HETEROGENEOUS CHEMISTRY OF IMPORTANCE IN DECISIONS
CONCERNING THE ENVIRONMENTAL IMPACT OF ENERGY
PRODUCTION AND THE SITING OF NEW ENERGY SOURCES

Progress Report
For the Period
March 1, 1979 - February 29, 1980

MASTER

A. W. Castleman, Jr.
Professor of Chemistry

The Regents of the
University of Colorado
Boulder, CO 80309

February 1980

Prepared for
THE DEPARTMENT OF ENERGY
Under Contract No. EP-78-S-02-4776

DISCLAIMER
This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

EB
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

BRIEF SUMMARY OF RECENT ACCOMPLISHMENTS

It is well recognized that the results from studies concerning the formation and properties of small clusters provide an important key for elucidating gas-to-particle conversion processes. As a result of our work in this area, it is now clear that there is an intimate relationship between the ability of a small cluster to become stabilized and its formation of a charged transfer complex upon cluster growth. The results of studies conducted in our laboratory have provided invaluable evidence concerning the factors governing the stability and structure of small clusters of both positive and negative ions of atmospheric interest. A combination of these data has also been useful in assessing the stability of these charged transfer complexes and has provided important insight into the incorporation of various species in the aqueous phase surrounding an aerosol droplet; thereby, important new information concerning their potential reactivity has been acquired.

Data on bonding involving a variety of negative and positive ions also enable an assessment of the influence of temperature and water vapor partial pressure on ion cluster distributions. Furthermore, in conjunction with the measurements, semi-quantitative quantum mechanical calculations lend insight into cluster structure. Comparison of measured enthalpies and entropies with the

classical liquid drop model have revealed its shortcomings in predicting nucleation, but a new correlation has emerged which is useful for assessing the contribution of bonding to the energy barrier and for predicting ion solvation energies. In the case of neutral clusters, evidence has been obtained for the existence of a clathrate-like structure involving 21 water molecules stabilized by a mobile proton. Clustering of water to neutral acid molecules has been found to lead to the formation of an electrolytic microdroplet with very few water molecules. The role of these various cluster species in condensation phenomenon and as pre-nucleation embryos to gas-to-particle conversion has been clarified.

Work in this field is important in understanding many other related problems in the atmospheric sciences. Included among these are questions concerning the fate of the products of ion cluster-ion cluster recombination, the influence of clusters in aerosol formation, the influence of small clusters and aerosols on the propagation of electromagnetic radiation, and the importance of small clusters and aerosol surfaces to atmospheric chemical reactions. From a basic point of view, it is evident that the results contribute to a more complete understanding of the forces between ions and neutral molecules. Research in this area is also particularly valuable in the field of interphase physics which is concerned with elucidating the molecular details of the collective effects responsible for phase transitions, nucleation phenomena, the development of surfaces, and ultimately the formation of the condensed state. It is, of course, well known that phase transformations of water vapor to the condensed state have a direct bearing on weather and climate. Likewise, it is recognized that atmospheric aerosols have a large percentage water content, and water vapor plays a major role in their formation processes.

In order to further advance these important areas of chemical physics, research is being conducted in our laboratory on: 1) the formation, stability,

and structure of ion-clusters both by high pressure mass spectrometric experiments and approximate molecular orbital quantum mechanical calculations; 2) the exchange of energy and angular momentum during ion-molecule association reactions using computer dynamics calculations; 3) related experimental and theoretical studies of nucleation and solvation phenomena; 4) laser photophysics of ion clusters including measurement of cross sections for photodissociation, fluorescence, and energy exchange by pulsed infrared techniques; 5) the growth, stability, and structure of weakly-bound van der Waals and charge-transfer complexes employing electric deflection techniques and taking advantage of the first-order Stark effect; and 6) the multiphoton ionization of metal atom clusters to probe the transition from the isolated atomic to the condensed metallic state, and to elucidate their electronic states and potential as sites for the catalytic conversion of absorbed pollutants.

