

Abstract: Combustion Behavior of High Purity, Dense Carbon Spheres at Atmospheric Pressure:

Part II: The True Order of Reaction and Temperature Limits of the Reaction Zones for the Internal Burning

Carbon spheres burning in air have been found to exhibit reaction behavior that qualitatively is in accordance with the classical Three-Zone concept of reaction mechanisms, in spite of the very high density and low internal surface area (0.3 sq.m. per gm.); but, quantitatively it differs in certain significant respects from other work, notably with respect to the order of reaction.

The carbon spheres are 1/2 in. dia. of ultrahigh purity, burned mostly in air, but also in other atmospheres (100% O₂) inside an electrically heated tube furnace as described in Pt. I.

Reaction rates were determined by graphical differentiation of the weight/time curves obtained by continuous weighing of the sample (as described in Pt. I) during burn-out. In these determinations a steady burning region could always be identified (though it was rather short on Zone II), and it was found that these data, and only these, were accurately reproducible.

Measurements were made over the temperature range 500 to 1200°C and the three Zones were identified as follows: Zone I, <750°C; Zone II, 900 to 1100°C; and Zone III, >1100°C. The identifications were made partly from the penetration depth measurements described in Pt. I, and partly from an Arrhenius plot. In Zone I, the activation energy was about 45kcal/mole and in Zone II was 23kcal/mole, both figures being in good agreement with other published values. In Zone III the "activation energy" could be quoted as 1.8kcal/mole which is roughly consistent with boundary layer diffusion control. In agreement with this, the reaction rate was also proportional to the square root of the mainstream gas velocity, and also in reasonable agreement with absolute calculations from boundary layer diffusion theory.

The significantly different result, however, was in the reaction order. On comparing rate data in air and in 100% oxygen it was observed that the reaction rate increased and, initially, this was interpreted (using the comparable gas or furnace temperature) as being due to a fractional order of reaction. However, measurement of the sample temperature showed that this also rose when the oxygen was increased, and plotting against sample temperature the points for air and oxygen all fell on the same line (with little scatter) on an Arrhenius plot. The

reaction is therefore zero order in Zone I, in disagreement with most other work reported. However, most of that other work used the furnace or gas temperature, not the sample temperature by thermocouples right in the carbon samples themselves. They then agree more or less with our first result before we measured the sample temperature directly. At the low reaction rates obtained, calculation indicated that the sample temperature should not be much above the gas temperature in Zone I but this has to be modified by two complicating factors not usually taken into account. The first is "ignition" of the solid, and the second is increased burn-up of CO by gas phase reaction.

Ignition is defined formally by the Semenov criterion and was found in our case to occur between Zones I and II, but with more porous carbon this could occur earlier. In accordance with this the Semenov temperature jump identifying ignition meant a significantly greater temperature difference after ignition than before. In further agreement with this, and in accordance with classical ignition theory, there was a small temperature range that was inaccessible to steady state because of the rapid temperature change on either ignition or extinction. This seems to be associated with the source of the reaction instability in Zone II identified and described in Part I.

The problem of the location of secondary burn up of the CO formed by primary reaction is one that seems to have attracted little attention. That it is slow, but that it does occur before the CO leaves the boundary layer is accepted. If the oxygen concentration increases it will presumably burn up faster and earlier, maybe in the carbon sphere pores, and will produce locally a higher temperature. This seems to be the source of the extra heat that is able to increase the sample temperature when the oxygen concentration is increased though the primary reaction is zero order.

The principal results are, then, that: (1) the reaction order is zero in Zone I. and 0.5 in Zone II, both consistent with desorption reaction control which is to be expected from the high activation energy; and (2) that the Zone II is considerably narrower (200° from 900 to 1100°C) than other work has indicated. (3) Activation energies, however, agree with previous work, though their identification of mechanism (desorption) in general does not.

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