Equilibrium constants for clustering of neutral molecules about gaseous ions

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Equilibrium constants for clustering of neutral molecules about gaseous ions

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A study of the clustering of neutral molecules to gas-phase ions was made using mass spectrometry. Equilibrium constants and the associated standard Gibbs free energy changes were determined for the attachment of H_2O, SO_2, and CO_2 to a number of positive and negative ions. Mixed clusters were studied, as well as clusters containing only one type of ligand. A total of 49 constants were measured for ligand association and switching reactions; a further 21 new constants could be derived from thermodynamic cycles. Clustering of N_2 about hydrated positive and negative ions was observed, but no equilibrium constants were determined. The observed trends in the cluster stabilities are explained by consideration of the properties of the ions and molecules. The ions used were produced by a high pressure source using aqueous solutions. This technique extends considerably the range of ions that can be studied.

I. INTRODUCTION

The pioneering work in the measurement of gas-phase ion solvation and equilibria was made by Kebarle and his co-workers,[1,2] and they have continued vigorous research activity in this field. This branch of chemistry finds application in the atmosphere where ions are continually produced[3] and react and cluster with both abundant and trace gases.[4]

The ions present in the ionosphere and stratosphere have been mass analyzed,[5–10] and recently such measurements have been made in the troposphere.[11,12] As well, ions formed in various air-like gas mixtures at 1 atm have been investigated in laboratory experiments.[13–16] In all cases cluster ions, especially hydrated ions, were seen. Castleman and his associates,[17,18] and Fehsenfeld and Ferguson and co-workers[19,20] have made an investigation of the bonding of atmospherically important species to ions.

In this paper the clustering of H_2O, SO_2, CO_2, and N_2 has been investigated on a series of ions chosen either for their importance in the atmosphere, for general interest, or for facilitating comparison with results of other workers. Of special interest were clusters with two different types of molecules attached (mixed clusters). Two types of ion–molecule reactions were investigated:

association reactions $I + N + M \rightleftharpoons I \cdot N + M,$

and

switching reactions $I \cdot A + B \rightleftharpoons I \cdot B + A,$

where I is an ion, which may already be a cluster ion, N, A, and B are associating neutral molecules, and M is a third body. Equilibrium constants, K (expressed in terms of partial pressures, in atm), and their associated standard Gibbs free energies, ΔG°, were determined at room temperature.

A number of mixed clusters have already either been simply observed[21,22] or studied with respect to their thermodynamic properties.[19,23–26] The recent study by Upschulte *et al.*[26] has the closest relationship to the present work.

Recently there has been considerable interest in producing ions of nonvolatile or thermally labile compounds for

mass spectrometry. Suitable techniques are those in which ions are produced with thermal or near-thermal energy.[27,28] In the technique of atmospheric pressure ion evaporation mass spectrometry[29–32] ions are produced with thermal energy by evaporation from the surface of tiny, charged droplets (spray produced ions). In this paper a method is developed to use spray produced ions to measure equilibrium constants for mixed clusters. These ions are very stable at high pressure so there is the capability to study slow reactions, and reactions with some degree of endothermicity. The ions are produced in an atmosphere free of the parent neutral and excited species. Some ions which are difficult to produce by other means are easily obtained. The ion spectra as observed by mass spectrometry are usually very clean. This feature, coupled with a fairly strong overall signal, allows even relatively inabundant ion species to be seen.

Since the ions are produced at atmospheric pressure it is convenient to study the establishment of equilibrium at 0.1–1 atm, and to introduce the ions into the mass spectrometer in a viscous flow of buffer gas, followed by rapid expansion and quenching of the reactions. It is believed that the method developed here will be a valuable complement to other methods of measuring equilibrium constants for gas-phase ion–molecule reactions.

II. EXPERIMENTAL

A. Apparatus

The ions were equilibrated in an atmosphere of known composition (the controlled atmosphere) and then mass analyzed in a quadrupole mass spectrometer. The ion source and equilibration chambers are shown in Fig. 1.

As compressed air escaped through the needle, GI in Fig. 1, the ionic solution was drawn up from a reservoir through LI and blown out as a plume of droplets. When a potential (~ 2000 V) was applied to the electrode, IE, these droplets became highly charged by induction. Large droplets were removed by impaction in an elbow, E. As the remaining fine droplets evaporated the ions also "evaporated" (by field desorption). All solutions were made $\sim 10^{-3}$ M in distilled water. For negative ions the sodium salt was used as
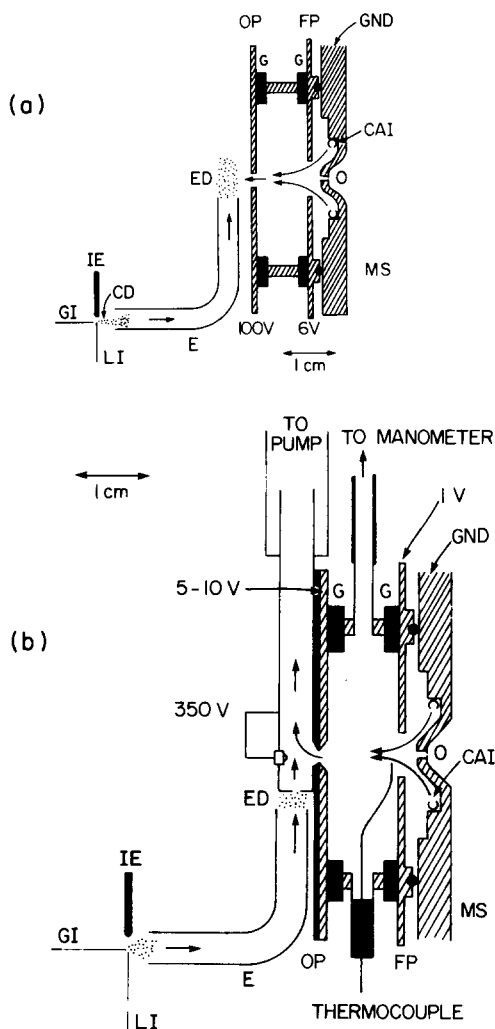
FIG. 1. The equilibration chambers used at (a) atmospheric pressure and (b) 0.06–0.3 atm showing also the sprayer and the interface to the mass spectrometer. CAI: controlled atmosphere inlet; OP, FP: outer and front plates; G: gasket; O: orifice forming the interface between regions of high and low pressure; MS: vacuum region of the mass spectrometer; GND: electrical ground; GI: gas inlet; LI: liquid inlet; IE: induction electrode; CD: spray of charged droplets; E: elbow; ED: evaporating droplets and ions.

against this flow into the chamber by the space charge of the spray (atmospheric pressure chamber) or by the potential applied to the tube (low pressure chamber). Once in the chamber a suitable field applied between OP and FP directed the ions toward the orifice. A rotary vacuum pump was used to lower the chamber pressure.

A representative circuit illustrating the preparation of the controlled atmosphere is shown in Fig. 2. The gas flows were controlled by mass flow controllers and a needle valve which were calibrated for the different gases used. The humidifier usually used consisted of 300 ml of distilled water through which the dry gas was bubbled. At very low flow rates the gas simply passed over the water surface. In either case the gas attained 100% relative humidity and the water vapor pressure in the equilibration chamber could be calculated from the pressures and the gas flow rate.

Both the nitrogen buffer and the nitrogen carrying the SO_2 were passed through a cold trap [dry ice and ethanol (96%)] to remove water vapor and other trace gases, especially those originating in the SO_2 arm. This trap decreased the contaminant concentration dramatically without affecting the passage of SO_2.

In spite of the fact that very clean, nonreactive materials were chosen for the gas preparation circuits (Teflon, Pyrex, stainless steel) there were some problems due to desorption of water vapor and adsorption of the reactive gases. The problem of water vapor desorption was dealt with by pumping down the system or by flushing with dry air. The amount of water vapor left after 45 min of pumping or 24 h of flushing was $< 10^{-6}$ atm. This was checked by running a standard ion spectrum, $Na^+ \cdot (H_2O)_n$, and comparing the observed hydrate distribution with the work of Kebarle.[33] The problem of adsorption of the reactive gases to the walls was solved by following the evolution of the ion spectrum in time after the addition of the reactive species. When no further changes were observed the concentration was considered equilibrated. Of the gases studied SO_2 was the slowest to equilibrate.
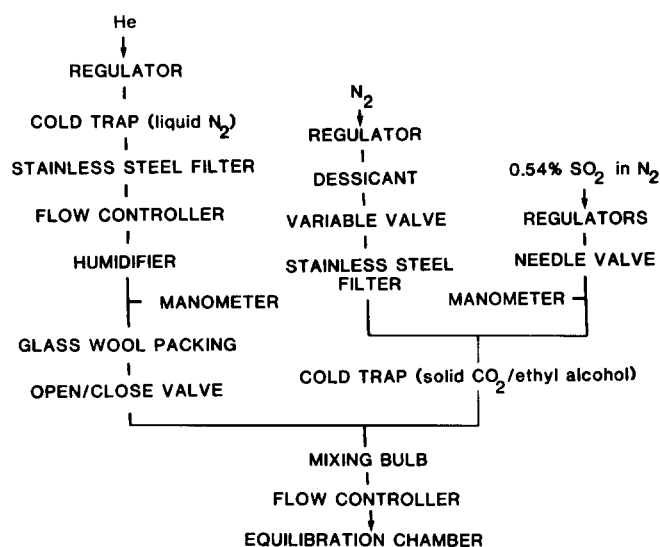
the solute (e.g., $NaClO_4$ for ClO_4^-), and for positive ions the chloride salt was used [e.g., $NH_3(CH_3)Cl$ for $NH_3(CH_3)^+$]. A positive potential applied to the electrode induced a negative charge on the droplets and vice versa.

The equilibration chambers were designed for use at different pressures: 1 and 0.06–0.3 atm. With the exception of the plate indicated by OP in Fig. 1(b), and the attached tube, which were brass, all metal parts were stainless steel. The sealing gaskets, G, were neoprene rubber.

The temperature of the gas in the chambers was the same as the surrounding metal surfaces, which was ambient temperature. The temperature was monitored with a thermocouple inserted in the chamber, or with a thermometer clamped nearby. The chamber pressure was measured with a mercury manometer.

The controlled atmosphere was introduced to the chambers through a circlet of small holes, CAI, surrounding the orifice of the mass spectrometer and exited through the opening in the outer plate, OP. The ions were directed

FIG. 2. Preparation of the controlled atmosphere for experiments involving both H_2O and SO_2.

Due to the long reactant equilibration times it was more convenient to change the identity of the ion being studied than the concentration of clustering neutral. Once the gas flow system was equilibrated, spectra were taken for all of the ions of interest. In general, at most two concentrations of clustering molecule could be run on one day. Thus, with few exceptions, the data used for each K determination were taken over several days.

A differentially pumped quadrupole mass spectrometer system developed by Thomson and Iribarne[30] was used to mass analyze the ions. A sample of the ions present in the reaction chamber was drawn into the vacuum region of the mass spectrometer in a viscous flow of the controlled atmosphere through the orifice, indicated by O in Fig. 1.

The ion counts were recorded through a pulse counting circuit. Ion masses could be scanned manually or automatically over any range from 0 to 520 amu. In the automatic mode the mass interval was swept repeatedly until a spectrum of sufficient intensity was obtained on a signal averager. At least 200 counts were accumulated for the smallest peaks of interest. The output from the signal averager was stored digitally on computer disk or tape and then analyzed using a package of highly interactive programs.

