STABILITY OF REACTION SYSTEMS

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THIS IS THE *first of a series of articles describing the development and operation of several new experiments as part of an undergraduate laboratory course for seniors in chemical engineering.* The course was initially offered at Princeton as an elective for seniors in the spring term following a fall lecture course in chemical kinetics and reactor design. Recently, the number of laboratory sessions was reduced and laboratory and lecture courses were combined into a single course required of all students majoring in chemical engineering.

Professor Richard H. Wilhelm provided inspiration and guidance for the successful development of the reactor laboratory. Other members of the faculty—Donald E. Jost, Ronald P. Andres, and James B. Anderson—were directly responsible for development of the experiments and instruction of students. Most of the experiments were designed, built and tested by graduate students of the department serving as teaching assistants.

The laboratory was designed to emphasize reactor properties rather than reaction properties. Four main ideas are illustrated: 1) Modes of operation (batch, CSTR, tubular flow), 2) Regimes of operation (predominance of chemical rates, mass transfer rates and heat transfer rates), 3) Classes of reactions (homogeneous, heterogeneous, biological), 4) Measurements of pertinent physical rate processes. In several of the experiments the coupling of chemical, thermal and diffusional efforts are illustrated. Many of the important experimental techniques for reactor studies are utilized.

Listed in Table I are a total of eleven experiments developed and utilized in the course. A number of the experiments have been used in laboratory courses by other departments and have been described in some detail previously (1, 2). In this series we will consider only those

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experiments which are sufficiently new to warrant a full description. The first of these demonstrates thermal effects for an exothermic reaction occurring at the surface of a catalytic wires.

METHANOL OXIDATION ON A PLATINUM WIRE

WHILE THE PHENOMENA of stability of reactor systems are familiar in everyday life (ignition and extinction of matches, etc.), the bridge between theory and practice needs considerable reinforcement before students develop an intuitive feel for stability phenomena in reactor systems. This experiment provides a demonstration of reactor operation in two stable stationary states together with ignition and extinction in a system whose thermal characteristics can be measured. Measurements of the heat generation and removal characteristics are used by students to predict the overall behavior of the system. These predictions are compared with actual behavior observed. In this way the theory of reactor stability is directly related to experimental observations.

The reaction system used stems from self-lighting cigarette lighters in which catalytic wires above an alcohol-saturated pad glow red hot when exposed to the air-alcohol vapors and ignite the alcohol on the pad. In the experiment a helium-oxygen mixture saturated at 0°C with methyl alcohol is passed over a short length of platinum wire in a heated chamber. Since the alcohol concentration is below that for a flammable mixture, reaction occurs only at the wire. Wire temperature is determined from electrical resistance measurements. The heat removal and heat generation characteristics at the wire are determined from measurements of electrical heat input required to maintain various wire temperatures at several chamber temperatures both with and without methanol present. To determine ignition and extinction temperatures for a negligible electrical heat input, the chamber temperature is varied slowly while the wire resistance is monitored. Since the wire does not glow red hot after ignition, all observations must be made by way of the wire resistance.

Table I. Reactor Laboratory Experiments

1. Batch Reactors: Hydrolysis of Acetic Anhydride.
2. CSTR Systems: Hydrolysis of Acetic Anhydride.
3. Tubular Flow Reactors: Hydrolysis of Acetic Anhydride
4. Gas Chromatography: Analysis of Alcohol-Ketone Mixtures.
5. Heterogeneous Catalysis: Isopropanol Dehydrogenation and Dehydration.
6. Diffusion and Reaction in Catalyst Pellets: TCC Catalyst Regeneration.
7. Stability of Reactor Systems: Methanol Oxidation on a Platinum Wire.
8. Biological Reactions: Kinetics of Yeast Growth.
9. Fluidized Beds: Study of Major Characteristics.
10. Diffusion in Porous Media: Knudsen Flow in Catalyst Pellets.
11. Diffusion in Packed Beds: Dye Tracer Studies.