Ion Cluster Experiments

High pressure mass spectrometric sampling of ion-drift cells is used in our laboratory for measuring bond energies and entropies. Its advantage lies in the fact that measurements can be made over a large range of pressures, temperatures, and electrical field parameters. Thereby, even in the formation of relatively large clusters, the attainment of equilibrium can be ensured.

The reaction cell and associated apparatus is shown schematically in Figure 1. Ions are produced by various methods depending on the nature of the ones to be investigated. In the case of negative ions this is usually accomplished by electron bombardment of gas phase molecules [1], while a thermionic source [2] is generally employed in the case of positive ones. Subsequent to their formation, the ions are focused into a thermally controlled reaction cell. The pressure is maintained sufficiently high (ca. 5 to 15 torr) such that the ions reside in the reaction cell for a time adequately long to ensure the attainment of equilibrium

between the various clustering-reaction sequences. The primary ions and ion clusters leak through a small orifice (typically 50 or 75 μm diameter) into a high vacuum region where they are mass analyzed and counted. From the measured ion intensities and known partial pressure of the clustering neutral, an equilibrium constant $K_{n,n+1}$ is determined for reactions of the type:

where $A^{\pm}$ designates a positive or negative ion, B the clustering neutral, and M the third-body necessary for collisional stabilization of the complex. Taking the standard state to be one atmosphere, and making the usual assumptions [2] concerning ideal gas behavior and the proportionality of the chemical activity of an ion cluster to its measured intensity, it follows that

$$\ln K_{n,n+1} = \ln \left| \frac{I_{n+1}}{I_n p_B} \right| = - \frac{\Delta G^{\circ}_{n,n+1}}{RT} = - \frac{\Delta H^{\circ}_{n,n+1}}{RT} + \frac{\Delta S^{\circ}_{n,n+1}}{R}$$

Here, I_{n+1} and I_n represent the respective measured ion intensities, p_B the pressure of clustering molecule B , $\Delta G^{\circ}_{n,n+1}$, $\Delta H^{\circ}_{n,n+1}$, and $\Delta S^{\circ}_{n,n+1}$ the standard Gibbs free energy, enthalpy, and entropy, respectively, R the gas-law constant, and T absolute temperature.

As part of the DOE sponsored program, thermodynamic quantities for the gas phase clustering equilibria of NO_3^- with water (see Appendix I), NO_2^- with CO_2 , NO_2^- with SO_2 , and I^- with HCl were determined with high pressure mass spectrometric techniques. The data for the NO_3^- system have been of great value in assessing the cluster stability for nitric acid water systems as discussed in a subsequent section. The data for the negative ion systems, together with earlier hydration results obtained in our laboratory, have established that the magnitude of the enthalpy changes for the association of the first neutral to a series of negative ions parallels the gas phase basicity of these anions. For any given ion, the relative order of the addition enthalpies among the neutrals was

found to be dependent on the polarizabilities of the neutrals and on the covalency in the ion-neutral bond. Dispersion of charge by a covalent bonding was found to significantly affect the succeeding clustering steps. The details of the results from these studies are discussed in Appendices A and I.

Considerations of Bonding and Solvation

Typical van't Hoff plots of data derived from the above experiments for the clustering of CO_2 with NO_2^- , Cl^- , CO_3^- , SO_3^- , and I^- and SO_2 with NO_2^- , and from which enthalpies and entropies can be deduced, are shown in Figures 2a and 2b. Analogous data were obtained recently for a number of negative and positive ion systems and have been used to demonstrate that the breakdown in the classical liquid-drop formulation of nucleation theory is based on the inability of the model to properly account for the configurational entropy of small clusters (structural features) rather than its inability to adequately describe bonding [3-5]. The application of recent laboratory data in explaining observations of negative ion cluster distributions in the lower ionosphere is discussed in Reference [6].