For association reactions the ion intensity ratio

$$R = [\text{I} \cdot \text{N}]/[\text{I}]$$

was determined for a number of different pressures of neutral reactant molecules, p_N. If an equilibrium distribution was sampled and detected without distortion, a plot of R vs

TABLE I. Conditions used in the equilibration chambers

Pressure (atm)	Gas flow (ℓ/min)	Buffer gas	Electric field (V/cm)
1	0.6	N_2 or He	75
~0.2	0.8	N_2	75
		He	5

p_N would yield a straight line with slope K passing through the origin. For each association reaction studied the equilibrium constant was found by doing a weighted least squares fit to this data. The fit was to a line constrained to pass through the origin. For switching reactions the equilibrium constant was found by taking a weighted average of the individual K's calculated for each p_A, p_B used.

B. Conditions for equilibrium of the ion distribution

The intensity distribution among ions which are in equilibrium should be affected only by the pressure of the clustering molecules and by the temperature. As is well known, the ion distribution can be changed by many experimental variables which affect the establishment of equilibrium, the maintenance of the equilibrium distribution, and the mass dependent detection efficiency.[2,34] These variables were investigated so that the proper conditions could be chosen for the experiment.

The conditions used in the equilibration chambers are given in Table I. The flow were sufficient to completely flush the chambers, and the fields were low enough that the ions

TABLE II. Equilibrium constants measured for the clustering of H_2O.

	T(K)[a]	p(atm)[b]	K(atm^{-1})	$-\Delta G^0$(kJ/mol)[c]	K_L(atm^{-1})[d]
$NH_4^+ \cdot (H_2O)_n + H_2O \overset{M}{\rightleftharpoons} NH_4^+ \cdot (H_2O)_{n+1}$					
$n = 1$, M = He	298	0.20	$(2.8 \pm 0.2) \times 10^6$	36.8 ± 0.2	$1.0(0.7–1.4) \times 10^{6\,e}$
$n = 2$, M = He or N_2	299	0.26	$(4.5 \pm 0.2) \times 10^4$	26.6 ± 0.1	$2(1–3) \times 10^{4\,e,o}$
M = N_2	300	0.1–0.3	$(6.0 \pm 0.2) \times 10^4$	27.44 ± 0.08	
$n = 3$, M = N_2	299	0.32	$(4.5 \pm 0.2) \times 10^3$	20.9 ± 0.1	$9(5–20) \times 10^{2\,e}, 7 \times 10^{2\,o}$
M = N_2	300	0.1–0.3	$(4.4 \pm 0.2) \times 10^3$	20.9 ± 0.1	
$NH_3(CH_3)^+ \cdot (H_2O)_n + H_2O \overset{He}{\rightleftharpoons} NH_3(CH_3)^+ \cdot (H_2O)_{n+1}$					
$n = 0$	298	0.18	$(7.1 \pm 0.6) \times 10^7$	44.8 ± 0.2	$1.1(0.6–2.3) \times 10^{8\,f,o}$
$n = 1$	299	0.20	$(3.1 \pm 0.1) \times 10^5$	31.43 ± 0.08	$7(4–13) \times 10^{4\,f,o}$
$n = 2$	299	0.20	$(6.1 \pm 0.2) \times 10^3$	21.67 ± 0.08	$1.9(0.3–12) \times 10^{3\,f,o}$
$NH_2(CH_3)_2^+ \cdot (H_2O)_n + H_2O \overset{He}{\rightleftharpoons} NH_2(CH_3)_2^+ \cdot (H_2O)_{n+1}$					
$n = 0$	298	0.20	$(4.4 \pm 0.1) \times 10^6$	37.90 ± 0.06	$3 \times 10^{6\,o}$
$n = 1$	299	0.20	$(3.5 \pm 0.1) \times 10^4$	26.00 ± 0.07	$3 \times 10^{4\,o}$
$n = 2$	299	0.20	$(1.13 \pm 0.05) \times 10^3$	17.5 ± 0.1	$500^{\,o}$
$NH(CH_3)_3^+ \cdot (H_2O)_n + H_2O \overset{He}{\rightleftharpoons} NH(CH_3)_3^+ \cdot (H_2O)_{n+1}$					
$n = 0$	299	0.20	$(3.7 \pm 0.2) \times 10^5$	31.9 ± 0.1	$4 \times 10^{5\,o}$
$n = 1$	299	0.20	$(1.32 \pm 0.06) \times 10^3$	17.9 ± 0.1	$600^{\,o}$
$n = 2$	300	0.26	$(2.9 \pm 0.2) \times 10^2$	14.1 ± 0.2	$50^{\,o}$
$N(CH_3)_4^+ + H_2O \overset{He}{\rightleftharpoons} N(CH_3)_4^+ \cdot H_2O$					
	299	0.20	$(2.52 \pm 0.09) \times 10^2$	13.76 ± 0.09	

TABLE II (*continued*).

	T(K)[a]	p(atm)[b]	K (atm^{-1})	$-\Delta G^0$(kJ/mol)[c]	K_L (atm^{-1})[d]
$Na^+(H_2O)_3 + H_2O \overset{He}{\rightleftharpoons} Na^+ \cdot (H_2O)_4$					$5 \times 10^{4\,g}$
	298	0.27	$(3.7 \pm 0.2) \times 10^4$	26.1 ± 0.1	$2 \times 10^{4\,h}$ $10^{4\,i}$ $(3 \pm 1) \times 10^{4\,j}$
$Cs^+ \cdot (H_2O)_n + H_2O \overset{N_2}{\rightleftharpoons} Cs^+ \cdot (H_2O)_{n+1}$					
$n = 1$	299	0.30	$(2.4 \pm 0.1) \times 10^4$	25.1 ± 0.1	$2 \times 10^{4\,g}, 4 \times 10^{4\,P}$
$n = 2$	299	0.30	$(3.4 \pm 0.1) \times 10^3$	20.20 ± 0.07	$10^{3\,g}, 3 \times 10^{3\,P}$
$Cs^+ \cdot H_2O \cdot SO_2 + H_2O \overset{N_2}{\rightleftharpoons} Cs^+ \cdot (H_2O)_2 \cdot SO_2$					
	299	0.32	$(7.5 \pm 0.8) \times 10^3$	22.2 ± 0.3	
$NH_4^+ \cdot (H_2O)_2 \cdot SO_2 + H_2O \overset{N_2}{\rightleftharpoons} NH_4^+ \cdot (H_2O)_3 \cdot SO_2$					
	299	0.31	$(6.9 \pm 0.6) \times 10^3$	22.0 ± 0.2	
$I^- \cdot (H_2O)_n + H_2O \overset{He}{\rightleftharpoons} I^- \cdot (H_2O)_{n+1}$					
$n = 0$	300	0.24	$(7.0 \pm 0.3) \times 10^3$	22.1 ± 0.1	$7 \times 10^{3\,k}$ $7(6-9) \times 10^{3\,l}$
$n = 1$	300	0.24	$(9.3 \pm 0.4) \times 10^2$	17.0 ± 0.1	$10^{3\,k}$ $6(4-9) \times 10^{2\,l}$
$I^- \cdot SO_2 + H_2O \overset{He}{\rightleftharpoons} I^- \cdot SO_2 \cdot H_2O$					
	300	0.24	$(3.54 \pm 0.05) \times 10^2$	14.64 ± 0.04	
$NO_3^- \cdot H_2O + H_2O \overset{He}{\rightleftharpoons} NO_3^- \cdot (H_2O)_2$					
	301	0.25	$(6.4 \pm 0.5) \times 10^3$	21.9 ± 0.2	$5 \times 10^{3\,m}$ $6(4-9) \times 10^{3\,n}$
$NO_3^- \cdot SO_2 + H_2O \overset{He}{\rightleftharpoons} NO_3^- \cdot SO_2 \cdot H_2O$					
	301	0.25	$(1.33 \pm 0.06) \times 10^3$	18.0 ± 0.1	

[a] The temperature given is an average value for the different data points. The temperature deviation over a data set may be as large as ± 1 K.

[b] The pressure given is a representative pressure at which K was determined. The pressure deviation may be as large as ± 0.05 atm.

[c] Calculated from $\Delta G^0 = -RT \ln K$, where T and K are as given in the Table.

[d] Values taken from the literature, and calculated at the temperatures given in column one. The limits of error for these K's are given in the brackets, or if not shown, are a factor of 2.

[e] Reference 23.
[f] Reference 35.
[g] Reference 36.
[h] Reference 37.
[i] Reference 38.
[j] Reference 39.

[k] Reference 40.
[l] Reference 41.
[m] Reference 19.
[n] Reference 42.
[o] Reference 62.
[p] Reference 63. Error a factor of 3.

were always kept at thermal energy. Experimental evidence was obtained that indicated there was no ion loss in the equilibration chamber due to diffusion.

As the ion distribution was sampled into the vacuum of the mass spectrometer there existed the possibility that it would be distorted by mass dependent ion losses due to diffusion to the walls of the chamber and/or association, stripping or unimolecular dissociation reactions during the expansion from high to low pressure. The detailed behavior of the ions during the sampling was dependent on the carrier gas, the pressure, the orifice diameter and thickness, and the electric field in the vicinity of the orifice. The influence of these factors on several clustering reactions was studied: He

and N_2 were used as carrier gases; pressures of 0.06–1 atm were used; orifice diameters of 10–100 μm and thicknesses of 2.5–25 μm were tried; the electric field in the expansion region ranged from 0–20 V/cm. The conditions chosen for the determination of the equilibrium constants were 0.06–0.3 atm and a 50 μm diam orifice, or 1 atm and an orifice 25 μm or less in diameter. Under these conditions the results were independent of buffer gas or orifice thickness. The electric field chosen was 1 V/cm. At lower fields diffusional loss of the lighter ions was seen; at the higher fields ligand stripping was evident.

The quadrupole control and counting circuit parameters were set to values which either minimized or eliminated

mass discrimination. The largest influence on mass discrimination was made by the quadrupole resolution controls. To estimate the degree of mass discrimination remaining at the chosen operating resolution, sequential spectra were taken for which only one peak was found: I^- or $I^- \cdot SO_2$. The integrated counts in each case were the same within 7%. Thus any residual mass discrimination was small.

Many possible sources of error in the peak intensities were eliminated in the studies just described. As well the possibility of effects due to instrumental drifting was eliminated. The error bars which are shown on the graphs in the next section include, for the error in the ion intensity ratio, the statistical error in the counts and any uncertainty in the background subtraction and, for the error in the pressure of the clustering neutral, the uncertainty in the determination of the concentration.

III. RESULTS

A. Measurements of equilibrium constants

1. Association of H₂O

Equilibrium constants were determined for the association of a water molecule to a number of different ions. The clustering reactions, experimental conditions, and measured equilibrium constants are given in Table II. Also shown, for comparison, are results from other laboratories. Typical spectra obtained in this study for the addition of a water molecule are shown in Fig. 3. From spectra such as these the ion intensity ratios could be determined. A plot of the ion
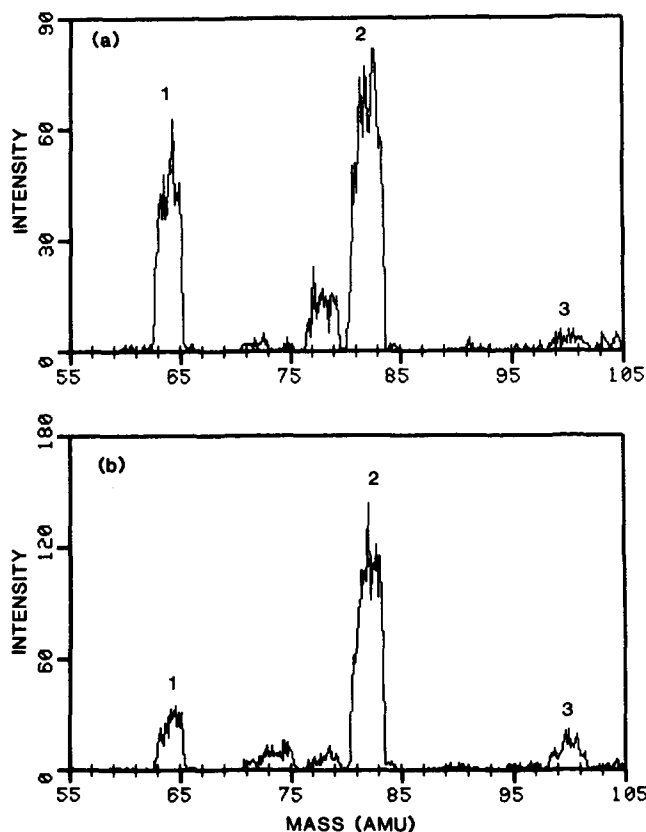
intensity ratios as a function of the water vapor pressure for $NH_2(CH_3)_2^+ \cdot (H_2O)_{1 \to 2}$ is shown in Fig. 4. As discussed before, the slope of the line fitted to the data points yields the equilibrium constant.