THEORETICAL BACKGROUND

THE PRESENTLY AVAILABLE theories of the thermal characteristics of reactors have been admirably summarized by Denbigh[4], Aris[5], Kramers and Westerterp[6] and Frank-Kamenetskii[7]. The methanol oxidation system used corresponds in many respects to a CSTR system. Except for end effects the wire temperature is essentially uniform. Reaction occurs at a single temperature and the system need not be considered a distributed-parameter system. A plot of the rate of heat generation by reaction against wire temperature has a sigmoid shape. At lower temperatures the reaction is rate-controlled while at higher temperatures the reaction is diffusion/transport-controlled. Depletion of reactants in the chamber is believed to be negligible under the conditions used. The process of transport of reactants and products is a combination of molecular diffusion with thermal and forced convection. A plot of heat removal rate against wire temperature shows the expected increase with difference between wire temperature and chamber temperature. The heat removal corresponds to that in a CSTR with a heat transfer surface. Heat removal from the wire occurs by radiation in addition to conduction and convection. For the methanol oxidation system the phenomena of multiple steady-states, ignition and extinction by monentary heating or momentary interruption of reaction, and spontaneous ignition and extinction can be explained in terms of the heat generation and heat removal curves. The analysis for this system has a direct parallel in the CSTR. Analysis of the transient behavior of this system is undoubtedly considerably more complicated than that of the CSTR and a direct

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parallel may not exist. Transient behavior is not examined with the present apparatus.

APPARATUS

A schematic diagram of the system and a photograph of the reactor are shown in Figures 1 and 2. The helium-oxygen mixture is supplied from a cylinder, passed through a rotameter and fed to a sparger immersed in methanol at 0°C. The saturated (or partially saturated) gas passes through a coil to the air-jacketed reaction chamber which contains the platinum wire. A by-pass of the sparger is provided. Reactor exit gases are vented within a fume hood. Hot air for the chamber jacket is supplied by a hair-dryer type of heat gun. Resistance of the wire is measured with a commercial Kelvin double bridge circuit. Electrical current for resistance measurements and for hating the wire is supplid by an automobile storage battery and a solid-state control circuit.
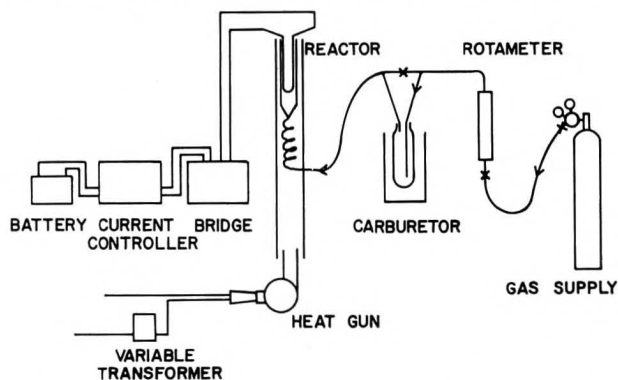

Figure 1. Schematic diagram of apparatus for determination of thermal characteristics of methanol oxidation on a platinum wire.

The 90% helium—10% oxygen mixture is purchased premixed in a conventional cylinder. The gas passes through a pressure regulator, shut-off valve, rubber tubing, control valve, and rotameter to the carburetor. Tygon tubing (¼-inch I.D.) is used downstream of the rotameter. The carburetor is a 2½-inch I.D., 8-inch long glass cylinder containing methanol in which a fritted-glass sparger is placed. The carburetor is immersed in ice water contained in a 4½-inch I.D. wide-mouth vacuum flask. The carbureted gas passes to the reactor. A carburetor by-pass tube is provided with a pinch clamp.

The reactor chamber is a ⅞-inch I.D. glass tube, 6 inches long, contained at the top of a second glass tube (2-inch I.D., 18 inches long) through which hot air from a heat gun is blown. The reactor feed gas passes through a tubing coil within the jacket for preheating prior to entering the reactor. The platinum wire is suspended in a horizontal loop at the center of the reactor. Exhaust gases from the reactor and the jacket are vented at the top of the reactor assembly. The heat capacity of the system is deliberately low so that rapid temperature
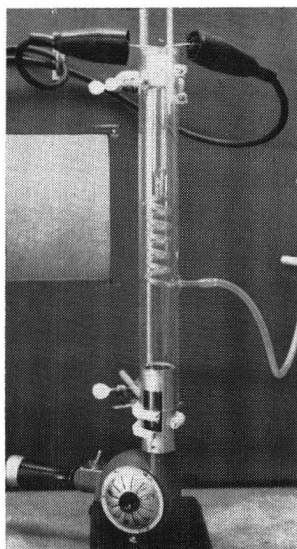
Figure 2. Air-jacketed reaction chamber.