Recent data for selected negative ion-ligand systems are shown in Table II. The results for the NO_2^- - SO_2 , NO_2^- - CO_2 , and I^- - HCl studies were obtained with DOE support. (See Appendix A.) Interestingly, the relative pattern of bond energies for the association of one neutral molecule to a negative ion was found to be the same for water (a protic polar molecule), sulfur dioxide (an aprotic polar molecule), or carbon dioxide (a non-polar molecule). (See Table I.) Theoretical calculations based on the approximate quantum mechanical procedure CNDO/2 were made in our laboratory. These have been successful in explaining the relative bonding of higher order clusters of H_2O about HCO_3^- , CO_3^- , NO_2^- , and NO_3^- . (See Reference [1].)

In the case of positive ions, the Extended Huckel method accounts for the

finding that the bonding of NH_3 to the alkali metal ions is stronger than that of H_2O . [2]. In the case of the closed shell ions, the relative bond energies of various ligands is found to correlate with differences in ionization potentials [2].

The most interesting finding is that all of the gas phase negative and positive ion-hydration data, as well as the positive ion ammoniation values, can be related to the liquid phase single ion heats of solvation by a simple correlation [7]. Referring to Figure 3, it can be seen that the ratio of ΔH°_{solv} (standard heat of solvation) to the summed gas phase enthalpies, $\Delta H^\circ_{0,n}$, approaches a value which is independent of the nature of the ion. This is intimately related to the Born equation which expresses the energy necessary to place a charge in the cavity of a dielectric medium. The details are summarized in Appendices B and E.

Experiments are now in progress to elucidate the structure of ion clusters and the dynamics of decomposition utilizing laser techniques. In particular, measurements of ion cluster photodissociation cross-sections and fluorescence are being made with visible CW lasers. Preliminary evidence for a bound excited state of SO_2^- has been obtained as part of a related study. Experiments with pulsed infrared lasers are being planned to investigate energy transfer mechanisms and the dynamics of cluster dissociation.

Theory of Ion Molecule Association Reactions

During the course of our experimental studies we observed that the apparent equilibrium constant for many cluster association reactions varied with the electric field. In situations where there is insufficient reaction time for equilibrium to be established, the equilibrium constant is found to diminish exponentially with the field energy. However, in other cases there is very little effect at low values of field energy E/N ; here, E is the electric field intensity and N is the number density of the gas phase molecules. A gradual decrease in

the apparent equilibrium constant is only evident at relatively high values of the energy imparted by the electric field.

The equilibrium constant for an association reaction is also given by the following expression:

$$K_{n,n+1} = \frac{k_f}{k_r}$$

where k_f is the forward reaction for the formation of the association complex and k_r is its rate of unimolecular decomposition. Since it was obvious that the apparent decrease in the equilibrium constant with field energy was due to a change in the rate of clustering or cluster break-up, theoretical studies were initiated in our group to investigate the energy dependence for such reactions.

Five major approaches are available for treating capture collision rate constants for ion molecule reactions: These include Langevin theory, the locked dipole approximation, Barker-Ridge theory, the average dipole orientation theory (ADO), and the angular momentum conserved theory AADO. An examination of these various theories showed that there is an inconsistency in the theoretical developments in all cases except for the Langevin theory. Within the framework of an average ion dipole interaction potential, as part of another grant we developed a generalized approach which properly accounts for the conservation of both total energy and total angular momentum. The general approach, termed TEAMS, was found to satisfactorily account for the energy dependence of association reactions over a wide range of conditions. The details are given in Reference 8.

Subsequently, we developed a two-dimensional collision dynamic model for ion molecule association reactions. (See Appendix H.) The results of our study show that there are both capture and non-capture orbiting trajectories which often display multiple reflective collisions. (See Figure 4.) It is found that, due

to the non-isotropic nature of the long-range dipole interaction potential, coupling of angular momentum and energy between the collision coordinate and the dipole internal rotational coordinate becomes quite significant even at large radial separations. Along with the dipole self rotation, these effects result in an effective potential profile with multiple centrifugal barriers. The height of these barriers is found to increase with decreasing radial separation.