In the determination of K for the addition of the first water molecule to $NH_3(CH_3)^+$ a spectrum run at $p_{H_2O} = 1.4 \times 10^{-5}$ atm gave a limiting value of $K > 3.3 \times 10^7$ atm^{-1}. A second spectrum, run at $p_{H_2O} = 3.6 \times 10^{-6}$ atm (the lowest H_2O pressure that was reliable), required 5 h of accumulated counts to obtain adequate statistics. Thus for practical reasons this was the only spectrum used to determine the value.

2. Association of SO₂

The equilibrium constants determined for the addition of a SO_2 molecule to the ions studied are given in Table III. The clustering of SO_2 to $I^- \cdot H_2O$ and to ClO_4^- were studied at only one SO_2 concentration. Thus the K for the formation of $ClO_4^- \cdot SO_2$ must be considered tentative. However as will be discussed later there is additional evidence to support the value obtained for $I^- \cdot H_2O \cdot SO_2$.

The influence of SO_2 on spectra in which the core ions were Br^-, Cl^-, or F^- was studied. The addition of 9×10^{-7} atm of SO_2, the smallest reliable concentration, was sufficient to transform the spectra so that the dominant ions became $Br^- \cdot SO_2$, $Cl^- \cdot SO_2$, and $F^- \cdot SO_2$. The hydrates of these ions were not present in the spectra of Br^- or Cl^-. It was possible to calculate a limit for K for the attachment of SO_2 to Br^- and Cl^-, but not to F^- because the bare ion was not seen.

Typical spectra and data plots obtained in this study are shown in Figs. 5 and 6.

3. Association of CO₂

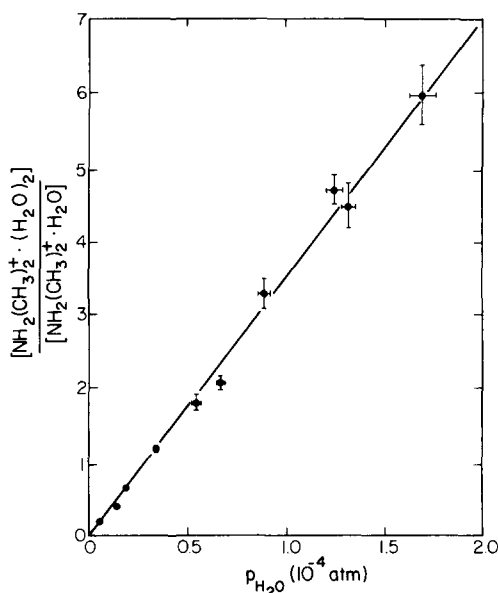The equilibrium constants determined for the association of a CO_2 molecule to a number of different ions are

FIG. 3. Spectra of $NH_2(CH_3)_2^+ \cdot (H_2O)_n$ aged in a controlled atmosphere containing (a) 5.4×10^{-5} atm H_2O; (b) 1.2×10^{-4} atm H_2O. The values of n are indicated in the spectra.

FIG. 4. Ion intensity ratios plotted as a function of water vapor pressure for the reaction $NH_2(CH_3)_2^+ \cdot H_2O + H_2O \overset{He}{\rightleftarrows} NH_2(CH_3)_2^+ \cdot (H_2O)_2$.

TABLE III. Equilibrium constants measured for the clustering of SO_2.

	$T(K)$[a]	p(atm)[b]	K (atm^{-1})	$-\Delta G^0$(kJ/mol)[c]
$I^- \cdot (H_2O)_n + SO_2 \overset{M}{\rightleftharpoons} I^- \cdot (H_2O)_n \cdot SO_2$				
$n=0$, M = He, N_2, or air	301 ± 2	0.2–1	$(3.2 \pm 0.2) \times 10^6$[d]	37.5 ± 0.2
$n=1$, M = He	300	0.24	$(1.4 \pm 0.1) \times 10^5$	29.6 ± 0.2
$Br^- + SO_2 \overset{He}{\rightleftharpoons} Br^- \cdot SO_2$	300	0.25	$>4 \times 10^9$	>55
$Cl^- + SO_2 \overset{He}{\rightleftharpoons} Cl^- \cdot SO_2$	300	0.25	$>2.6 \times 10^9$[e]	>54
$NO_3^- + SO_2 \overset{He}{\rightleftharpoons} NO_3^- \cdot SO_2$	299	0.21	$(2.1 \pm 0.1) \times 10^7$[f]	41.9 ± 0.1
$ClO_4^- + SO_2 \overset{air}{\rightleftharpoons} ClO_4^- \cdot SO_2$	298	1	$(1.4 \pm 0.2) \times 10^4$ (tentative)	23.7 ± 0.4
$NH_4^+ \cdot (H_2O)_n + SO_2 \overset{N_2}{\rightleftharpoons} NH_4^+ \cdot (H_2O)_n \cdot SO_2$				
$n=1$	300	0.24	$(4.4 \pm 0.3) \times 10^4$	26.7 ± 0.2
$n=2$	300	0.26	$(4.5 \pm 0.3) \times 10^3$	21.0 ± 0.2
$n=3$	299	0.31	$(4.3 \pm 0.5) \times 10^2$	15.1 ± 0.3
$Cs^+ \cdot (H_2O)_n + SO_2 \overset{N_2}{\rightleftharpoons} Cs^+ \cdot (H_2O)_n \cdot SO_2$				
$n=0$	300	0.24	$(6.3 \pm 0.3) \times 10^3$[g]	21.8 ± 0.1
$n=1$	300	0.26	$(1.27 \pm 0.08) \times 10^3$	17.8 ± 0.2
$n=2$	299	0.32	$(3.8 \pm 0.2) \times 10^2$	14.8 ± 0.2
$H_3O^+ \cdot (H_2O)_n + SO_2 \overset{N_2}{\rightleftharpoons} H_3O^+ \cdot (H_2O)_n \cdot SO_2$				
$n=3$	300	0.24	$(1.17 \pm 0.07) \times 10^3$	17.6 ± 0.2
$n=4$	300	0.24	85 (factor of 2)	11 ± 4
$Na^+ \cdot (H_2O)_3 + SO_2 \overset{N_2}{\rightleftharpoons} Na^+ \cdot (H_2O)_3 \cdot SO_2$				
	300	0.24	$(3.1 \pm 0.1) \times 10^3$	20.05 ± 0.08

[a] The temperature given is an average value for the different data points. The temperature deviation over a data set may be as large as ± 1 K.
[b] The pressure given is a representative pressure at which K was determined. The pressure deviation may be as large as ± 0.05 atm.
[c] Calculated from $\Delta G^0 = -RT \ln K$, where T and K are as given in the Table.
[d] Compare with a K at 301 K of $(9 \pm 2) \times 10^4$ atm^{-1} (Ref. 43).
[e] Compare with a K at 300 K of $7(4-10) \times 10^{10}$ atm^{-1} (Ref. 43) and 8.3×10^{10} atm^{-1} (Ref. 20). The numbers in brackets give the limits of error.
[f] Compare with a K at 300 K of 10^7 atm^{-1} (Ref. 20) and 2×10^6 atm^{-1} (Ref. 44).
[g] Compare with a K at 300 K of $7 \times 10^3 (\pm \times 4)$ atm^{-1} (Ref. 63).

summarized in Table IV. As an example, spectra illustrating the clustering of CO_2 to NO_3^- are given in Fig. 7. The ions $NO_3^- \cdot CO_2$ appear at mass 106, and there is also a peak at 108 due to $NO_3^- \cdot H_2O \cdot N_2$. At the low resolution used to minimize mass discrimination these peaks are unresolved. The fraction of the doublet due to $NO_3^- \cdot CO_2$ was determined at higher resolution, and applied to the low resolution doublet intensity. The ion intensity ratios are plotted in Fig. 8.

Carbon dioxide was observed to cluster to $NO_3^- \cdot H_2O$ and to $Na^+ \cdot (H_2O)_3$, but K's could not be determined because the data do not show the proper relationship between the intensity ratios and p_{CO_2} for equilibrium.

4. Switching reactions

For experiments which were run at known concentrations of both H_2O and SO_2 it was possible to calculate equilibrium constants for ligand switching reactions. These K's,

and other relevant data, are summarized in Table V.

The negative ion reactions involve the switching of a SO_2 molecule for a H_2O molecule in $I^- \cdot (H_2O)_{1,2}$ and $NO_3^- \cdot (H_2O)_{1,2}$. All of the data used to determine these constants were taken at $p_{SO_2} \sim 9 \times 10^{-6}$ atm. The individual values for the constants are shown in Fig. 9 as a function of the water vapor pressure used. The lines show the weighted average of the K's.

Equilibrium constants were measured for the switching of a SO_2 molecule for a H_2O molecule for the positive ions $NH_4^+ \cdot (H_2O)_3$ and $Cs^+ \cdot (H_2O)_{2,3}$. The data are shown in Fig. 10. In this data set both p_{H_2O} and p_{SO_2} were varied.

B. Application of measured K's to thermodynamic cycles

Transitions between the different ions of the families of cluster ions are summarized in Figs. 11–14 for the core ions NH_4^+, Cs^+, Na^+, H_3O^+, NO_3^-, and I^-. The transitions for
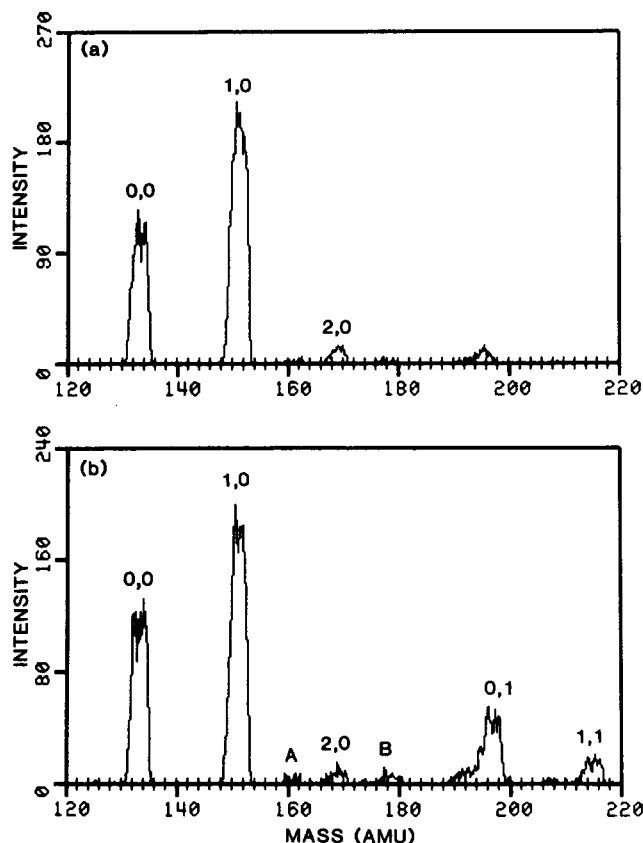
FIG. 5. Spectra of $Cs^+ \cdot (H_2O)_m \cdot (SO_2)_n$ aged in a controlled atmosphere containing (a) no SO_2; (b) 7×10^{-5} atm SO_2. The values of m, n are indicated in the spectra. The peaks labeled A, B are $Cs^+ \cdot N_2 \cdot (H_2O)_{0,1}$.

which equilibrium constants have been measured in this study are indicated by solid arrows.

