

**FEASIBILITY OF REMOVING GASEOUS CONTAMINANTS
FROM MANNED SPACE-CABIN ATMOSPHERES
BY IONIC PROCESSES**

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ABSTRACT

The application of ionic processes to the purification of manned space-cabin atmospheres was investigated in anticipation of a need for a radically new atmospheric purification system for some of the presently scheduled space journeys. Processes considered are (1) ion-molecule reactions of contaminant molecules with specific added molecule ions (O_2^+ , O_2^-) and (2) clustering of contaminant molecules about specific ions (H_3O^+). Either reaction type can lead to charging of the contaminant molecules (or molecules derived therefrom), allowing collection by an externally applied electric field. Ion-molecule reactions were found to be potentially useful for removal of a large class of contaminant species. However, charge-trapping reactions involving such species as water and oxygen--occurring or energetically capable of occurring concurrently or subsequently to the desired reaction--could interfere, thereby allowing no clear-cut decision as to the applicability of ion-molecule reactions to purification. Clustering was investigated in greater detail than ion-molecule reactions. Detailed calculation of ion-polar molecule interaction energies for typical molecules were carried out to better accuracy than has been done heretofore. Competing reactions with water molecules will occur in the presence of water vapor. However, if the ecological balance of the cabin would allow nearly complete and specific removal of water vapor, then clustering could be used to remove highly polar contaminants. A short experimental program to demonstrate feasibility is recommended.

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Section I

INTRODUCTION

A lightweight unit of low energy consumption and long service life for the purification of manned cabin atmospheres is urgently needed. Systems now available are unsuitable for some of the space journeys planned for the near future. In the search for new purification methods adaptable to such a unit, one attractive possibility that has been suggested is the extension of the well-known and highly effective technique of electrostatic precipitation of aerosols (White, 1963) to particles of molecular size. Because general knowledge and the present (essentially nonexistent) state of the art are not sufficient to justify initiation of a development program, a feasibility study of the basic concept must be completed to efficiently determine the practicability of this method. Accordingly, this investigation of the feasibility of electrostatic precipitation for removal of gaseous trace contaminants from cabin atmospheres was undertaken.

The results of only the initial phase of the study--a nonexperimental study of means of implementing this concept and of predicted problems that may be encountered--are presented. The initial study shows that electrostatic purification of an atmosphere from molecularly dispersed contaminants is promising under certain conditions and for restricted classes of contaminants. The power expended per unit weight of removed contaminant can be expected to be considerably higher than in the case of aerosols.

Section II

SUMMARY

Three promising modes of operation were studied:

1. Injection of negative molecular ions of lesser electron affinity than a class of contaminants, allowing them to react with the contaminants within a sweeping electric field, and collecting the discharged negative ions at the anode. (The negative oxygen molecular ion is a possible choice as a reagent ion.)
2. Injection of positive molecular ions of greater ionization potential than a class of contaminants and, by a procedure similar to that above, collection of discharged positive ions at the cathode. (The positive oxygen molecular ion is a natural choice as reagent ion in this case.)
3. Injection of stable ions into the contaminated atmosphere and allowing them to react with polar contaminants to form stable clusters, which would then be collected at the appropriate electrode. (Protons or alkali metal ions are natural candidates in this case.)

Modes 1 and 2 depend on the hypothesized occurrence of rapid charge-exchange reactions of reagent ion with the contaminant; the slowness or absence of subsequent reactions that transfer charge to innocuous species; and the nongeneration of charge-trapping molecular species within the purifier by, say, the ion generation process. However, if these conditions are

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satisfied, two large classes of contaminants could be collected in modes 1 and 2. In mode 3, clustering of the contaminant can be expected to be subject to extreme competition from innocuous polar constituents of the atmosphere, particularly water vapor. This means that only a very restricted group of compounds are potentially collectable by mode 3--for example, alcohols, acids, amines, and aldehydes. A practical purifier might employ at least two of these modes in successive purification steps.

The experimental study to follow will consist of: (1) development of usable ion sources; (2) development of a collecting electrode (possibly made of porous sintered metal powder) such that discharged ions can be removed (along with some atmosphere) from the interelectrode space; and (3) tests of the effectiveness of these three modes on synthetic atmospheres starting with the atmospheric composite thought to be most favorable for the mode under test and in succeeding tests, progressing toward a realistic composition for a breathable atmosphere.

Section III

PERTINENT PHYSICAL PROPERTIES OF MOLECULAR SYSTEMS

In this section, the fundamental properties of molecules that could effect their removal from a gaseous environment by electrostatic means are considered, and the limitations on attempting to collect uncharged molecular species directly by electrostatic means are indicated.

