaction at small change in external radius. Then the penetration depth stabilized with some further reduction of external radius. However, this only seemed to be a quasi-stable situation since after still further burn-out the penetration depth then either jumped to 100% (at the lower temperature) or dropped to zero (at the higher temperatures). The impression given is that Zone II is inherently unstable with a penetration depth that never fully stabilizes and that either has to increase or decrease.

The extensive kinetic and mechanistic significance of and conclusions from these results are given in the companion paper, Part II, also submitted for consideration.

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