Since the sum of the ΔG^0 values around any closed loop must be zero, cycles for which all ΔG^0 values were known could be used as a check on the internal consistency of the results, and loops for which all but one ΔG^0 value were known could be used to calculate the unknown value.

FIG. 6. Ion intensity ratios plotted as a function of SO_2 partial pressure for the reaction $Cs^+ \cdot H_2O + SO_2 \overset{N_2}{\rightleftharpoons} Cs^+ \cdot H_2O \cdot SO_2$.

The cycles summed for internal consistency gave good results. The largest error in ΔG^0 indicated was ~ 0.3 kJ/mol for $I^- \cdot (SO_2)_{0 \to 1}$.

The ΔG^0 values which could be calculated are indicated in the figures by dashed arrows. Fifteen such values could be found from K's measured in this experiment. They are summarized in Table VI. With the introduction of the ΔG^0 values from the literature for the following reactions:

$$Cs^+ + H_2O \overset{M}{\rightleftharpoons} Cs^+ \cdot H_2O,$$

$$\Delta G^0 = -34.2 \text{ kJ mol}^{-1} \text{ (Ref. 45)},$$

and

$$H_3O^+ \cdot (H_2O)_3 + H_2O \overset{M}{\rightleftharpoons} H_3O^+ \cdot (H_2O)_4,$$

$$\Delta G^0 = -23.4 \text{ kJ mol}^{-1} \text{ (Ref. 46)},$$

shown in Figs. 12 and 13 by dotted arrows, a further six K's could be determined. They are summarized in Table VII.

TABLE IV. Equilibrium constants measured for the clustering of CO_2.

	$T(K)^a$	K (atm^{-1})	$-\Delta G^0$(kJ/mol)^b
$I^- + CO_2 \overset{He}{\rightleftharpoons} I^- \cdot CO_2$	298	3.8 ± 0.2^c	3.3 ± 0.1
$NO_3^- + CO_2 \overset{He}{\rightleftharpoons} NO_3^- \cdot CO_2$	298	91 ± 3	11.18 ± 0.08
$Cs^+ \cdot (H_2O)_n + CO_2 \overset{He}{\rightleftharpoons} Cs^+ \cdot (H_2O)_n \cdot CO_2$			
$n = 0$	301	55 ± 2^d	10.03 ± 0.09
$n = 1$	301	7.0 ± 0.4	4.9 ± 0.1
$NH_4^+ \cdot (H_2O)_2 + CO_2 \overset{He}{\rightleftharpoons} NH_4^+ \cdot (H_2O)_2 \cdot CO_2$	299	8.4 ± 0.4	5.3 ± 0.1
$H_3O^+ \cdot (H_2O)_3 + CO_2 \overset{He}{\rightleftharpoons} H_3O^+ \cdot (H_2O)_3 \cdot CO_2$	300	<26	<8

^{a} The temperature given is an average value for the different data points. The temperature deviation over a data set may be as large as ± 1 K. The buffer gas pressure was (0.25 ± 0.05) atm.
^{b} Calculated from $\Delta G^0 = -RT \ln K$, where T and K are as given in the Table.
^{c} Compare with a K at 298 K of (1.4 ± 0.3) atm^{-1} (Ref. 43).
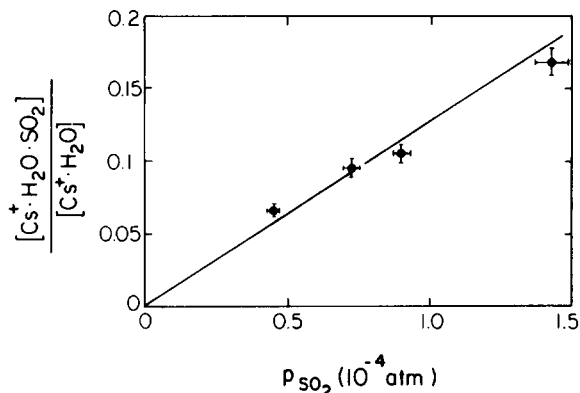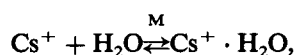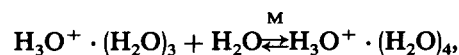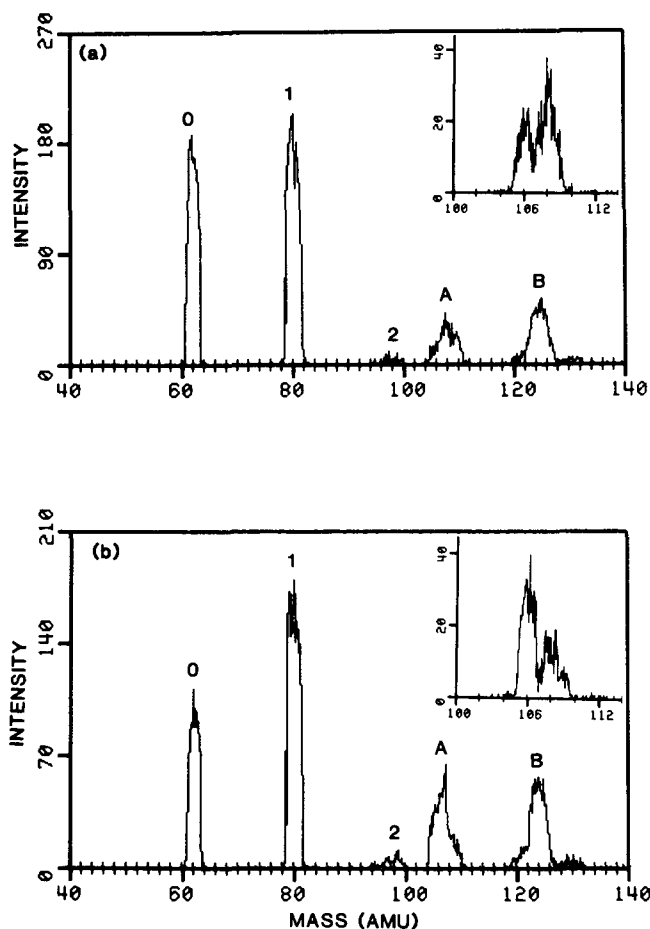^{d} Compare with a K at 301 K of 20 $(\pm \times 3)$ atm^{-1} (Ref. 63).

FIG. 7. Spectra of $NO_3^- \cdot (H_2O)_n$ aged in a controlled atmosphere containing (a) 1.36×10^{-3} atm CO_2, (b) 5.4×10^{-3} atm CO_2. The values of n are indicated in the spectra. The peak indicated by A is the unresolved doublet $NO_3^- \cdot CO_2$ and $NO_3^- \cdot H_2O \cdot N_2$. This doublet is shown resolved in the insets. The peak indicated by B could be $NO_3^- \cdot H_2O \cdot CO_2$. The increased hydration in (b) reflects the fact that the CO_2 was not dried.
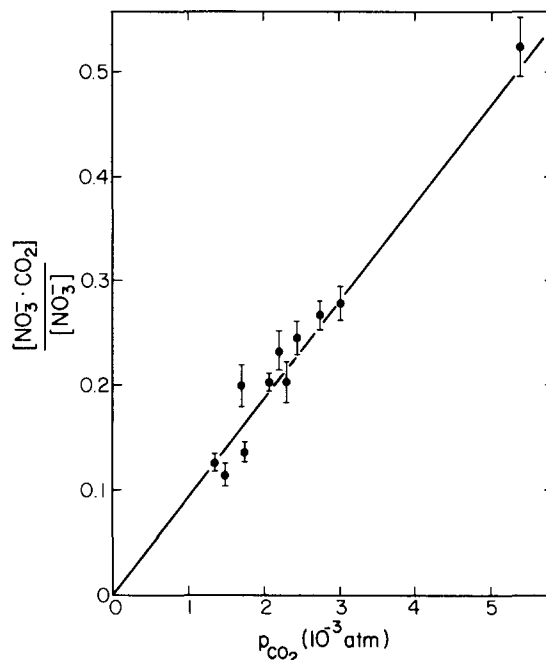
FIG. 8. Ion intensity ratios plotted as a function of CO_2 partial pressure for the reaction $NO_3^- + CO_2 \overset{He}{\rightleftharpoons} NO_3^- \cdot CO_2$.

C. Other observations of clustering

Nitrogen was observed to cluster with ClO_4^-, $OH^- \cdot CO_2 \cdot H_2O$, $I^- \cdot (H_2O)_{0,1}$, $Br^- \cdot (H_2O)_{0,1,2}$, $NO_3^- \cdot (H_2O)_{0,1}$, $Cl^- \cdot (H_2O)_{1,2}$, $OH^- \cdot (H_2O)_{1,2}$, $Cs^+ \cdot (H_2O)_{0,1}$, $NH_4^+ \cdot (H_2O)_{1,2}$, $Na^+ \cdot (H_2O)_{2,3}$, and $H_3O^+ \cdot (H_2O)_{3,4}$. The association of N_2 with $Br^- \cdot (H_2O)_n$ and $Cs^+ \cdot (H_2O)_n$ is clearly seen in Fig. 15. The spectra show ions which have been aged in dry air in the atmospheric pressure chamber with an applied ΔV of 100 V.

TABLE V. Equilibrium constants measured for the switching of SO_2 for H_2O.

	T(K) (± 1 K)	Buffer gas	p(atm) (± 0.05 atm)	K	ΔG^0(kJ/mol)[a]
$I^- \cdot (H_2O)_n + SO_2 \rightleftharpoons I^- \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$					
$n = 1$	300	He	0.25	$(3.9 \pm 0.1) \times 10^2$	-14.88 ± 0.06
$n = 2$	300	He	0.25	$(1.43 \pm 0.07) \times 10^2$	-12.4 ± 0.1
$NO_3^- \cdot (H_2O)_n + SO_2 \rightleftharpoons NO_3^- \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$					
$n = 1$	301	He	0.25	$(1.0 \pm 0.1) \times 10^{2}$ [b]	-11.5 ± 0.3
$n = 2$	301	He	0.25	20 ± 2	-7.5 ± 0.3
$NH_4^+ \cdot (H_2O)_3 + SO_2 \rightleftharpoons NH_4^+ \cdot (H_2O)_2 \cdot SO_2 + H_2O$					
	299	N_2	0.32	$(7.7 \pm 0.2) \times 10^{-2}$	6.37 ± 0.06
$Cs^+ \cdot (H_2O)_n + SO_2 \rightleftharpoons Cs^+ \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$					
$n = 2$	299	N_2	0.32	$(5.6 \pm 0.1) \times 10^{-2}$	7.16 ± 0.04
$n = 3$	299	N_2	0.32	$(1.15 \pm 0.07) \times 10^{-1}$	5.4 ± 0.2

[a] Calculated from $\Delta G^0 = -RT \ln K$, where T and K are as given in the Table.
[b] Compare with a K at 300 K of 67 (Ref. 20) and with a K at 296 K of 300 (Ref. 19). The error in the latter value is a factor of 2.
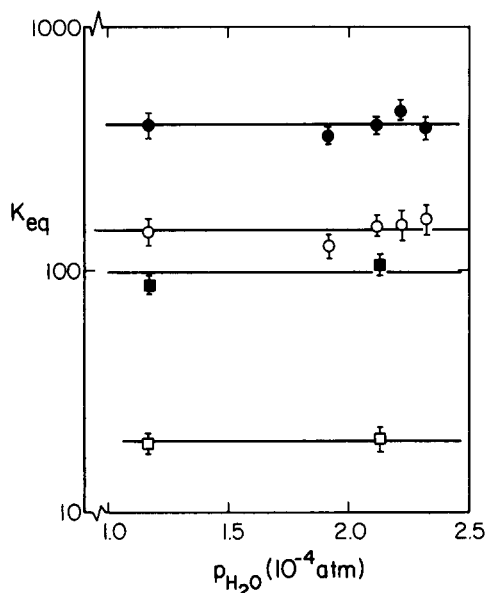
FIG. 9. Equilibrium constants for the ligand switching reactions $I^- \cdot (H_2O)_n + SO_2 \rightleftharpoons I^- \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$ for $n = 1$●, $n = 2$○, and $NO_3^- \cdot (H_2O)_n + SO_2 \rightleftharpoons NO_3^- \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$ for $n = 1$■, $n = 2$□.