Figure 3. Circuit diagram for current controller.

equilibrium can be obtained. The heat gun is wired for control of its heating current with a variable transformer.

The platinum wire (0.003 to 0.005 inch diameter, about 1.5 inches long) is spot welded to two copper rods (3/32-inch diameter, tinned) held by a Teflon plug inserted (loose fit) in the top of the reaction chamber. Holes in the plug allow gas exit and insertion of a thermometer. Since wires are easily melted by overheating, spare assemblies are kept on hand. Spot welding is accomplished with a commercial spot-welding machine common to vacuum tube shops.

A Kelvin double bridge circuit is required for measuring the wire resistance because of the low resistance and the high currents which are used. Since three resistance ratios must be equal for balancing the bridge, a mechanical linkage of two ratios is essential for rapid measurements. With a slightly modified commercial bridge (General Electric, No. 9069199G) resistance measurements are made in a few seconds. The platinum wire and the copper rods (negligible resistance assumed) holding the wire are incorporated in the bridge.

The current control circuit is shown in Figure 3. An automobile storage battery provides sufficient current for more than five hours of experimentation. The circuit provides smooth control of current to the wire (and bridge) with the turn of a single dial. No feedback control is provided. Two ammeters, necessary for determining the power input to the wire, are included in the control box.

For reasons of safety, the reactor assembly and carburetor are located behind Plexiglas shields located within an exhaust hood. Provided the methanol concentration in the helium-oxygen mixtures does not exceed that corresponding to saturation at 0°C, the carbureted gas is not flammable at temperatures below 200°C. With higher methanol concentrations or at higher temperatures, the mixture may be flammable and/or explosive. To minimize the severity of a possible explosion, the volumes of carbureted gas contained in the reactor and in the carburetor are minimized.
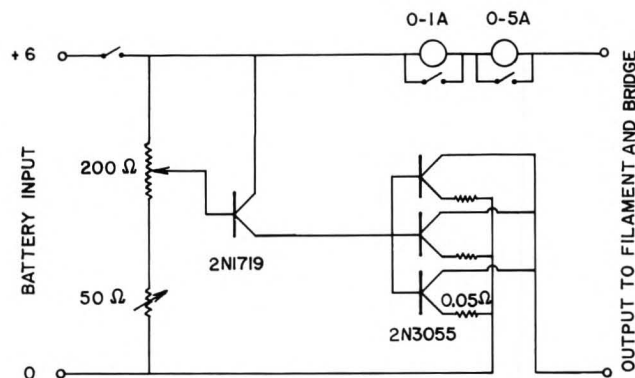
PROCEDURE

Prior to measurements, the storage battery is charged and the methanol flash is cooled to 0°C. The platinum wire is flashed at a yellow heat in air to remove any contaminants. During experiments occasional flashing at a yellow heat helps to maintain a constant catalytic activity, but also risks melting the wire.

Initial observations of spontaneous ignition and extinction are made in order to check the activity of the wire and set a gas flow rate for which these phenomena are observable with chamber temperatures in the range 25-200°C. Usually flow rates in the range of 10 to 20 percent of full scale on the rotameter are suitable.

With a fixed flow rate and reaction chamber temperature the resistance of the wire is measured for a range of wire currents. Measurements without methanol in the feed give the heat removal-wire temperature curve since the heat removal is equal to the electrical heat input. If it is assumed that the heat removal for a given wire temperature is unaffected by the presence of the methanol, then the heat of reaction can be taken as the difference in electrical heat inputs with and without methanol present.

