

Some Experimental Techniques Used in Carbon Reaction Studies

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1. INTRODUCTION

Although research on carbon has proliferated unbelievably in the last decade, there are indications of a growing dichotomy between two somewhat disparate points of view regarding the objectives of the research. On the one hand, university-oriented work has tended to be of the so-called "pure" or "fundamental" variety, often concentrating on small, very specialized points and utilizing many highly-elaborate techniques of an impressive level of sophistication. Industrial research on the other hand has, of necessity, to be of an applied nature, and often contains a high component of empiricism. These latter are sometimes referred to as engineering studies. The two respective points of view can be summed up in the phrases "Know Why" and "Know How."

It is a truism to say that the Know Why ought to illuminate the Know How, but recently there has been increasing skepticism of the part of some investigators that this is possible, and in this lies the source of the dichotomy. The problem is best seen by way of an example. In the measurement of activation energies, for instance, it seemed possible at one time that if the energies could be measured for different carbons under known conditions then the value, or range of values for the different carbons, was likely, to imply a particular mechanism. However, recent work [1] on the adsorption isotherms at low temperatures have shown the evident existence of a range of possible and overlapping alternate steps in the reaction each with its own individual energy. Therefore, it would seem that any activation energy not determined by these very precise methods must be only an average with an evident ambiguity of interpretation. The problem is then compounded when we consider that, when the detailed mechanisms were elucidated, this was by using ultrapure, highly specialized "research" carbons, such as Spheron 6, whereas industrial carbons have the additional complexities of different degrees of graphitization, accessibility, and reactivity, of binder and filler, together with modifying factors due to ash, permeability, porosity, isotropism or lack of it, etc. It is, therefore, a very real question whether the "pure" and so-called "engineering" studies really have sufficient in common to make attempts at cross-correlations and interpretations worthwhile.

As we have ourselves been concerned primarily with more "engineering" studies, we have therefore been somewhat exercised by this very question. Whilst not finding the description sufficiently important to quarrel about, it does nevertheless seem to us that our studies do in fact lie more or less between the two (what might therefore legitimately be called technological studies if one looks for a name). Our conclusions are that cross-correlations between studies of different levels of fundamentality are in fact possible, if applied with caution; and also that the unfortunate dichotomy that has started to develop will have to be closed.

The first consideration to be examined was whether the lack of interpretation in terms of fundamental mechanisms actually mattered. After all, the carbon industry has existed quite successfully for decades (centuries if one includes charcoal burning) without access to the information now being developed. However, the last 10 or 20 years has been an increasing sophistication in carbon manufacture, paralleled by much more varied and extreme uses, which has been itself largely the stimulus for the increased research; and it is clear that we now require a matching sophistication in knowledge of reaction behavior of actual carbons as manufactured for industrial processes.

Now, when we consider the behavior of industrial carbons with the attendant complexity of reaction in real situations, it seems to us that, so long as we can unravel the complexity due to the real situation, the only factor likely to disturb any mechanistic interpretation is the parameter modification due to the presence of two or more components (such as filler, binder, ash, etc.). Here it is true that kinetic parameters such as frequency factors, activation energies and so on will be averages of some sort; but this does not seem to be an insuperable objection since all it means is that behind the average we measure is some (unknown) statistical distribution of the parameter values. Any such statistical distribution must itself be determined by composition and other material properties; and the use of an average value does not seem to be any less relevant than the use, for example, of average properties of gasses such as velocity, or energy, or temperature. In the case of carbon studies, the more fundamental work may in time determine the statistical distributions of the relevant parameters due to variable material compositions and properties, and this will be of immense assistance in filling out any interpretation. In the meantime, lacking such information, we may legitimately assume (till proved otherwise) that the background distributions are rather narrow, so that any kinetic constants obtained by experiment are presumed to be close to unique--and therefore mechanistically interpretable--values.

To us, the more important problem at this stage is the unambiguous experimental determination of these (statistical) property parameters, and this is primarily a matter of experimental design. The problem is that many of the more applied (engineering) methods of experimentation lack definition so that there can be considerable uncertainty what property a measured value is really related to--even before one starts to consider the problem of the statistical average. The activation energy, for example: it is true that the value measured is the weighted statistical average of all possible adsorption energies; or could it be the average of all possible desorption energies? This is typical of the type of ambiguity that can arise.

