Experimental Techniques for Studying Surface Chemistry in Smog Chambers

Laura T. Iraci, Jeffrey C. Johnston and David M. Golden
SRI International, Menlo Park, CA

Chemical reactions occurring on the walls of environmental chambers provide a large fraction of the radical species which initiate gas phase smog chemistry, but the nature and magnitude of these processes have not received focused attention. For example, the empirical models used in conjunction with the UNC and Riverside smog chambers contain different reaction schemes and product distributions for the adsorption and reaction of NO_2 on surfaces. In addition, several parameters are often adjusted empirically when environmental chamber data is analyzed. The current understanding of wall chemistry and its parameterization in models are briefly reviewed here.

Determination of the fundamental processes involved in wall reactions is needed for prediction of heterogeneous radical generation in different chambers under a variety of conditions. Techniques available for quantitative study of these heterogeneous processes include Knudsen cell, flow tube, and aerosol methods. The use of these methods in our laboratory is demonstrated, and their applicability to the study of environmental chamber wall processes is discussed.

It has long been known that the gas-phase chemistry which occurs in an irradiated environmental chamber cannot be reproduced in a mathematical model without the inclusion of an initial radical source in the model. This is generally presumed to be some (adjustable) quantity of nitrous acid (HONO) which is photolyzed to yield OH radicals at the start of the experiment and at the start of the model run. The formation of this HONO is generally attributed to heterogeneous formation from NO_2 and H_2O at the wall.

An additional, constant source of OH is often added to model schemes to better fit the experimental data. The physical basis for this OH production is less clear but may relate to a photostimulated HONO production channel also occurring at the walls.

The results obtained from fitting chamber data thus depend significantly on the choices made in the representation of the wall-induced radical sources. To properly extrapolate reactions studied in smog chambers beyond the experimental conditions and into models of the real atmosphere, molecular mechanisms of wall effects are needed. Only with a proper accounting of the radical sources can we be certain that the correct gas-phase reaction rates are obtained and that additional processes are not masked by the tunable parameterizations of wall chemistry.

As a first step in achieving a molecular understanding of the wall reactions, several studies must be undertaken:

- **Identify conditions which lead to HONO production.**
  what surfaces are active? how does wall history affect HONO production?
  are there surfaces more inert than Teflon? what is the role of light?

- **Quantify HONO production rate as a function of measurable chamber parameters.**
  temperature, time, relative humidity, wall exposure history, hν, NO_2

- **Determine if OH is directly emitted from Teflon surfaces or if a second, photoinduced mechanism leads to HONO formation throughout an experiment.**
  hv needed? O_2? H_2O? hydrocarbons? is HONO produced in the chamber throughout the experiment?

- **Express OH production rate in terms of parameters which apply to all chambers.**

These and other studies will foster the development of an explicit wall mechanism that can be incorporated into models in a manner analogous to the current detailed treatment of gas phase reactions.

Proposed Experiments to Characterize Wall-Induced Radical Formation:

HONO adsorption to and desorption from Teflon

Characterize outgasing of Teflon

vs. RH, T, time, hν, NO_x and HC history
watch for HONO, OH, other NO_x?

What species are involved in HONO formation?

$NO_2 + H_2O$ (+ hν) + surface
$NO_2 + H_2O + O_2$ (+ hν) + surface
is O_2 needed? what surfaces are more or less active?

Investigate mechanism using isotopes
Does the O come from NO_2 or H_2O?

$H_2{}^{18}O + NO_2 \rightarrow H^{18}ONO$ (Sakamaki et al., 1983)