Measurements of heat removal and heat input by reaction for a range of wire temperatures are taken at several chamber temperatures. It is usually found that heat input by reaction is dependent almost solely on wire temperature and affected only slightly by chamber temperature. The thermal characteristics of the system under normal operating conditions make it impossible to determine the heat input by reaction in the vicinity of the steeply rising portion of the heat input-temperature curve. Interpolation is necessary in this region.

The experiment is concluded with measurements of the chamber temperatures for spontaneous ignition and extinction. These points are located approximately at first, then more accurately by changing chamber temperatures at a slower rate to allow thermal equilibration of the chamber-jacket assembly.

STUDENT PERFORMANCE

Students are in general able to obtain satisfactory results in a 3-hour period. Because the apparatus is simple, only a few minutes are required for examining it and preparing for opera-

tion. Students then seem baffled at the various heat inputs and outputs involved and may spend half an hour discussing these and arguing among themselves over procedures. Once measurements of heat removal and heat release by reaction are underway, data accumulation is rapid. The groups that plot the data immediately are able to gain a full understanding of the thermal characteristics of the system and predict stability behavior on the spot. Other groups may adopt and follow a procedure without fully understanding it and fail to determine the significance of their data until after they leave the laboratory. Questions directed to the students during the laboratory help prevent this situation.

The initial confusion, even for well-prepared students, in relating theory and practice in this experiment indicates the need for the exercise. In the course of the experiment this confusion is usually replaced by understanding and an intuitive feel for this system, and it is hoped, for the stability of reactors in general.

Thermal characteristics determined at the ignition temperature in one experiment are shown in Figure 4. Similar curves were obtained at other temperatures. The ignition and extinction temperatures could be predicted within 20-30°C from the room temperature measurements.
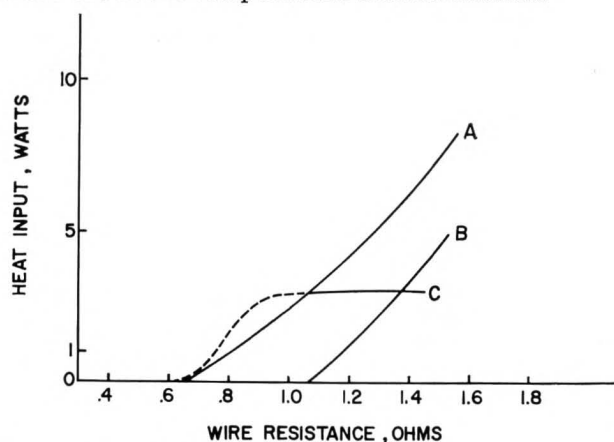

Figure 4. Thermal characteristics of reactor at the ignition temperature (188°C). Curve A—electrical heat input for helium-oxygen flow without methanol. Curve B—electrical heat input with methanol present. Curve C—heat released by methanol oxidation (difference of curves A and B).

DEVELOPMENT OF THE EXPERIMENT

The system was first built for operation with air saturated with methanol at 0°C. The reaction chamber was maintained at room temperature only. Under these conditions reaction at an elevated wire temperature was not sustained without a large electrical heat input. Although meas-

urements of heat removal and heat released by reaction could be made and transitions between stationary operating points were observed, self-ignition and extinction did not occur. The use of a heated reaction chamber, which necessitates the use of a less flammable gas mixture, allows observations of ignition and extinction with a negligible electrical heat input.

Experience indicates that an easily operated, continuously variable current control and an easily operated Kelvin bridge are essential to rapid measurements. In an early version of the apparatus, current was controlled by switching resistors in series with the platinum wire and the bridge lacked mechanical linkage of resistors. Several minutes were required for each measurement in this version.

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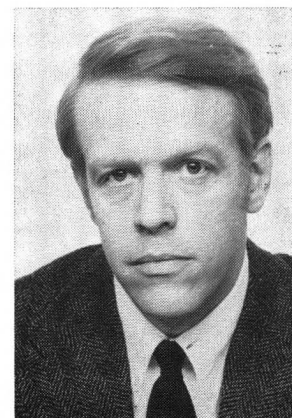
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