Methods were described by which ion-molecule reaction equilibria can be determined in the gas phase. The resulting data provide equilibrium constants and energy changes for reactions in the absence of solvent and in the presence of a controlled small number of solvent molecules. [The SCI indicates that this paper has been cited in more than 555 publications.]

A New Phase for Ionic Reactions
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Ionic reactions in solution are of fundamental importance in chemistry and biochemistry. The complete understanding of these reactions is made difficult because the behavior of the ions is dominated by strong interactions with a large number of solvent molecules. The role of the solvent could be much better understood if the same reactions could be studied in the complete absence of solvent and then in the presence of a controlled small number of solvent molecules.

We could show that such studies are possible in the gas phase on application of special mass spectrometric techniques. Central to these studies was the finding that ion-molecule equilibria can be observed in the gas phase. Our much-cited paper contains a description how such equilibria can be determined and provides a summary of the first data obtained in our and other laboratories.

At the time, we had just started mass spectrometric work at gas pressures in the 10^-6 torr range. These were “ultrahigh” pressures by mass spectrometric standards, conventional mass spectrometers are operated in the 10^-4 torr range. Our foray into ultrahigh pressures was motivated by the intention to solve problems of radiation chemistry. It was suspected that ion-molecule reactions make important contributions to the overall chemical change occurring in irradiated gases, but nobody had tried to detect the ions that were actually present at near-atmospheric pressures.

Our initial observations were very difficult to interpret. We could not relate the masses of the observed ions to the gas that was irradiated. Thus, nitrogen gas did not lead to ions made up of units of mass 14. Instead, a group of about 10 ions with a constant mass difference of 18 units among ions was observed. It took considerable time before we realized that these ions were due to H_2O^+(H_2O)_n ion-water clusters. Since chemicals almost always have impurities, there were many frustrations before we realized that some of the impurity reactions are of the greatest interest These often involved the most stable ions in the given system and these ions would interact with gaseous solvent molecules like H_2O and reach equilibrium. Measurement of these equilibria led to ion-solvent molecule bond energies. Gradually conditions for measurement of other equilibria such as proton transfer (acid-base), electron transfer (oxidation reduction), and others were developed in our and other laboratories. These results are the main present source of gas phase ion-molecule thermochemical data. The availability of these experimental data stimulated a large number of quantum chemical calculations, because these reactions, due to the absence of solvent, were accessible to ab initio calculation. Furthermore, the ion-solvent molecule binding energies provided data on the basis of which ion-molecule pair potentials could be developed. Such potentials are required for the theoretical modeling of ions in liquid solutions.