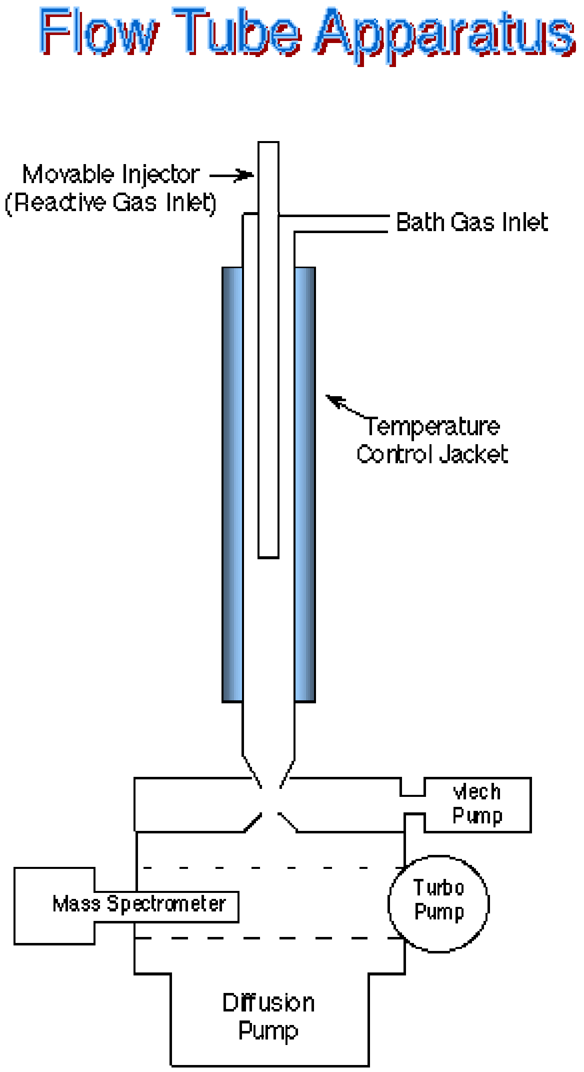
Does the N come from new NO_2 reacting at surface, or from old species already trapped?

Add $^{15}NO_2$ to Teflon aged with $^{14}NO_2$ and/or $H^{14}NO_3$; look for $HO^{15}NO$ vs. $HO^{14}NO$. Add $N^{18}O_2$ and H_2O; look for $HON^{16}O$ vs. $HON^{18}O$

Available Techniques:

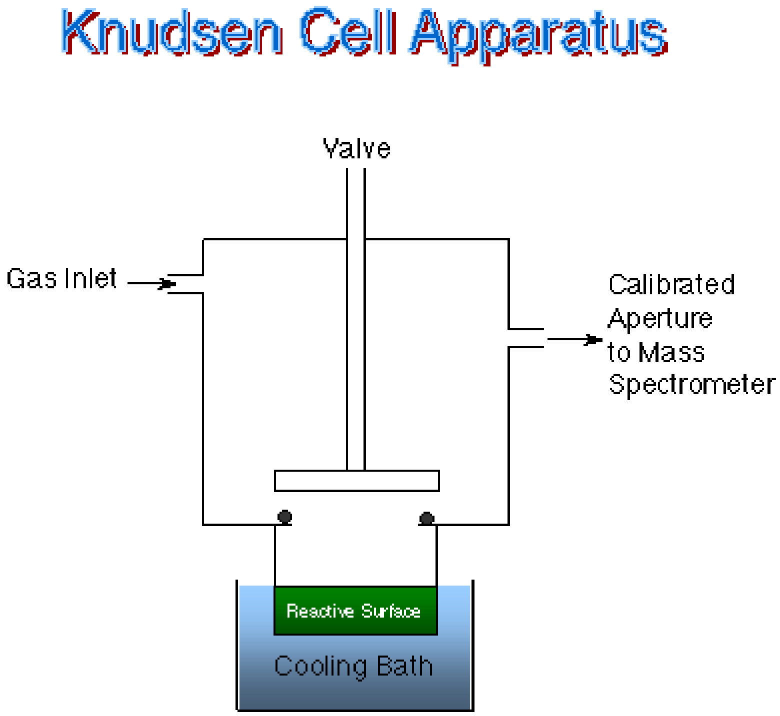
Two basic experimental arrangements are applicable to these studies. The first is the traditional flow tube, which can be designed and operated with a coated wall or with flowing aerosol particles to provide the reactive surface. A movable injector allows for the variation of interaction time between gas and surface. A second standard technique for studying gas-surface interactions is the Knudsen cell, which measures loss of a reactant to wall surfaces in competition with escape from the cell.

Many analytical tools are available for the monitoring of processes in either the flow tube or Knudsen cell arrangement. Mass spectrometry is commonly used to identify and quantify stable reactants and products. Spectroscopic techniques such as laser-induced fluorescence or resonance enhanced multi-photon ionization can be used to monitor short-lived species inside the reactor. This allows for the detection of radicals which must be measured in-situ before they are lost to downstream surfaces. Lastly, infrared spectroscopy can be used to detect gases in a static cell, allowing longer interaction times than those accessible with a flow tube or Knudsen cell.