To eliminate such ambiguities requires good experimental design, and this is jointly a matter of technique and of instrumentation. Recently we described a technique, with some brief outline of the instrumentation that we were able to show did eliminate much ambiguity [2]. In this paper our purpose is to re-summarize the technique (for completeness) and to amplify the information on the instrumentation in the belief that this may be of value to those concerned with the more precise, unambiguous "engineering" values of kinetic constants, but still measured on such a basis that there is some hope of applying a valid mechanistic interpretation. This is not to say that we think this is the only technique able to develop kinetic information on the basis required, but we believe it to be the most fully developed so far. The point we are making is that the time has come to start closing the gap between the "fundamental" and "engineering" studies on carbon reactions, so that the latter are as valid as the former for obtaining kinetic data and mechanistic interpretations of behavior.

2. ESSENTIALS OF THE EXPERIMENTAL METHOD

2.1. General - In the studies of heterogeneous reactions it is of great importance that experimental data are obtained which define both the state of the reacting surface and the state of the fluid that influences the course of the reaction. This also requires a precisely known solid geometry. The need for meaningful data in research on carbon-oxygen reactions is especially acute; the reason being that within a temperature span of several hundred degrees and a pressure span of one atmosphere, many of the elementary steps of reaction change from dominant to nondominant, e.g., adsorption of reactants, desorption of products, diffusion of reactants to the surface, diffusion of reactants through the carbon, etc. Coupled with the problems of heat exchange and continuous changes in the diffusion rates and surface area that occur due to consumption of carbon, an experimenter is faced with a formidable task of analyzing the kinetics of the reaction [3]. An experimental system is thus required capable of generating data whose interpretation would be unambiguous.

To determine process kinetics of carbon reactions information is needed about the sample weight, rate of weight change, temperature of carbon and gas, sample geometry, gas composition, and the surface area and permeability of the carbon. To obtain such data we have developed a technique in which a carbon sample is suspended in a vertical furnace, continuous records of sample weight, sample geometry, and sample and gas temperatures are obtained (Fig. 1). In addition gas composition inside and around the sphere can be measured at regular time intervals. Other data which are obtainable on samples that were partially reacted then quenched at the desired level of burnout are an independent check of porosity profiles and the BET surface area.

In the experimental technique which was developed a carbon sphere is used because of its well defined geometry and symmetry during burnout. The reactant flow velocity is kept low so that the heat and mass transfer conditions are well defined. From continuous measurement of weight and diameter the average density change can be established. When temperature measurements are included, the Arrhenius plot of reaction rate can be developed, together with information about the heat release rates inside and outside the carbon sample.

2.2 Temperature Measuring System - The temperature of the carbon sphere was measured by imbedded thermocouples. A small hole about 0.3 mm. in diameter was drilled in the carbon sphere. One lead of a Pt-Pt-13% Rh Thermocouple was threaded through the hole and a butt weld was made to the other lead. Then the hot junction was pulled back to the desired location in the sphere. To insulate the thermocouple leads from the sphere, they were shielded by quartz capillary tubing or flame plated with silica prior to insertion into the sphere. As many as three thermocouples were used to record the inside temperatures at one time.

The thermocouple leads above the sphere were threaded through an eight-inch long ceramic support rod. Alternatively, a section of a metal-shielded thermocouple was stripped of its metal cladding and ceramic insulation to expose thermocouple leads ready for insertion. An ice bath was used for the cold junction.

The gas temperature was measured using shielded thermocouple assemblies with bare hot junctions. Micromanipulators were used to position the beads at precise locations around the carbon sphere.

The temperature recording system consisted of millivolt suppression circuits and amplifiers for adjustment of the recording scale, a 24 channel recording oscillograph, and a precision potentiometer for independent spot checks of thermocouple outputs.

2.3. The Weighing System - The weighing of the carbon sphere was made using a conventional analytical balance with an automatic recording attachment. A continuous record of the sample weight was obtained either on a potentiometric recorder or using one of the channels in the recording oscillograph. Typical reduced records of weight loss and temperature measurements are shown in Figure 2.

In the base of the balance a hole was drilled to receive a ceramic rod that was connected to one of the balance pans. At the other end of the ceramic rod was a small platinum wire loop to which the ceramic rod with the thermocouples and the carbon sphere was connected. The carbon sphere was thus suspended from the balance on two ceramic rods connected by hooks and loops. This arrangement permitted easy disconnection of the thermocouple assembly from the balance and allowed the furnace to be moved for insertion of a new test sample.