An investigation of the effect of the electric field in the equilibration chamber on N_2 clustering was made. As the field was increased (e.g., to 1000 V/cm) the degree of N_2 clustering decreased.

For some solutions peaks corresponding in mass to the ion clustered with its salt could be seen. The clusters $I^- \cdot NaI$, $Cl^- \cdot NaCl$, $ClO_4^- \cdot NaClO_4$, and $NO_3^- \cdot NaNO_3$ were observed.

IV. DISCUSSION

A. Clustering of H_2O, SO_2, and CO_2

1. The equilibrium constants: An overview

The equilibrium constants determined for the association of H_2O to ions other than the $NH_m(CH_3)_n^+$ are sum-
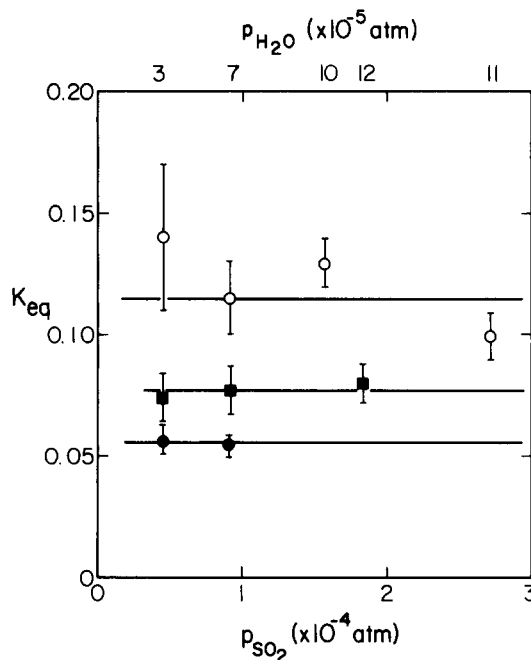
FIG. 10. Equilibrium constants for the ligand switching reactions $Cs^+ \cdot (H_2O)_n + SO_2 \rightleftharpoons Cs^+ \cdot (H_2O)_{n-1} \cdot SO_2 + H_2O$ for $n = 2$●, $n = 3$○, and $NH_4^+ \cdot (H_2O)_3 + SO_2 \rightleftharpoons NH_4^+ \cdot (H_2O)_2 \cdot SO_2 + H_2O$■. The water vapor partial pressures used for the different sets of data points are shown across the top of the figure.

marized in Fig. 16. Inspection of Fig. 16 reveals some interesting features. The equilibrium constants for the association of H_2O to all the ions studied decrease in a regular way as the degree of hydration of the ions is increased. If the positive ions with x ligands are considered, there is enhanced attachment of the next water molecule if one of the ligands is CO_2 or SO_2. For negative ions decreased attachment of H_2O is seen if the first ligand is SO_2.

The equilibrium constants determined for the association of SO_2 are summarized in Fig. 17. There is a regular decrease in the equilibrium constants for SO_2 addition as the
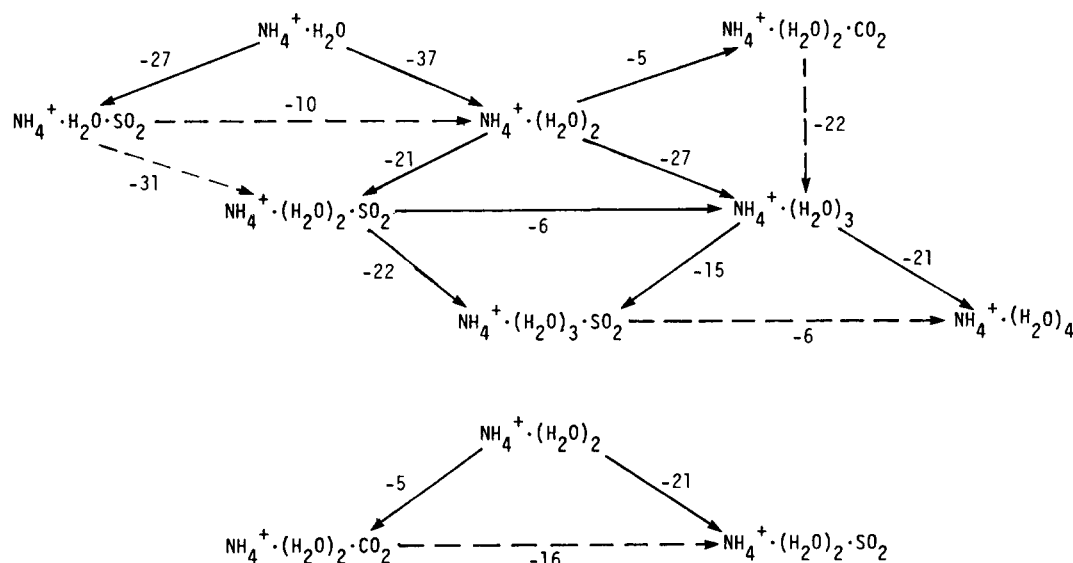

FIG. 11. Summary of reactions involving NH_4^+, H_2O, SO_2, and CO_2 for which K and ΔG^0 were measured (—) and derived (---). The values of ΔG^0 in kJ/mol are shown.
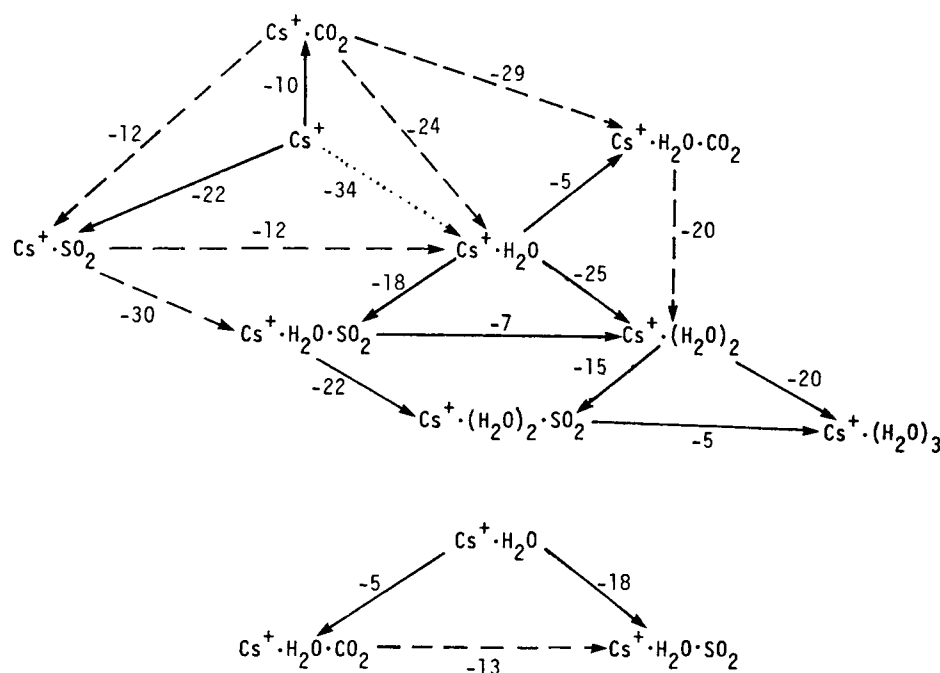
FIG. 12. Summary of reactions involving Cs^+, H_2O, SO_2, and CO_2 for which K and ΔG° were measured (—) and derived (---). The values of ΔG° in kJ/mol are shown. The ΔG° indicated by (· · ·) was taken from Ref. 45.

hydration of the ions is increased. Comparison of Figs. 16 and 17 leads to the observation that the stability of attachment of H_2O and SO_2 for different ions is $Na^+ > NH_4^+ > Cs^+$, $NO_3^- > I^- > ClO_4^-$, with H_2O more stable on the positive ions and SO_2 more stable on the negative ions.

This difference in stability is clearly illustrated in Fig. 18 where the K's for the exchange of H_2O for SO_2 are summarized. As the degree of hydration of the ion cluster increases, the K's for switching of SO_2 for H_2O on negative ions and H_2O for SO_2 on positive ions decrease, and the K's for switching of H_2O and SO_2 for all positive ions approach the

same value.

The displacement of H_2O by SO_2 in $Cl^- \cdot (H_2O)_{1,2}$ and $NO_2^- \cdot H_2O$ was seen by Fehsenfeld and Ferguson.[19] They also observed that the more hydrated ion $[Cl^- \cdot (H_2O)_2]$ showed a smaller preference for SO_2. Upschulte et al.[26] ob-
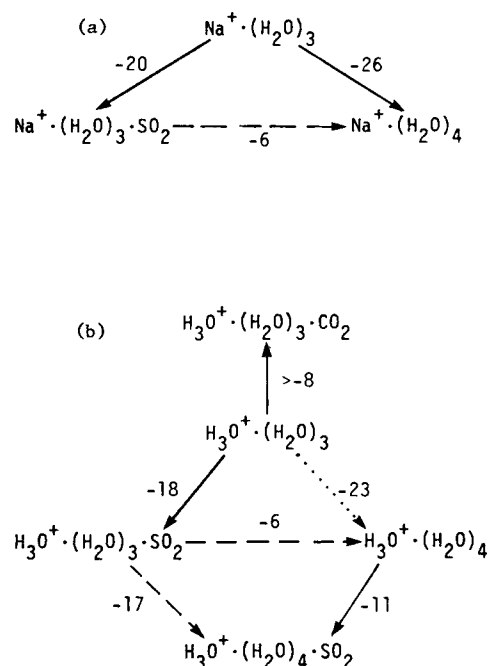

FIG. 13. Summary of reactions involving H_2O, CO_2, and (a) Na^+, (b) H_3O^+ for which K and ΔG° were measured (—) and derived (---). The values of ΔG° in kJ/mol are shown. The ΔG° indicated by (· · ·) was taken from Ref. 46.
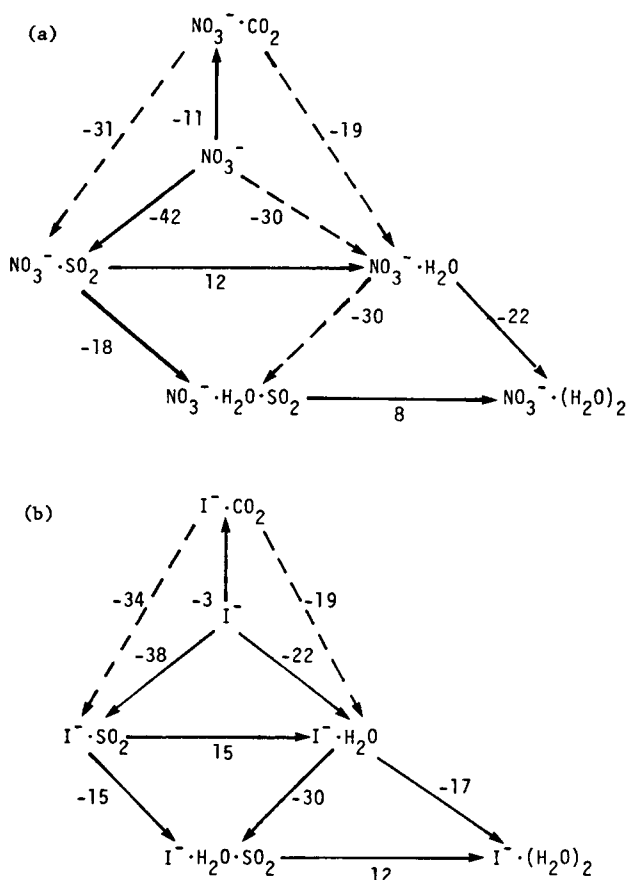
FIG. 14. Summary of reactions involving H_2O, SO_2, CO_2, and (a) NO_3^-, (b) I^- for which K and ΔG° were measured (—) and derived (---). The values of ΔG° in kJ/mol are shown.