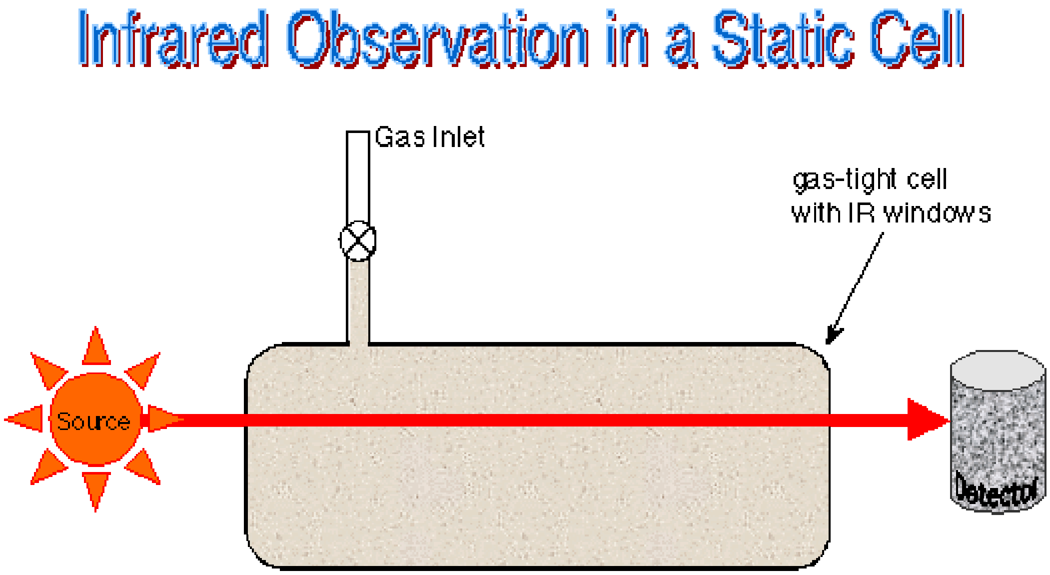


Operating a coated-wall flow tube would allow the glass surface to be coated with FEP Teflon, the same material used for chamber bags and wall coatings. The maximum interaction time in a flow tube is on the order of ten seconds, and the experimentalist has good control over conditions such as temperature, relative humidity, total pressure, fraction of O_2 present, identity of the carrier gas, and the light field available for photolysis. Because the Teflon surface area is well-known, rate coefficients are easily determined.

In contrast, an aerosol flow tube is designed to continually supply fresh surface area via particles roughly 0.1 – 1 um in diameter. The surface area can be greatly increased over that available in a coated-wall apparatus, allowing the observation of less efficient processes. In addition, the Teflon particles can be pre-treated before their introduction into the flow tube, facilitating studies of the effect of previous exposure to HNO_3, NaCl, etc. Particles can also be pre-treated with organics if desired.


Knudsen Cell Apparatus

The Knudsen cell, commonly used for uptake and kinetic measurements, allows the stationary reactive surface to be exposed for minutes to hours. This makes the technique especially well-suited to studies of wall saturation/passivation and regeneration processes. Our current cell is glass coated with FEP Teflon prepared from an aqueous suspension that is dried and annealed in place. Our cell walls would age similarly to those of smog chamber but can easily be stripped and recoated to start with fresh Teflon. Controlling the wall temperature is straightforward, something which cannot be said of an aerosol flow tube arrangement. In addition, other coatings or inserts of Teflon previously used in a smog chamber are easily accommodated.



Infrared Observation in a Static Cell

Walls could be coated, or Teflon wool or film could be placed in the cell.

A static cell coupled with infrared detection of the gases inside would be ideal for long-duration studies of the loss or release of gases from wall materials. Questions such as: how much NO_2 is lost to the walls over the course of an 8 hour experiment? or how much HONO is present the next morning? could be addressed. Also, the time evolution of species after a step-wise change in conditions can be monitored.

In summary, many aspects of wall-induced chemistry in smog chambers can be addressed by systematic lab studies. Several established experimental techniques are available, and combining the strengths of multiple methods will allow us to study problems from different perspectives. The goal of studying these processes is to develop a physically-based understanding of reactions at the walls and the adsorption/desorption behavior of gases present in chamber experiments. This will facilitate a realistic extrapolation of chamber data to the atmosphere. In addition, studies of heterogeneous

HONO formation are directly relevant to polluted urban areas, which contain many stationary and airborne surfaces and often exhibit increased levels of ambient HONO.