CHEMICAL REVIEWS

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Introduction: Atmospheric Chemistry—Long-Term Issues

It had long been assumed that the Earth's atmosphere is a vast, unalterable reservoir. It seemed that nothing humans would do could really alter or significantly influence the atmosphere. This long-held view was first cast into doubt by small-scale alterations such as the London fog and the Los Angeles smog, modified by visible regional-scale changes such as acid precipitation, and finally shattered by unmistakable global-scale changes such as the Antarctic ozone hole. Changes in climate, predicted and observed in the past, go further and show how other parts of the Earth system, especially the oceans, are also involved and can be altered by human activities.

Clearly, human-induced emissions are small compared to the mass of the atmosphere. Why, then, can such small emissions have such large influences? There are several reasons. First, even small amounts of certain molecules can catalyze change (e.g., catalytic ozone destruction in the stratosphere). Second, they can be much more efficient than the major constituents of the atmosphere in bringing about some specific changes (e.g., greenhouse gases that are thousands of times more efficient than CO_2). Third, small emissions over a long period of time can add up to a significant amount. The key to the extent of a molecule's impact on the atmosphere is what happens to it in the atmosphere and how, in turn, that change influences the atmosphere. Therefore, atmospheric chemistry is a study of how a molecule introduced into the atmosphere is altered by the oxidizing medium of the atmosphere and, in turn, how this alteration affects the atmospheric composition and atmospheric properties.

Let us examine what can happen to a molecule that is introduced into the atmosphere. Figure 1 is a depiction of most of the processes experienced by a molecule upon entry into the atmosphere. Central to these changes are the chemical processes. Other transformations such as uptake by ocean, precipitation scavenging, deposition to ground, or reactions in other Earth system components also involve chemistry. In this thematic issue, the focus is on the transformations occurring within the atmosphere.

The majority of the chemical alterations in the atmosphere are brought about by sunlight, by free radical reactions, and by reactions in or on condensed media floating about. Sunlight, which directly interacts with and alters the molecules, is also the source of most of the highly reactive atmospheric free radicals. Thus, photolytic processes play a crucial role in the atmosphere. The abundances of the free radicals are very small, usually less than one part in a billion of air. The low abundances are understandable since it is precisely because they are reactive that they are consumed, unlike the unreactive species that can build up to higher abundances. However, it is these free radicals with small abundances that transform most species in the atmosphere. Thus, free radical kinetics is key to our understanding of atmospheric chemistry. The condensed media are highly variable in terms of location, duration of existence, properties, and ability to alter a gas-phase species. Yet, because they provide pathways for reactions that are not feasible (or too slow) in the gas phase, heterogeneous (reactions on surfaces) and multiphase (reactions of gas-phase species taking place via their entry into a liquid droplet) processes play vital roles. Quantifying these processes is essential for understanding what happens to a species upon its entry into the atmosphere and how this molecule alters the atmosphere. Such an understanding presupposes that the "background" state of the atmosphere that exists prior to the introduction of the molecule is also known. Again, the same chemistry in the "background" atmosphere also needs to be understood.

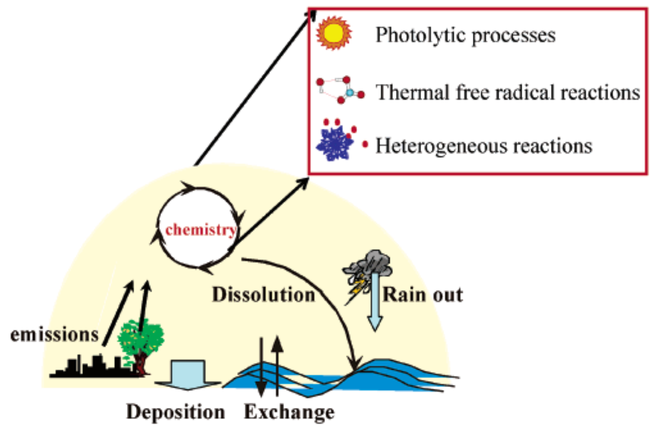

Figure 1. Schematic of the various transformation pathways for a species emitted into the atmosphere. The central role of chemistry in the atmosphere is highlighted, and the specific processes are noted.

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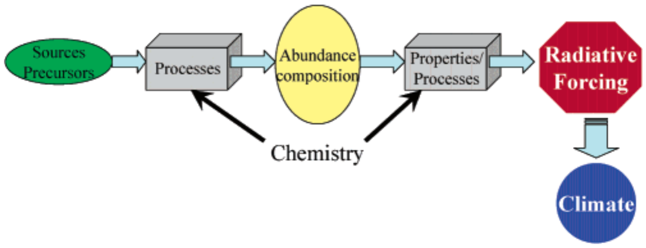

Figure 2. Block diagram showing the central role of processes and properties in addressing societal issues such as climate. Chemistry plays a key role in connecting emissions to abundances to impacts.

One of the reasons for the large emphasis on atmospheric science is society's need to understand and predict the influence of humans on the Earth system. Let us consider the currently important issue of climate change. Figure 2 shows, in a block diagram, the conceptual steps in connecting the emission of a greenhouse species (or its precursor) with the climate impact of that species. Clearly, the two crucial steps involved are based on chemical processes. Understanding the chemical processes is thus key for prediction and for any action by the society, which to a first order is altering the emissions. Such steps are critical because one cannot simply use the currently measured abundances and the observed trends of species to predict the future. The steps involved in predicting the future are mostly the same as those needed for hind-casting. Such hind-casting is essential for validating our understanding of the atmospheric chemical processes to assess how well the recorded changes can be accounted for.