The most interesting finding from these studies is that a reduction in the initial impact parameter between the molecule and the ion does not always lead to a capture collision. For certain initial orientations of the dipole and certain dipole rotational temperatures, "bulls-eye" patterns are actually found. In such cases a further reduction in the impact parameter leads to a non-capture collision. (See Reference [9].)

Neutral Clusters: Hydrogen Bonded Systems and Charged Transfer Complexes

Studies of the properties of van der Waal's and similar weakly bound clusters are of considerable interest since they provide a basic understanding of the forces responsible for neutral cluster stability. Investigations of the formation of clusters involving water molecules are of particular value since they provide insight into the nature of hydrogen bonded systems existing not only in the gaseous state but also as liquid water and ice. An intriguing possibility to follow the course of change continuously from the gaseous to the condensed state is provided by molecular beam techniques. Such studies are presently underway in our laboratory [10].

Recently, as part of another activity we have made a detailed study of water clusters produced by supersonic expansion techniques. A mass spectrometric analysis of the resulting cluster distribution reveals a number of interesting features corresponding to weakly bound clusters containing six, eight, ten, and

twelve molecules, respectively. The observations can be accounted for in terms of simple RRK arguments based on internal energy considerations in conjunction with a consideration of the kinetics of growth mechanisms in supersonic free jet expansions. It is found that the formation of these small clusters occurs through well-defined ring closures, with structures similar to those occurring in bulk ice crystals being exhibited.

Electron impact ionization of larger clusters reveals [10] special structures at clusters $H^+(H_2O)_n$ where n equals 21, 26, 28, and 30. Each of these corresponds to known unit cell structures for clathrates in the condensed phase, and it is speculated that what is actually observed in the gas phase is a cluster with an analogous structure which is stabilized by a mobile proton [11]. Studies made as part of the DOE sponsored program with both heavy and light water revealed a preference for the heavy isotope to become enriched in the cluster. This is consistent with the suggestions regarding the formation mechanism.

Based on our model, the cluster involving 21 water molecules about an H^+ ion is a pentagonal dodecahedron. Our findings, and related explanation, are especially intriguing since they account for the observations of Searcy and Fenn [12], Burke [13], and Rabalais et al. [14]. The work in the first two references is based on studies of the expansion of a weakly ionized gas; the results of Rabalais et al. give evidence of the formation of similar species during the ion bombardment of ice surfaces.

Research is also in progress in our laboratory on the formation of mixed clusters of species which form charge-transfer complexes, and ultimately ion pairs, upon solvation in the condensed phase. An especially intriguing question to which the present results have implications concerns the fate of the products of the recombination of positive and negative ion clusters upon interaction. It

has been suggested [15] that, rather than result in charge neutralization, the interaction of highly hydrated clusters may lead to a species having an unusually large residual dipole moment, that is, a cluster which is overall electrically neutral, but which has separated charges contained within.

In order to provide information on this possibility, as well as on the nature of interactions between ion-pairs in solution, we have undertaken studies of clustering between nitric acid and water molecules. Clusters corresponding to $(HNO_3)_x(H_2O)_y$ (where $1 \leq x \leq 6$ and y ranged to 20) were observed. For large values of y , and in situations where $x=1$, species of the type H_3O^+ clustered to water and NO_3^- clustered to water (analogous to the recombination products of these two hydrated ion species) will eventually form. The experimental technique consists of a supersonic expansion to produce mixed clusters of nitric acid in water, followed by subsequent analysis of the products by mass spectrometry. Some recent results are shown in Fig. 5 which is a plot of the relative intensity of cluster beams versus mass to charge ratio. It is interesting to note, as shown in the insert of Fig. 5, that a suitable plot of the mole fraction of the water component of the nitric acid clusters, plotted versus the number of nitric acid molecules in the cluster, rapidly approaches a constant value. The limiting value of this ratio corresponds to the bulk phase azeotrope for the nitric acid-water system. (See details in Appendix G.)