TABLE VI. ΔG^0 and K values derived from thermodynamic cycles for which all ΔG^{0}'s were measured in this work.

	T(K) (± 1 K)	$-\Delta G^0$(kJ/mol)	K
$NH_4^+ \cdot (H_2O)_2 \cdot CO_2 + H_2O \rightleftharpoons NH_4^+ \cdot (H_2O)_3 + CO_2$	299	22.2 ± 0.1	$(7.4 \pm 0.4) \times 10^3$
$NH_4^+ \cdot (H_2O)_2 \cdot CO_2 + SO_2 \rightleftharpoons NH_4^+ \cdot (H_2O)_2 \cdot SO_2 + CO_2$	300	15.7 ± 0.2	$(5.4 \pm 0.4) \times 10^2$
$NH_4^+ \cdot H_2O \cdot SO_2 + H_2O \rightleftharpoons NH_4^+ \cdot (H_2O)_2 + SO_2$	299	10.1 ± 0.2	58 ± 7
$NH_4^+ \cdot (H_2O)_3 \cdot SO_2 + H_2O \rightleftharpoons NH_4^+ \cdot (H_2O)_4 + SO_2$	299	5.8 ± 0.3	11 ± 2
$NH_4^+ \cdot H_2O \cdot SO_2 + H_2O \overset{M}{\rightleftharpoons} NH_4^+ \cdot (H_2O)_2 \cdot SO_2$	300	31.1 ± 0.3	$(2.6 \pm 0.3) \times 10^5$ atm^{-1}
$Cs^+ \cdot H_2O \cdot CO_2 + H_2O \rightleftharpoons Cs^+ \cdot (H_2O)_2 + CO_2$	300	20.2 ± 0.2	$(3.3 \pm 0.3) \times 10^3$
$Cs^+ \cdot H_2O \cdot CO_2 + SO_2 \rightleftharpoons Cs^+ \cdot H_2O \cdot SO_2 + CO_2$	300	13.0 ± 0.2	$(1.8 \pm 0.2) \times 10^2$
$Cs^+ \cdot CO_2 + SO_2 \rightleftharpoons Cs^+ \cdot SO_2 + CO_2$	300	11.8 ± 0.1	$(1.1 \pm 0.1) \times 10^2$
$Na^+ \cdot (H_2O)_3 \cdot SO_2 + H_2O \rightleftharpoons Na^+ \cdot (H_2O)_4 + SO_2$	299	6.0 ± 0.2	11 ± 1
$NO_3^- \cdot CO_2 + SO_2 \rightleftharpoons NO_3^- \cdot SO_2 + CO_2$	299	30.7 ± 0.1	$(2.3 \pm 0.2) \times 10^5$
$NO_3^- + H_2O \overset{M}{\rightleftharpoons} NO_3^- \cdot H_2O$	299	30.4 ± 0.3	$(2.0 \pm 0.3) \times 10^5$ atm^{-1} [a]
$NO_3^- \cdot H_2O + SO_2 \overset{M}{\rightleftharpoons} NO_3^- \cdot H_2O \cdot SO_2$	301	29.4 ± 0.3 29.5 ± 0.3	$(1.3 \pm 0.1) \times 10^5$ atm^{-1}
$NO_3^- \cdot CO_2 + H_2O \rightleftharpoons NO_3^- \cdot H_2O + CO_2$	298	19.2 ± 0.3	$(2.3 \pm 0.3) \times 10^3$
$I^- \cdot CO_2 + SO_2 \rightleftharpoons I^- \cdot SO_2 + CO_2$	300	34.2 ± 0.2	$(8.9 \pm 0.7) \times 10^5$
$I^- \cdot CO_2 + H_2O \rightleftharpoons I^- \cdot H_2O + CO_2$	299	18.8 ± 0.2	$(1.9 \pm 0.1) \times 10^3$

[a] For comparison, K's from the literature (atm^{-1}): 8×10^4 ($\pm$ factor of 2) (Ref. 47), 1.1×10^5 ($\pm$ factor of 2) at 296 K (Ref. 19), 1.6 $(1.1-2.4) \times 10^5$ (Ref. 42), where the numbers in the round brackets give the limits of error.

served that H_2O clusters more strongly to Na^+ than does SO_2 [at 300 K $K(Na^+ + H_2O) = 4.4 \times 10^{12}$, $K(Na^+ \cdot H_2O + H_2O) = 5.4 \times 10^9$, $K(Na^+ + SO_2) = 2 \times 10^9$, all in atm^{-1}]. Their K reported for the switching of H_2O for SO_2 on Na^+ (5×10^3 at 300 K) extrapolates well from the results reported here.

Inspection of the equilibrium constants listed in Table IV for the clustering of CO_2 to various ions leads to the observation that the K's are smaller than for the association of H_2O or SO_2 to the same ions. There does not seem to be a preference for positive or negative ions as the degree of attachment is $NO_3^- > Cs^+ > I^-$. Consistent with the observations for H_2O and SO_2, the attachment K is smaller for more hydrated ions.

A summary of the equilibrium constants for the exchange of H_2O and SO_2 for CO_2 is given in Fig. 19. It is clear that CO_2 is readily replaced by either H_2O or SO_2. The preference for SO_2 is much stronger for the negative ions than the positive. The preference for H_2O is about the same for positive and negative ions.

TABLE VII. ΔG^0 and K values derived from the thermodynamic cycles for which a ΔG^0 value was taken from the literature.

	$-\Delta G^0$(kJ/mol)[a, b]	$K^{a, c}$
$Cs^+ \cdot SO_2 + H_2O \overset{M}{\rightleftharpoons} Cs^+ \cdot SO_2 \cdot H_2O$	30.2	$2(1-3) \times 10^5$ atm^{-1}
$Cs^+ \cdot CO_2 + H_2O \overset{M}{\rightleftharpoons} Cs^+ \cdot CO_2 \cdot H_2O$	29.1	$1.2(0.7-2) \times 10^5$ atm^{-1}
$Cs^+ \cdot CO_2 + H_2O \rightleftharpoons Cs^+ \cdot H_2O + CO_2$	24.2	$2(1-3) \times 10^4$
$Cs^+ \cdot SO_2 + H_2O \rightleftharpoons Cs^+ \cdot H_2O + SO_2$	12.4	$1.5(0.9-2) \times 10^2$
$H_3O^+ \cdot (H_3O)_3 \cdot SO_2 + H_2O \overset{M}{\rightleftharpoons} H_3O^+ \cdot (H_2O)_4 \cdot SO_2$	16.8	$8(5-14) \times 10^2$ atm^{-1}
$H_3O^+ \cdot (H_2O)_3 \cdot SO_2 + H_2O \rightleftharpoons H_3O^+ \cdot (H_2O)_4 + SO_2$	5.8	$10(6-17)$

[a] $T = 300$ K.
[b] An error in ΔG^0 of 1.2 kJ/mol was used.
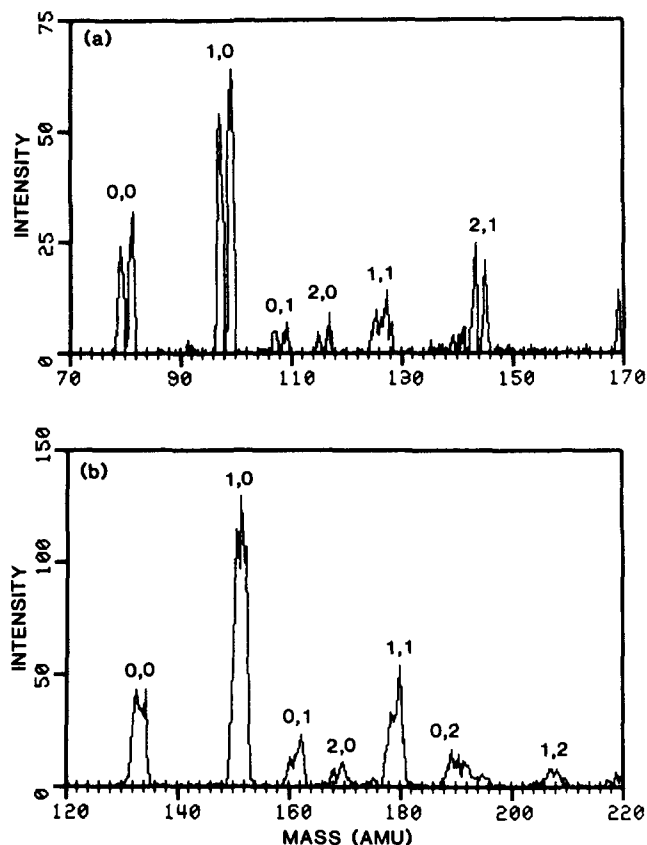[c] The limits of error are given in the round brackets.

FIG. 15. Spectra of (a) $Br^- \cdot (H_2O)_m \cdot (N_2)_n$ and (b) $Cs^+ \cdot (H_2O)_m \cdot (N_2)_n$, taken through the atmospheric pressure equilibration chamber containing purified air. The values of m, n are indicated in the spectra.

