Enclosed flow tube injector system for low temperature kinetic studies

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A new enclosed injector system for low temperature kinetic studies is described. This system offers a number of advantages over more conventional designs of moveable inlet injectors. The enclosed injector prevents the introduction of contaminants into the flow reactor. In conventional designs, ambient contaminants adsorbed onto the outside of the injector could be transported into the flow reactor. The enclosed injector exposes the reactant gas to the same length of inlet tubing at a uniform temperature regardless of the injector position. In addition, the enclosed injector minimizes temperature gradients in the flow reactor caused by heat transfer along the injector. This is a particular problem when the flow reactor is operated near atmospheric pressure at reduced temperatures. Finally, this design is significantly more compact than conventional injector designs. This system has been successfully employed in studies of the heterogeneous reaction of N₂O₅ with sulfuric acid aerosols over the temperature range 225–293 K.

I. INTRODUCTION

The flow tube technique has been one of the most widely used methods to acquire kinetic data. Initially employed around 1930 to study reactions of atomic hydrogen and oxygen with various compounds,¹ ² this technique was later applied by many researchers to study important reactions of atoms and radicals. For a comprehensive review of this technique, its extensive applications, and the associated detection methods, the reader is referred to the review by Howard.³

Figure 1 shows a schematic diagram of a typical flow tube reactor employing a moveable injector. Reactants, such as atomic or molecular radicals, are introduced through one of the sidearms and mixed with the main carrier gas flow entering the other sidearm. The carrier flow generally defines the physical properties of the flow reactor gas stream while a temperature-regulated jacket defines the maximum length of the reaction zone. An additional reactant is introduced into the flow tube through the moveable injector. Kinetic measurements are carried out by varying the distance between the point where the two reactants are mixed and the detector. In addition to the moveable inlet injector shown in the figure, variations on this technique include moveable detectors, moveable discharge sources, and a series of fixed position inlet and/or sampling ports along the flow reactor length.

Because of its simplicity, a large number of kinetic studies employ moveable injector designs similar to Fig. 1. However, this simple design presents several practical disadvantages when carrying out laboratory studies simulating the earth’s stratosphere where temperatures of interest typically range between 210 and 240 K. Stratospheric reactions are generally studied using pressures below ambient, thus placing stringent requirements on the integrity of the sliding injector seal. This becomes particularly important when water vapor and/or other trace ambient gases may be involved in the reactions under study. For water vapor in particular, adsorption onto the cold outer wall of the injector can produce a significant "leak" into the reactor, even for reactor pressures near ambient. An additional complication arises when the warm injector, which is initially near ambient temperature, is moved into the cold flow reactor. This introduces temperature gradients, which may result in turbulence, especially at high flow reactor pressures. Such turbulence in turn can contribute to the background wall decay rate as well as cause an uncertainty in the knowledge of the velocity profile and therefore in the conversion of injector position into residence time.

Finally, some gases of stratospheric interest, such as dinitrogen pentoxide (N₂O₅), decompose both homogeneously and heterogeneously in the warm sections of a moveable injector. With the simple design of Fig. 1, the extent of decomposition changes with injector position since the temperature profile along the injector changes. As a result, the background wall decay may become large; severely complicating the data analysis, as will be further discussed in Sec. III.

The above problems would clearly be greatly reduced if the injector is completely isolated from the ambient environment and maintained at a uniform temperature. In the present design, we accomplish this by mounting the entire injector and drive mechanism in a temperature-controlled enclosure. The drive mechanism is connected to a crank, which is external to the enclosure, through a vacuum seal. Reactant gas is introduced into the moving injector by means of a coiled Teflon tube. Details of the design are given in Sec. II. An additional advantage of this design is that it requires a total length of only twice the desired injector travel; traditional designs require a length of three times this travel. The present injector design has been used successfully in measur-
II. ENCLOSED INJECTOR DESIGN

Figure 2 shows a detailed schematic of the enclosed injector, associated components, and the suspended flow reactor (27). The injector system is constructed from a triple-wall stainless steel cylinder 106.7 cm long × 12.7 cm in diameter. Stainless steel flanges are welded on both ends. Viton O rings (24) form a seal between the inner chamber and the plates at the top (2) and bottom (23) of the injector enclosure as well as the seal (25) for the flow reactor (27).