New experiments are now underway which utilize the Stark effect, coupled with an inhomogeneous electric deflection method. The technique, termed DEADHOTSS (deflection of electrically aligned dipoles via a hexapole orientation technique Stark spectroscopy) utilizes the focusing properties of an inhomogeneous electric field for the case of molecules having a component of the dipole moment lying along an axis of rotation of the molecular complex. Results have now established that dipole moments can be accurately measured by this tech-

nique. A number of molecules having structures equivalent to symmetric and asymmetric rotors have been studied. Their dipole moments could be easily measured to an accuracy of 3% by this method. Experiments are in progress to determine the point at which a large dipole moment increase takes place upon successive hydration in the nitric acid-water cluster system.

Multiphoton Cluster Ionization Experiments

During the past year considerable effort was directed toward the construction of a major facility for studying the nature of surfaces which may be of importance in assessing the environmental impact of new energy sources. A new medium resolution quadrupole mass spectrometer was designed and built in our laboratory. The apparatus consists of a triply differentially pumped vacuum system comprising: a high-pressure clustering source suitable for either low-temperature cluster formation or metal-atom cluster formation with a high temperature oven, a *uv* light source and monochromator was obtained for doing the multiphoton ionization experiments as a function of wave length. In addition, a double hemispherical energy analyzer was designed and built which will enable 20 *m eV* resolution for measurements of the energy state from which an electron is removed from the small cluster via the multiphoton ionization experiments. Experiments are currently in progress to optimize beam configuration and ionization geometry.

References

- [1] (a) R.G. Keesee, N. Lee, and A.W. Castleman, Jr., *J. Am. Chem. Soc.*, **101** (10) 2599 (1979)
(b) N. Lee, R.G. Keesee, and A.W. Castleman, Jr., *The Properties of Clusters in the Gas Phase: IV. Complexes of H₂O and HNO_x Clustering on NO_x⁻*, *J. Chem. Phys.* (in press, Jan. 15, 1980 issue)
- [2] A.W. Castleman, Jr., P.M. Holland, D.M. Lindsay, and K.I. Peterson, *J. Am. Chem. Soc.*, **100** 6039 (1978)
- [3] (a) A.W. Castleman, Jr., *Kinetics of Ion Molecule Reactions*, Pierre Ausloos, Ed. (Plenum Press, N.Y. 1979) p.295
(b) A.W. Castleman, Jr., *Advances in Colloid & Interface Science Nucleation* A. Zettlemoyer, Ed. (Elsevier Press, Oxford, 10, 1979) pp. 73-128
- [4] A.W. Castleman, Jr., P.M. Holland, and R.G. Keesee, *J. Chem. Phys.*, **68** 1760-1767 (1978)
- [5] (a) A.W. Castleman, Jr., *A Reconsideration of Nucleation Phenomena in Light of Recent Findings Concerning the Properties of Small Clusters, and a Brief Review of Some Other Particle Growth Processes*, *J. Astrophys. & Space Sci.*, **65** 337 (1979)
(b) A.W. Castleman, Jr., *J. Aerosol Sci.*, **10** 183-185 (1979)
- [6] R.G. Keesee, N. Lee, and A.W. Castleman, Jr., *J. Geophys. Res.*, **84** 3719 (1979)
- [7] N. Lee, R.G. Keesee, and A.W. Castleman, Jr., *On the Correlation of Total and Partial Enthalpies of Ion Solvation*, *J. Phys. Chem.* (submitted)
- [8] E. Hsieh and A.W. Castleman, Jr., *A Reconsideration of the Theory of Capture Cross Sections for Ion-Molecule Reactions and a Total Energy and Angular Momentum Conserved Average Charge-Dipole Interaction Theory*, *J. Chem. Phys.* (submitted)
- [9] E. Hsieh, A.W. Castleman, Jr., and B. Upschulte, *Ion-Molecule Capture Collisions: Molecular Dynamic Simulations of Two-Dimensional Charge-Dipole Collision Dynamics*, *J. Chem. Phys.* (submitted)
- [10] V. Hermann, B.D. Kay, and A.W. Castleman, Jr., *Evidence for Structures in Large Gas Phase Clusters Involving H₂O*, *J. Chem. Phys.* (submitted)
- [11] P.M. Holland and A.W. Castleman, Jr., *A Model for the Formation and Stabilization of Charged Water Clathrates*, *J. Chem. Phys.* (submitted)
- [12] J.Q. Searcy and J.B. Fenn, *J. Chem. Phys.*, **61** 5282 (1974)
- [13] R. Burke, private communications
- [14] J.W. Rabalais, et al., *J. Am. Chem. Soc.*, **101** 1951 (1979)
- [15] Dr. Eldon Ferguson (NOAA), private communications