The equilibrium constants for the association of H_2O with $N(H)_m(CH_3)_r^+$ ($m + r = 4$) hydrates are summarized in Fig. 20. Inspection of this figure shows that the K's for hydration decrease as the hydration of the ion increases, and as r increases. The decrease in the K's for $r \leqslant 2$ appears smooth; for $r = 3$ there seems to be a discontinuity between the addi-
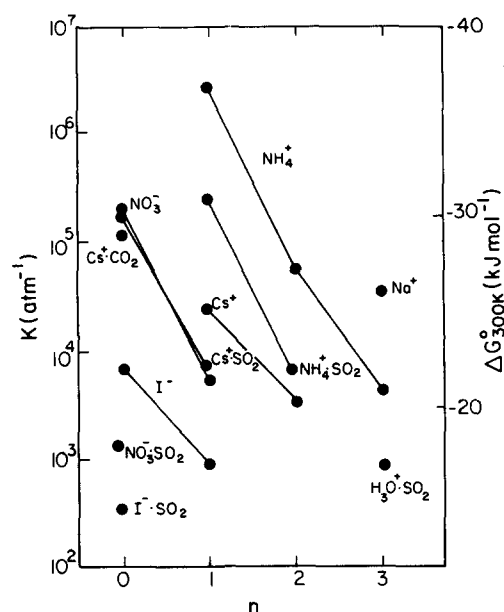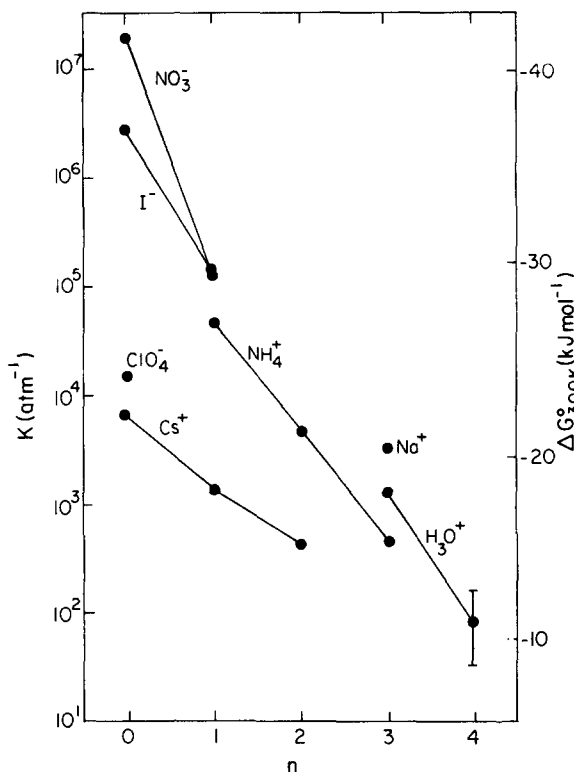

FIG. 17. Summary of the equilibrium constants determined for the association of SO_2 to ions. The number of water molecules associated with each cluster ion is indicated by n. The scale for ΔG^0 at 300 K is shown.

tion of the first and second water molecules. The decrease in the K's for addition of the first H_2O molecule to ions with $r \leqslant 3$ seems to be smooth. There is a discontinuity between $r = 3$ and $r = 4$. These observations are consistent with a change in cluster stability after the build up of a shell of four CH_3 and/or H_2O around the nitrogen core of the ion.

FIG. 16. Summary of the equilibrium constants determined for the association of H_2O to ions. The number of water molecules associated with each cluster ion before the new addition is indicated by n. The scale for ΔG^0 at 300 K is shown.
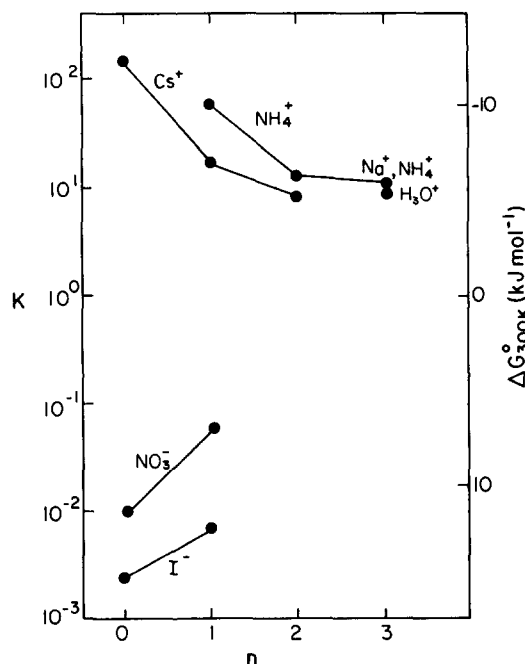

FIG. 18. Summary of the equilibrium constants determined for the exchange of H_2O for SO_2. The number of water molecules associated with each cluster ion is indicated by n. The scale of ΔG^0 at 300 K is shown.
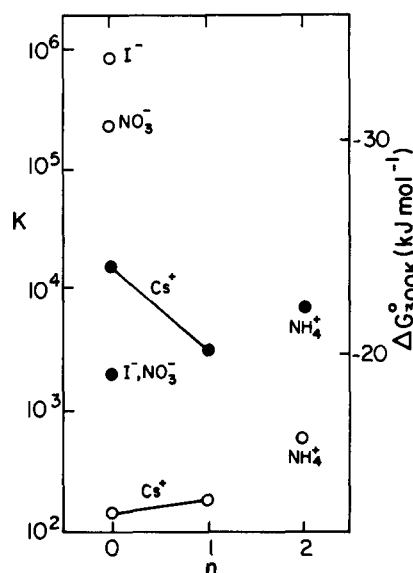
FIG. 19. Summary of the equilibrium constants determined for the exchange of H_2O for CO_2 (●) and SO_2 for CO_2 (O). The number of water molecules associated with each cluster ion is indicated by n. The scale of ΔG° at 300 K is shown.

2. Bonding in clusters

a. H_2O, SO_2, or CO_2. For electrostatic bonding and ions with closed electronic shells (alkali and halide ions) the most important property of the ion regarding the stability of the
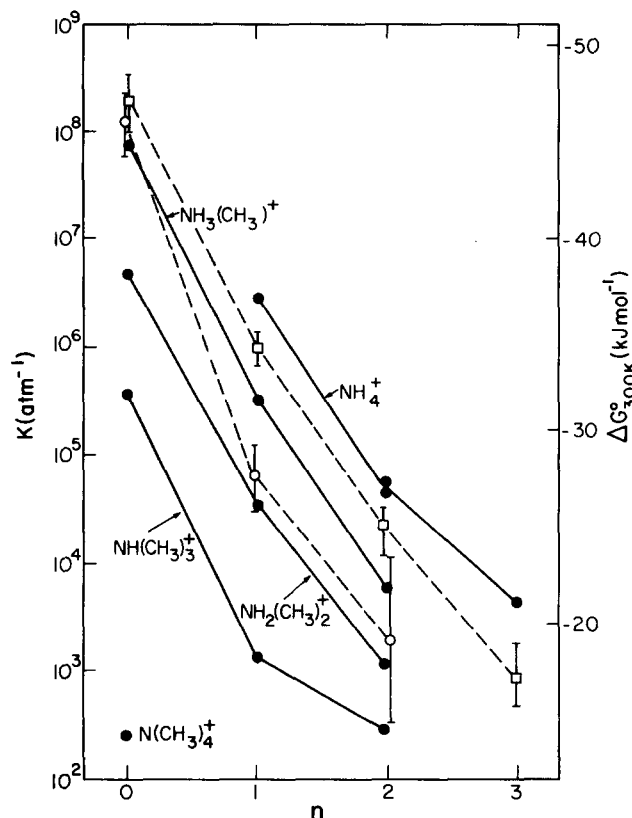

FIG. 20. Summary of the K's measured for the reactions $N(H)_m(CH_3)_r^+ \cdot (H_2O)_n + H_2O \overset{M}{\rightleftharpoons} N(H)_m(CH_3)_r^+ \cdot (H_2O)_{n+1}$ with $m + r = 4$. For comparison, results from Ref. 23 for hydration of $NH_4^+ \cdot (H_2O)_n$ (□) and from Ref. 35 for hydration of $NH_3(CH_3)^+ \cdot (H_2O)_n$ (O) are shown. The scale of ΔG° at 300 K is shown.

neutrals attached is the ion size. The smaller the ion the greater the stability of the cluster. Molecular ions may have properties which can influence bonding in other ways. For example the ions H_3O^+ and NH_4^+ allow the possibility of hydrogen bonding with water molecules. The ability of a neutral molecule to bind electrostatically to an ion is primarily determined by its dipole and quadrupole moments, and by polarizability. These values are listed in Table VIII for the neutral molecules studied in this work.

The interaction between ions and molecules can be quantitatively treated by an electrostatic model as long as the bonding is purely electrostatic and does not have a covalent contribution. Covalent bonding is suspected in ion–molecule clusters when the binding energy for a ligand to an ion is greater than for the same ligand to a different ion with similar properties, especially size and polarizability.[38] As well, a significant decrease in the bond energy for succeeding ligand attachments indicates dispersion of charge, caused by partial charge transfer to the first neutral ligand added.[17] Covalent bonds are directional and in giving rigidity to the bond may produce stereochemical effects which are absent for purely electrostatic bonds.
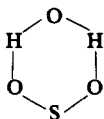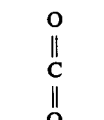
Electrostatic[41,49–52] and quantum mechanical[39,53,54] calculations for the clustering of water molecules to alkali or halide ions have shown that the bonding is almost completely electrostatic. The possibility of covalent bonding between the first SO_2 ligand and negative ions has been suggested by other authors[19,43] to explain the high stability of the corresponding clusters. However, there should be more consideration given to the possible differences between H_2O and SO_2 in their electrostatic interactions with ions. The dipole moment of SO_2 is smaller than that of H_2O, but the charge distribution is quite different. This may have a large influence on the dipole interaction. The quadrupole moment of SO_2 is much larger than that of H_2O. The quadrupole moment of H_2O is repulsive to negative ions and attractive to positive ions when the dipole is attractively aligned.[50] The present results, and observations made by Castleman et al.[55] for mixed clusters, indicate that for SO_2 the quadrupole moment is attractive to negative ions and repulsive to positive ions when the dipole is attractively aligned. As well, the polarizability of SO_2 is much larger than that of H_2O and if the geometry is such that SO_2 can approach the negative ions more closely this may have a large effect. No calculations considering these points have been done yet.

Another possible explanation for the difference in stability between H_2O and SO_2 ligands is that water molecules can cluster to ions in structures stabilized by hydrogen bonds. In fact H_2O molecules can cluster in chain structures which can be weakly preferred over cyclic structures.[56] Perhaps this interligand bonding can account for some of the difference in the stability of successive additions of H_2O and SO_2 in ion clusters.

The clustering of CO_2 to ions is governed by its polarizability and quadrupole moment. The degree of preference for H_2O or SO_2 over CO_2 as a clustered ligand is consistent with H_2O and SO_2 being more strongly bound because of their dipole moments.

A comparison of the K for the attachment of CO_2 to Cs^+

TABLE VIII. Molecular properties. Taken from a table given in Ref. 48, with the original references listed by letter.

Ligand	Dipole moment (D)	Dipole polarizability a_z, a_y, a_x (Å^3)	Quadrupole moment Q_{zz}, Q_{yy}, Q_{xx} (10^{-26} esu/cm^2)	Axes
H_2O	1.85[a]	1.452, 1.651, 1.226[b]	− 0.13, − 2.5, 2.63[c]	
SO_2	1.63[d]	2.653, 4.273, 4.173[d]	1.3, 4.0, − 5.3[e]	
CO_2	0[a]	4.05, 1.95, 1.95[f]	− 4.32, 2.16, 2.16[g]	
N_2	0[a]	2.39, 1.46, 1.46[h]	− 1.2, 0.6, 0.6[i]	

can be made with the prediction of the electrostatic calculation of Spears.[50] The presently measured K is 55 atm^{-1}, whereas the predicted K is ~ 3 atm^{-1}. A comparison of Spears' results for other ions and neutrals with experimental results from the literature[50] shows that the predicted K may be as large as 10 atm^{-1}. There is still a very large difference between the presently measured K and the predicted value. This may be explained by some covalent character to the bond formed. Castleman et al.[55] reports finding stronger binding than predicted electrostatically for the cluster $Na^+ \cdot CO_2$ and so expect that there is some covalent character to that bond.

b. Mixed clusters. It was of interest to see whether or not the mixed clusters observed had greater stability than clusters with only one type of ligand. This greater stability would result from an attractive interaction between the different clustered ligands. The mixed clusters observed in this study had intermediate stability between clusters with only one type of ligand. This trend is clearly seen in the data for the Cs^+ cluster ions shown in Table IX.