Ethanol coolant is circulated between the inner and middle walls while the outer annulus serves as an insulating vacuum jacket. The base plate (23) contains a number of vacuum feedthroughs for a thermocouple, the coolant inlet, and the gas and aerosol inlets. A slow flow of dry air enters and exits through needle valves connected to ports in the base (28) and top (29) flanges, respectively. The enclosure pressure is controlled by these needle valves and is monitored by a pressure gauge connected to the inlet port. The enclosure pressure and temperature are maintained near those of the flow reactor.

One reactant gas (N₂O₅ in the present study) enters the system through the inlet port (20), and passes through a coiled length of 3 mm o.d. PFA Teflon tubing (17). This Teflon coil contracts or expands as the injector moves. The gas then passes through a Teflon elbow (15), through the Delrin connector head (12) and into the injector tube (16). This tube consists of a 120 cm length of 6.35±0.05 mm o.d. glass-lined stainless steel tube (Scientific Glass Engineering, Inc., Austin, TX). Precision o.d. tubing is needed to effect a good sliding seal over the entire range of injector travel. The glass-lined stainless steel injector achieves the stiffness of stainless steel and the inertness of glass. A Thompson linear ball bearing (13), mounted in the Delrin connector head, slides on a linear guide shaft (7). This acts as a guide for movement of the injector. A Warner R-0502 ball nut assembly (11) is also mounted on the Delrin connector and runs on a Warner ball lead screw (1). The lead screw is supported on both ends by ball bearings (4) mounted in the top and bottom plates. The lead screw protrudes through the top plate and is sealed by a Teflon-encapsulated Viton O ring (6) mounted in the top plate. An identical O ring (18) forms the sliding seal around the injector near the bottom of the enclosure. This seal achieves the inertness of Teflon and the mechanical usability of Viton. A Chevron seal (3) external to the top of the injector chamber prevents ambient moisture from reaching the internal O ring and causing ice buildup. This Chevron seal is readily changed without opening up the chamber enclosure.

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The injector is moved in and out of the flow reactor by turning an external crank; this crank (not shown) is coupled to the lead screw via a pair of toothed timing pulleys. The pulleys and lead screw, which protrude from the injector enclosure, are enclosed in a loose-fitting plastic bag which is flushed with dry nitrogen to prevent ice buildup. Since the injector and the Teflon coil are completely enclosed in a constant temperature environment, the extent of decomposition of the reactant gas does not change with injector position. A stainless steel guide rod (not shown) passes through the center of the Teflon coil and into the base plate to prevent the Teflon coil from entangling with the injector tube.
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The performance of the enclosed injector system can be
judged by the integrity of the sliding injector seal, the magni-

dude of flow reactor temperature gradients, the degree of
reactant gas decomposition with injector movement, and the
ease of system use without encountering major problems.

With a Teflon-encapsulated Viton O ring forming the
seal around the injector (18), the enclosed injector system
has been in operation for over eight months at temperatures
of 215–293 K without any major problems. The Viton seal
initially employed was eventually attacked by the acidic
aerosol, which caused a dramatic increase in the injector slid-
ing friction. The more inert Teflon seal deformed at lower
temperatures resulting in leakage. Leakage across this seal
can have a number of detrimental effects on low temperature
kinetic studies. In addition to those discussed in Sec. I such
leakage will (1) affect the gas flow rate and therefore the
residence time in the flow reactor, (2) introduce impurities
from the injector enclosure into the flow reactor, and (3)
introduce corrosive flow reactor gas and aerosol into the
injector enclosure leading to corrosion of the injector drive
mechanism. The Teflon-encapsulated injector O-ring seal
maintained an excellent sliding seal throughout the tempera-
ture range 215–293 K, even with a 227 Torr pressure differen-
tial across the seal; we measured no change in the injector
enclosure pressure as the flow reactor pressure was reduced.
In addition, the total gas flow entering the reactor was typi-
cally within 3% of that measured at the output, again imply-
ing a good sliding seal.