The issues of major interest in atmospheric chemistry have changed with societal concerns and new discoveries; they will change in the future. However, the basic pathway for tackling problems of today is the same as that for the past and will likely be the same for the future (with some modifications). The approach is to break the transformations into their basic chemical steps and quantify them in the laboratory, determining the emissions and deposition processes, incorporating them in numerical models, and checking model results with observations (a reality check!). Thus, process understanding—from the fundamental chemical kinetics and photochemistry, heterogeneous and multiphase reactions, biological and other processes that lead to emissions, and alterations in other parts of the Earth system—is essential.

Inclusion of the process understanding is necessary in modeling atmospheric changes, be it the stratospheric ozone depletion, recovery of the ozone layer, improvements in the regional air quality, or the global climate change. Such process understanding has to be distilled into accurate, yet manageable complexity, for inclusion in atmospheric models. This "simplification" demands a better understanding than an empirical representation.

This thematic issue exemplifies these process-understanding steps in all these areas. Such information will be of use today and in the future. Currently, the main long-term issues of atmospheric chemistry are climate, regional and urban air quality, and stratospheric ozone changes. Other emerging issues include the role of the atmosphere in transporting and transforming toxic substances (e.g., mercury), indoor air quality, alterations to the biosphere, and the overall biogeochemical cycling of various elements.

There are two papers in this thematic issue, one on atmospheric motion and one on evaluation of laboratory data for atmospheric modeling, which may be viewed as being outside atmospheric chemistry. However, these two areas are of central concern to atmospheric chemistry, and, therefore, atmospheric chemists in particular and chemists in general need to be aware of them. First, the Earth's atmosphere is fluid, constantly moving and mixing. This is a key aspect of the atmosphere because the concentration, and hence the influence, of a species depends not only on what happens at the location of interest but also on what happened elsewhere. In some cases, the atmospheric motion can be separated from chemistry if the time scales for motion and chemical change are vastly different. However, in most of the cases of importance to the societal issues of the day, such a separation is not feasible. A basic understanding of the dynamics of the atmosphere and a little familiarity with the terminology in this field is needed for atmospheric chemists to interface with the dynamicists and to fully appreciate the inseparability of chemistry and dynamics. It is hoped that the article by Shepherd will familiarize chemists with this area, provide pointers for more information, and enable chemists to have a meaningful discussion with atmospheric dynamicists. Second, evaluation of laboratory data is a critical element in atmospheric chemistry because models need to use consistent and vetted input parameters so that answers obtained by models can be used for policy decisions. Therefore, a great deal of emphasis is placed on the accuracy of the input data. The modeling community has relied on expert panels to evaluate and recommend the best available data for atmospheric modeling. Thus, there is a tradition spanning roughly the past three decades in using evaluated data for atmospheric models. Cox has described the process of data evaluation in this issue.

Atmospheric chemistry spans from the fundamental understanding of reactions to accurately measuring reaction rate and photochemical data for gas-phase processes. Papers by Smith, Troe, Golden, and Donahue address the fundamental kinetics issues. The papers by Atkinson, Bedjanian, and Orlando address kinetics of organics, halogen oxides, and alkoxy radical, respectively. Herrmann covers the kinetics in liquid phase. Donaldson, Slanger, and Matsumi address the role of photochemical processes.

Heterogeneous and multiphase chemistry is one of the prominent areas that has emerged since the discovery of the ozone hole and the realization of the extremely important role played by these processes. A wide variety of heterogeneous and multiphase reactions is addressed in this issue by the following papers: Abbatt on interactions with ice, Finlayson-Pitts and Rossi on sea salt chemistry, and Grassian on dust. Other articles also address this topic.

In addition, the important area of emissions is exemplified by the paper by Fall on oxygenated organic compounds.

Atmospheric chemistry often revolves around following the path of an element or a chemical moiety from its emission to chemical processing in the atmosphere to its removal and assessing the impact of this species on the atmosphere. The following papers address some these issues: Carpenter on iodine, Plane on metals, Cohen on nitrogen oxides, Francisco on alternative fuels and new refrigerants, Goldstein on volatile organics, Kurylo on atmospheric lifetimes, and Mellouki and Rudich on organic compounds.

Measuring the isotopic composition of chemicals and their changes in the atmosphere has provided a powerful method for identifying and quantifying atmospheric budget and processes. The paper by Brenninkmeijer, and that by Goldstein mentioned above, exemplify the advantages, and also the limitations, of this approach.

Atmospheric measurements of chemicals and an understanding of their abundances are telling and essential for evaluating our overall understanding. The confidence in using predictive models of the atmosphere is developed by comparing model results with atmospheric observations. Further, atmospheric observations have led to unexpected discoveries. Papers by Heard and Reeves describe the current state of knowledge on odd hydrogen species derived via atmospheric observations. Of course, measurements cannot be made without suitable instrumentation. Many of the major atmospheric discoveries have come about because of advances in measurement capabilities and the unexpected findings that emerged from such measurements. Some recent developments in measurement capabilities have come about in the area of cavity ring-down spectroscopy, and the papers by Brown and Jones address them.

This thematic issue is not just a collection of reviews; the reviews contain new interpretations and opinions of authors. Sometimes, the opinions and approaches were not those liked by the reviewers. Yet, opinions and conclusions were encouraged to provide further thought and future research.

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