The results of Upschulte et al.[26] for the association of H_2O and SO_2 to Na^+ extrapolate well from the results on mixed clusters given in Figs. 16, 17, and 18. At 300 K they find $K(Na^+ \cdot H_2O + H_2O) = 5.4 \times 10^9$, $K(Na^+ \cdot SO_2 + H_2O) = 9.5 \times 10^9$, $K(Na^+ \cdot H_2O + SO_2) = 2.9 \times 10^6$, all in atm^{-1}.

TABLE IX. ΔG^0's for formation of Cs^+ cluster ions.

	− ΔG^0(kJ mol^{-1})
Cs^+	0
$Cs^+ \cdot CO_2$	10
$Cs^+ \cdot SO_2$	22
$Cs^+ \cdot H_2O$	34
$Cs^+ \cdot H_2O \cdot CO_2$	39
$Cs^+ \cdot H_2O \cdot SO_2$	52
$Cs^+ \cdot (H_2O)_2$	59
$Cs^+ \cdot (H_2O)_2 \cdot SO_2$	74
$Cs^+ \cdot (H_2O)_3$	79

c. Effect of increased hydration and methyl substitution. As the degree of hydration of the cluster ion increased, K's for association of H_2O and SO_2 decreased. This is due to ligand–ligand repulsions, and for large enough n, perhaps not seen here, the inability of the neutral to approach the ion as closely. There is also a tendency for the entropy change in association reactions to be larger in a negative sense for progressive addition of neutral molecules[43,57] implying greater structure in the cluster.

The convergence of the K's for the switching reactions of H_2O for SO_2, as the degree of hydration increased, for the positive ions studied is probably due to the associated water molecules masking the character of the central ion.

It is of interest to see the effect of the substitution of the hydrogens of NH_4^+ by the methyl groups, and so to see the influence of the methyl "shell". As more methyl groups are added, the ion becomes physically larger so that the clustering water molecules cannot approach as closely. It is expected that the transitions for successive hydrations should be smooth for up to four attached groups, whether bonded CH_3 or clustered H_2O. In this experiment the bond strengths (ΔH's) were not determined, but, for NH_4^+ and $NH_3(CH_3)^+$ hydration ΔG^0 and ΔH^0 are well correlated[23,35] so the cluster stability (ΔG^0) may be considered as indicative of the bond strength.

The expected shell influence was not seen for the addition of the third H_2O to $NH_2(CH_3)_2^+$. This could be due to the third H_2O still being able to squeeze in close to the ion, or to hydrogen bond to one of the water molecules. A small change in the stability does appear for the second H_2O attachment to $NH(CH_3)_3^+$. The similarity in the ΔG^0 values for the attachment of the second and third water molecules implies that they are similarly bonded; the second and third H_2O may then be outside the shell formed by the three CH_3 and the first H_2O.

It can be seen that the difference in ΔG^0 for the first hydration of NH_4^+ and $NH_3(CH_3)^+$ is quite small, and that there is a regular progression to lower ΔG^0 for $NH_m(CH_3)_r^+$ as r takes values 1, 2, 3. There is a large decrease in ΔG^0 at

$N(CH_3)_4^+$, showing a strong shell effect when the four groups around the N are methyls.

3. Validity of the equilibrium constants

Since the apparatus used in this experiment had not been applied to the measurement of equilibrium constants before, it is appropriate to comment on the validity of the values obtained. The experimental procedure was carefully investigated to ensure the reliability of the technique. However additional confirmation can come from comparison of the K's measured in this work with results of the well-established techniques of Kebarle and Castleman. In general the agreement in the K's is within a factor of 3. Considering the nature of the experiment this is very good agreement and supports confidence in the present measurements. Additional confidence comes from the consistency of the thermodynamic cycles. Many of the ΔG^0's are determined from independent spectra and so the fact that the $\Sigma(\Delta G^0)$'s are zero within error means that the different values support each other and are reliable.

The value reported by Keesee et al.[43] for K for the attachment of SO_2 to I^- is ≈ 35 times smaller than that determined in this experiment. The reason for this large discrepancy is not understood at present, but the thermodynamic cycles support the K found in this work.

Even though the value for the equilibrium constant for the association of SO_2 to $I^- \cdot H_2O$ was derived from only one spectrum, the fact that this K gives such consistent results in the cycles supports the value as correctly representing the equilibrium constant.

B. Clustering of N_2

Nitrogen molecules were observed clustered to a variety of simple and cluster ions, both positive and negative. However in this series of experiments, appropriate conditions for the measurement of equilibrium constants were not found. Nonetheless some interesting features were observed.

In the spectra illustrating the attachment of SO_2 to NO_3^- and I^- there was an apparent enhancement of the N_2 clustering relative to the bare or hydrated ion as p_{SO_2} was increased. There was also some distortion of the hydrate distribution. This implies that the reactions with H_2O and N_2 do not relax fast enough to maintain equilibrium under conditions in which reactions with SO_2 preferentially remove some of the ions present. The conclusion drawn is that the relaxation times are $\tau_{N_2} > \tau_{H_2O} > \tau_{SO_2}$, and so a long relaxation time for N_2 clustering (and declustering) is indicated.

The effect of an increased electric field on the clustering of N_2 and H_2O to Br^- was to decrease the amount of N_2 attached. This could support either a long τ for the attainment of equilibrium or collision-induced dissociation for the N_2 clusters. As expected, the change in field had no effect on the H_2O clustering since the τ is shorter and the clusters are strongly bound. This effect of the field in the equilibration chamber on the nitrogen clusters rules out the possibility that the clusters are being formed in the free jet expansion.

The clustering of N_2 to simple ions has been observed in other laboratories and some equilibrium constants and rate constants have been reported.[58] The attachment of N_2 to cluster ions was observed by Kadlecek[22] and Thomson[59] but equilibrium constants were not measured. The ions they observed were $H_3O^+ \cdot (H_2O)_n \cdot N_2$, $NH_4^+ \cdot (H_2O)_n \cdot N_2, NH_4^+ \cdot (NH_3)_n \cdot N_2$ and $H_3O^+ \cdot (H_2O)_n \cdot N_2$, $NH_4^+ \cdot (H_2O)_n \cdot N_2$, $CO_4^- \cdot H_2O \cdot N_2$, respectively.

C. Implications for the atmosphere

It is clear from the broad spectrum of ions studied that ion clusters with water molecules as the ligands would be plentiful in the atmosphere. The number of H_2O clustered in equilibrium at tropospheric water vapor concentrations would be only a few more than in the clusters studied here.[33] Thus it is expected that mixed clusters with N_2 attached would be plentiful in the atmosphere. A very rough estimate is that perhaps 25% of the ion clusters would involve N_2.

Sulphur dioxide was observed clustered to positive ions with up to four water molecules attached. Since the interaction of SO_2 with negative ions is stronger it is expected to cluster at least as well to hydrated negative ions. The average concentration of SO_2 in the troposphere is ~ 0.2 ppb (parts per billion), but in cities concentrations as high as 2 ppm (parts per million) have been measured,[60] and near sources of SO_2 pollution the concentrations would be higher yet. The K's for switching reactions measured in this work predict that one hydrated positive ion in 10^5 would have an SO_2 attached. For negative ions, especially those with lower hydration, a small, but perhaps nonnegligible, number would have SO_2 attached (say 1 in 10^3).

The mole fraction of carbon dioxide in the atmosphere is constant at 3.5×10^{-4} up to about 90 km.[60] The K's for switching reactions indicate that at tropospheric conditions of 300 K and 80% RH only 10^{-6} of the ion clusters will have CO_2 attached. Thus CO_2 clustering in the lower troposphere would be negligible. However, higher in the atmosphere the concentration of H_2O is much smaller (mole fraction of $H_2O < 5 \times 10^{-6}$ at 15–45 km[60]) and clusters with CO_2 may be seen.

In fact there are very stable ion clusters involving CO_2 observed under tropospheric conditions. However these clusters, such as $OH^- \cdot CO_2$ and $O_2^- \cdot CO_2$, are assumed to be covalently bonded: HCO_3^- and CO_4^-.[19,61] Even though the electrostatic attachment of molecules such as N_2 and CO_2 may be weak, the fact that these clusters do exist opens the possibility of bimolecular reactions of the ion clusters with other trace gases of lesser abundance. These bimolecular reactions may not be possible for H_2O ligands due to the stronger bonding.

The large equilibrium constants seen for the attachment of a species like SO_2 to negative ions illustrates how the study of ion–molecule clusters in the atmosphere can be a tool for trace gas detection.

In these experiments O_2 was not observed to cluster with ions when air was used as a buffer gas. Thus it is expected that very few, if any, atmospheric cluster ions would have O_2 as a ligand.

D. Advantages of the sampling method used

There are definite advantages to introducing ions into the mass spectrometer in a viscous flow of gas followed by a rapid expansion. The experimental results of Kebarle and co-workers quoted in this paper were obtained under conditions of molecular flow. The experiments of Castleman and co-workers were run in the transition region (flows of intermediate nature between molecular and viscous). Under these conditions corrections need to be made for mass dependent transmission of ions through the orifice. However in the situation of viscous flow the ions are simply transported along in the flow of buffer gas and all masses are transmitted with equal efficiency so no corrections are necessary.

In ion clusters with a large number of bonds there is the possibility of the ion cluster distribution being distorted by unimolecular dissociation occurring in the mass spectrometer when sampling is via a molecular leak.[46,52] In the present experimental arrangement the ion clusters are rapidly cooled in the free jet expansion and the extent of unimolecular dissociation is correspondingly decreased.

Both undercorrection for the effect of transition region flow and unimolecular dissociation in the mass spectrometer would lead to apparent K's which are smaller than the true K's. As the present experiment is free of these sources of error it is interesting to note that even though the K's reported here agree well with the values of Kebarle and Castleman, where comparison is possible, they are always larger.

It must be stressed, however, that there is the possibility of association or stripping reactions occurring in the regions of very rapidly changing temperature and pressure in the jet. Conditions must be carefully chosen, and the influence of the jet well understood to ensure that these reactions do not occur. The occurrence of stripping or association reactions in the jet would lead to apparent K's which are smaller or larger, respectively, than the true equilibrium constants.

V. CONCLUSIONS

A new technique has been developed in which ions produced by a spray source can be used for the determination of equilibrium constants for gas-phase ion–molecule reactions. This technique has several unique and important advantages: (1) the use of the spray source extends the range of ions that can be studied; (2) the operation of the ion equilibration chambers at high pressures (0.1–1 atm) extends the number of reactions that can be studied; and (3) the ion sampling by means of a carefully studied free jet expansion eliminates any systematic error due to unimolecular dissociation or transition region flow. This new technique is ideally suited to the study of hydrated ions, especially the investigation of mixed clusters.

It was found that SO_2 clustered most strongly to negative ions and H_2O most strongly to positive ions. There is a possibility of some covalency in the negative ion–SO_2 bonding but further calculations are needed to check this point.

Clustering of CO_2 was weaker than that of H_2O or SO_2. This is consistent with the nature of the electrostatic interaction, but some covalency is indicated for the $Cs^+ \cdot CO_2$ cluster which is more stable than electrostatic calculations suggest.

Mixed clusters had stabilities intermediate between the clusters involving only one type of ligand.

It was shown that clustering of trace gases such as SO_2, and of weakly bound species such as CO_2 and N_2 can be of some importance in the atmosphere.

The study of the hydration of the series of methyl substituted ammonium ions demonstrated the weaker bonding of H_2O to the methyl groups.

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