Calibrated thermocouples were used to measure the
aerosol inlet temperature at the exit of the glass cone and the
wall temperature at the exit of the flow reactor. Temperature
gradients were typically \( \leq 0.2 \) K over the above temperature
range. At 273 K, no temperature gradient was measured. Un-
der similar flow and pressure conditions, the injector system
of Fig. 1 by comparison resulted in temperature gradients of
0.5 and 0.8–1.5 K at operating temperatures of 273 and 243
K, respectively.

The degree of reactant gas decomposition as a function
of injector position is quantitatively measured by the back-
ground wall decay rate \( k_{wall} \). This rate, which is measured
in the absence of aerosol, is dependent upon the condition of
the flow reactor walls, the presence of flow reactor tempera-
ture gradients, and the degree of reactant gas thermal de-
composition with injector movement. As discussed in Sec. I, ther-
mal gradients will cause turbulence and this may contribute to
the wall decay rate. In contrast to the enclosed injector
described here, such a situation has in fact been observed
using the simple injector system. For example at a flow tube
temperature of 273 K and a temperature gradient of 0.5 K,
we sometimes measured \( k_{wall} \) values a factor of 1.6–3.7
times higher than that predicted by diffusional transport
(Gormley and Kennedy).\(^5\)

As previously mentioned, the extent of decomposition
for gases like \( \text{N}_2\text{O}_5 \) will change with injector position using
the design of Fig. 1. As one increases the fraction of the
injector length protruding into the warm environment, more
\( \text{N}_2\text{O}_5 \) will thermally decompose to \( \text{NO}_2 \). This results in a
larger apparent \( k_{wall} \), as shown by the comparisons of Fig. 3.
As can be seen, the background \( \text{N}_2\text{O}_5 \) decay for the enclosed
injector (profile A, \( k_{wall}=0.00175 \text{ s}^{-1} \)) is over an order of
magnitude smaller than that for the simple injector (profile B,
\( k_{wall}=0.034 \text{ s}^{-1} \)) under similar conditions of temperature
(273 K), relative humidity (\( \leq 0.6 \% \)), and flow velocity (1.6
\text{ cm} \text{s}^{-1} \)). As the \( k_{wall} \) values become larger, it becomes more
difficult to separate out the gas phase reaction rate from those
occurring on the walls, particularly when the former is small.
In addition, as we often observe, high \( k_{wall} \) values are fre-
quently associated with a high variance. This in turn de-
grades the precision in the determination of reaction prob-
ability. In this particular case, the enclosed injector system
results in a reaction probability a factor 6 more precise than
the simple injector system.

In the present low temperature kinetic studies, water is a
reactant. Thus minimizing leakage of ambient water vapor
into the flow reactor, from either the O-ring seal (25) or the
sliding injector seal (18), is extremely important for achiev-
ing stratospheric water vapor concentrations below 10 parts-
per-million by volume (ppmv). The present injector design
achieves this. For example, at a flow tube temperature of 234
K, air with a controlled water vapor concentration was added
to the flow reactor and the concentration in the flow leaving
the reactor was measured by tunable diode laser absorption
spectroscopy (see Ref. 4 for details). With a water vapor
mixing ratio of 7.9 ppmv, the measured concentration was

\[ \text{FIG. 3. Background \text{N}_2\text{O}_5 \text{ wall decay curves for the enclosed injector sys-
tem (profile A) and the simple injector system (profile B) shown in Fig. 1.}
\]
within 1.8 ppmv of the added concentration, indicating a negligible ambient air leak rate.

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