Reprints Removed

TABLE I

RELATIVE ORDER OF A LIGAND BONDING TO NEGATIVE IONS

<u>Ligand</u>	<u>Negative Ions</u>			
H ₂ O	OH ⁻ > F ⁻ > O ₂ ⁻ > HCO ₃ ⁻ > NO ₂ ⁻ >	Cl ⁻ > NO ₃ ⁻ > CO ₃ ⁻ >	I ⁻	
SO ₂		NO ₂ ⁻ > SO ₂ ⁻ > Cl ⁻ >	SO ₃ ⁻	
CO ₂	O ₂ ⁻ >	NO ₂ ⁻ >	Cl ⁻ >	CO ₃ ⁻ > SO ₃ ⁻ > I ⁻

TABLE II

THERMODYNAMIC PROPERTIES OF NEGATIVE ION CLUSTERS
RECENTLY MEASURED IN OUR LABORATORY

$A^- B_n + B \xrightleftharpoons{M} A^- B_{n+1}$									
$-\Delta H^\circ_{n, n+1}$ (kcal/mole)						$-\Delta S^\circ_{n, n+1}$ (gibb/mole)			
Ligand	ion	(0,1)	(1,2)	(2,3)	(3,4)	(0,1)	(1,2)	(2,3)	(3,4)
H ₂ O	Cl ⁻	14.9	12.6	11.5	10.9	19.7	20.5	22.4	24.8
	I ⁻	11.1	9.9	9.3		19.3	20.3	21.0	
	CO ₃ ⁻	14.1	13.6	13.1		25.2	29.6	32.5	
	HCO ₃ ⁻	15.7	14.9	13.6	13.4	24.1	29.1	30.2	33.3
	NO ₂ ⁻	15.2	13.6	11.7	11.6	23.8	26.4	25.8	29.0
	NO ₃ ⁻	14.6	14.3	13.8		25.0	30.3	33.2	
CO ₂	Cl ⁻	8.0				19.6			
	I ⁻	5.6				18.2			
	CO ₃ ⁻	7.1				21.8			
	NO ₂ ⁻	9.3				24.2			
	SO ₃ ⁻	6.5				20.7			
SO ₂	Cl ⁻	21.8	12.3	10.0	8.6	23.2	22.7	23.1	23.2
	NO ₂ ⁻	25.9	9.0	6.6		36.8	16.8	13.4	
	SO ₂ ⁻	24.0				33.8			
	SO ₃ ⁻	13.3				18.9			
	I ⁻	12.9	10.1	9.2		20.2	21.6	24.7

FIG. 1

FIG. 2a

FIG. 2b

Trajectory for an Ion-Dipole
Capture Collision

FIG. 4a

Trajectory for a Non-Capture
Ion-Dipole Collision

FIG. 4b

FIG. 5