Prior to each run the test samples were weighed on an analytical balance to determine the exact original weight. Also with the cold sample suspended from the balance, a calibration run was made to simulate weight changes that would occur during sample burnout by adding weights to the proper pan.

2.4. The Sample Size Measuring System - The diameter of the carbon sphere was measured with a micrometer prior to placing of thermocouples in the sphere. After the insertion of the sphere in the furnace and its suspension from the balance, the size changes would be measured optically. To do this a telescope-projector was constructed through which one could measure the sphere visually or obtain a photograph at desired time intervals. Figure 1 shows the schematic of the size measuring system. Above the top of the furnace we have a 45° mirror which sends a projected light source through a transparent watch glass (with a hole to allow the ceramic rod to connect to the rod from the balance). The light passes vertically through the furnace tube exiting through a quartz window at the bottom of the furnace. A second 45° mirror connected to a movable telescope deflects the light through an iris diaphragm and focusing eye piece to a ground glass screen. After focusing, the ground glass screen was normally removed and a camera inserted in its place.

When the temperature of the carbon was less than about 800°C , a 1500 joule flash was used to project the shadow of the sphere onto the film. At higher temperatures the radiation intensity from the carbon sphere was sufficient for self-recording of the sphere image on ASA 125 film. An electric sequential timing switch was used to trigger the flash gun, camera, and a timing mark on the oscillograph. During a normal run the sphere was photographed about sixty times at X8 magnification.

2.5. The Furnace and Gas Feeding System - The electrical furnace contained a vertical tube which was two (2) inches in diameter by eighteen (18) inches long. The hot zone of nearly uniform temperature was about twelve (12) inches long located in the center of the furnace. On the bottom of the furnace was a water cooled brass cap containing various gas inlet ports and a quartz window in the center. One thermocouple extended through the brass cap to measure gas temperatures below the suspended carbon sphere. The furnace temperature-control thermocouple was located behind the heating elements. A proportional band controller was used to keep the furnace temperature constant. The top of the furnace was covered by a loose-fitting transparent glass lid. A hole was drilled in the lid to allow thermocouples as well as the carbon support rod to pass through.

The gasses were normally passed through molecular sieves and Drierite columns before being metered through rotameters and passed to the furnace. The pressure of gas entering the rotameters was also monitored.

3.6. Gas Sampling - A gas sampling system was developed in which a 0.1 mm. I.D. capillary steel tube was attached to the thermocouple assembly and suspended from the balance together with the carbon ball.

Gas was withdrawn both from the center of carbon sphere and from the vicinity of the sphere and analyzed using a Fisher gas chromatograph. By taking samples at regular intervals, changes in the gas composition inside the furnace could be established.

3. AMBIGUITIES AND FAILURES OF METHODS

3.1. Thermocouples - A thermocouple inserted in a carbon sphere or in a gas stream will under many circumstances indicate a temperature that is different from the true temperature of the solid or fluid at the hot junction. First, a large thermocouple will represent a large heat sink and, therefore, changes in the temperature of the material being measured will not be accurately reflected in changes in the thermocouple's readings. The goal therefore is to use as small a thermocouple as possible. Radiation exchange between the thermocouple and the surroundings is another source of error. A thermocouple exposed to walls which are at different temperature than the surrounding gas will indicate an intermediate temperature. Here it is also desirable to have a thermocouple as small as possible--the smaller the diameter of the hot junction the smaller will be the error. When the thermocouple leads are less than about 0.25 mm. and unsupported in the length of several centimeters, a serious error may develop due to vibration and movement of thermocouple leads. The vibrating thermocouple will indicate temperature fluctuations when in reality there are none. A good reference on thermometry in flames is "Flame Structure" by Fristrom and Westenberg [4], although they do not include discussion of the suction pyrometer (or HVT).

In measuring the internal temperature of an electrical conductor (like carbon) the thermocouple leads, except for the hot junction, have to be insulated from the conductor because the thermocouple will otherwise indicate some averaged temperature of the conductor rather than the temperature of the hot junction.

Another source of error in the measurement of temperature with very fine thermocouples are stray and induced currents due to furnace heating circuitry, on-off controller switching, starting and stopping of miscellaneous electrical equipment, etc. Here the recommendation is use grounded and shielded extension and thermocouple leads, amplifiers with high frequency noise filtering devices and constant voltage supply transformers. In our experience we had to use all these devices.

3.2 Gas Sampling - To obtain an accurate concentration profile while a gaseous chemical reaction is taking place, is quite difficult. First, the flow pattern of the gas around the sampling probe should not be significantly affected. Second, the chemical reaction must be quenched; otherwise, the composition of the gas as given by subsequent analysis will not be the same as that which enters the probe.

We found that during sampling of the gas from inside the carbon sphere, the hole through which the probe was inserted became enlarged. This indicated, of course, that, during sampling, a disturbance of the gas concentration profile occurred. Further information on gas sample probes is given in reference (4.).

3.3. Flow Pattern Inside the Furnace - The design of the gas feed system, the size of the furnace, and the gas throughput rate significantly influence the concentration and flow pattern of gases inside the furnace. Because the furnace, feed lines, tees, filters, etc., act as reservoirs, the change in gas concentration at the carbon sample surface normally does not follow a discontinuous change as one switches from inert to reacting gas or vice versa. After opening a valve, it is, therefore, most desirable to know when the concentration of the reacting gas reaches 95 or 98 percent of the desired value. Indeed, at low flow rates and with large holdup vessels it may take half an hour or longer to achieve a desired gas concentration around the sample.

To determine whether the flow pattern inside the furnace meets the desired characteristics, a plot of logarithm of concentration at the desired location versus time will indicate either the degree of back mixing, or the extent to which the reactor approaches plug flow conditions. The steeper the negative slope on the plot described, the closer the reactor approaches plug flow conditions (Fig. 3). If the concentration of the gas to be displaced, (nitrogen), approaches an asymptotic condition, then there exists the possibility of dead-end hold-up storage zones in the feed system, or of leakage of undesirable gas into the system.

4. SOME RECENT RESULTS

During the five years that the experimental technique has been in operation, and in process of gradual improvement, several significant experimental findings about carbon-oxygen reactions have been obtained.

First, the simultaneous measurement of both sample size and weight provided a direct method by which the data could be separated into the three zones of reaction. Thus, it was possible to construct an Arrhenius plot of the rate data in which the three major zones could be identified. The Arrhenius plot was constructed using the true sample temperature (not the furnace or gas temperature) which was measured by thermocouples within the carbon sphere. No meaningful analysis of the effect of oxygen concentration on the apparent reaction rate could be made without the sample temperature measurements. It was found that the apparent rate increased with increasing oxygen concentration but so did the sample temperature. The net result was that, regardless of the oxygen concentration, all data described a single rate curve at low temperatures (Zone I). It was concluded, therefore, that the chemical reaction was zero order.

In the further analysis of the data a definite conflict was apparent. If the reaction order was truly zero in the chemically dominant regime, why did the temperature of the carbon sphere reacting in oxygen exceed its temperature when reacting in air? This conflict was resolved only after temperature profile measurements were made of the sphere and of the surrounding gas. From these, heat exchange balances were made between the reacting sphere and the surrounding environment using a digital computer. These calculations revealed that in Zone I the heat release for the carbon-oxygen reaction amounted to that required to convert all carbon to CO_2 within the carbon sphere. But, for the case when oxygen concentration was low, such complete burn-up of the primary reaction product, CO, did not occur within the carbon boundaries; thus the temperature of the carbon reacting in air did not rise to as high a value as it did in pure oxygen.

In Zones II and III, the burn-up of carbon monoxide occurred outside the carbon sphere, as substantiated by gas sampling and temperature profile measurements and confirmed by heat balance calculations. It was also found that within a certain carbon porosity range a region of combustion instability existed between Zone II and Zone III during which the temperature of carbon oscillated by as much as 70 degrees and with a period of up to 100 seconds (Fig. 4).

5. CONCLUSIONS

Temperature, weight and size measurements of reacting carbon spheres can be made simultaneously in an electrically heated furnace. Combining these measurements with gas sampling, surface area, and density profile determinations, the progress and process of heterogeneous solid-gas and of subsequent gas phase reactions can be established. Measurements of atmospheric conditions gave results revealing the true

order of chemical reaction of carbon with oxygen, allowed the determination of the depth of penetration of the reaction zone into carbon, established the presence of an oscillatory combustion phenomena, etc. Problem areas to be encountered by the experimenter with the above techniques are pointed out.

These results show the importance and value of adequate experimental techniques designed to deliver results whose interpretation will be unambiguous.

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