The characteristics of a molecule that are mainly involved in interaction with an electrical field are its charge, its permanent dipole, and its polarizability tensor. Very few molecules of any contaminant will acquire a charge under the ambient conditions prevailing in a manned cabin. A permanent dipole is possessed by a large but not inclusive class of contaminants. Polarizability is a universal characteristic and is possessed in varying degree by all molecules; it results in a field-dependent dipole when a molecule is placed in an electric field.

The intrinsic electrostatic properties having universal applicability to contaminants are their polar properties. To exert a force on a polar molecule, it is necessary to place it within an inhomogeneous electric field. Assuming that the effect due to a permanent dipole will be much larger than that due to an induced dipole, for the types of molecules under consideration, one may estimate the order of magnitude of the effect for a molecule possessing a representative dipole moment. On this basis, a simple calculation, based on a time-averaged dipole along the field direction (Fowler and Guggenheim, 1939, pp. 633-43) shows that the average drift velocity $\langle u_x \rangle$ will be given by

$$\langle u_x \rangle = \frac{DM^2}{6(kT)^2} \frac{d(E_x^2)}{dx} \quad (1)$$

where D = diffusion constant of the contaminant species in question in the atmosphere at the prevailing pressure

M = dipole moment in electrostatic units

k = Boltzman's constant

T = absolute temperature

E_x = x component of an electric field assumed to possess only an x-component which varies only with x, the distance along some convenient coordinate axis.

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At pressures of several hundred torr, $D \sim 0.1 \text{ cm}^2/\text{sec}$, and a reasonable dipole moment is $2 \times 10^{-18} \text{ esu}$. Substitution of these values will show that a steeply varying electric field will be necessary, for example, a change of 100 stat volts/cm in 10^{-7} cm to achieve drift velocities of the order of cm/sec.

Two parameters--temperature and pressure--can be changed so as to enhance this velocity at a given field strength. However, a decreasing pressure requires a decreasing maximum electric field strength to avoid electric discharge, and this is likely to more than nullify any benefit from decreasing pressure. To demonstrate this, insert Paschen's law (Loeb, 1965, pp. 538-39) which says the field strength at breakdown is roughly proportional to pressure and the classical kinetic theory's dependence for diffusion on temperature and pressure, to obtain

$$\langle u_x \rangle = \frac{D_0 p_0}{T_0^{1/2}} \frac{B^2 M^2 p}{3k^2 L T^2} \quad (2)$$

Here D_0 = the diffusion constant under some reference pressure and temperature, p_0 and T_0

B = ratio of field strength to pressure at breakdown

L = a length characterizing the interelectrode spacing.

It is assumed that (dE_x/dx) is a constant.

Increasing pressure, decreasing interelectrode spacing, increasing potential drop, and low temperature enhance the drift velocity. An atmosphere compounded for high dielectric strength (large B) and low collision cross section for molecular diffusion (small D_0) would also be desirable. These latter requirements are somewhat conflicting, but the first (large B) is probably the most important, provided the atmosphere's collision cross section is kept within reasonable bounds because of the unavoidable contribution to collision cross section by the contaminant molecules.

For oxygen-nitrogen atmospheres, the quotient $p/LT^{3/2}$ must be of the order of $10^8 \text{ dyne cm}^{-3} \text{ deg}^{-3/2}$ or greater to achieve appreciable drift velocities. At reasonable temperature and pressures this implies interelectrode spacings of the order of microns. Since the factors that determine B are restricted by the requirement of breathability, one can expect

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less than an order of magnitude change in B (Loeb, 1961, Chapters 8 and 9). These considerations lead to the conclusion that, to exploit intrinsic molecular characteristics, it would be necessary to construct a micro-electrode array. It would also be difficult to develop methods whereby the concentrated contaminant could be removed from the surface of small electrodes. Further, there are some contaminants with no dipole moment and with low polarizability that would not be easily collected by this means. To exploit this approach in a more practical manner would require ingenuity and considerable research. One possibility would be to abandon all thought of construction of such delicate microelectrode structures and try an indirect approach. For example, requisite inhomogeneous electric fields exist in the neighborhood of gaseous ions, charged aerosol particles, and ion-bombarded dielectric particles on conducting electrodes (McDaniel, 1964, p. 665, and Loeb, 1961, pp. 826-28).

The exploitation of the field in the neighborhood of gaseous ions will be discussed below in detail under the section on clustering to concentrate impurities. Investigation of the use of charged aerosols for removal of contaminants was rather arbitrarily excluded from consideration because (1) the weak electric fields about an aerosol particle, as compared to those about an ion, made this approach apparently less promising and (2) such an approach seemed too far removed from the subject of this research as defined in the contract. (Also excluded is the study of ion-bombarded dielectric films as collection media.) These possible approaches are mentioned here to place them on the record for possible future exploitation.

Section IV

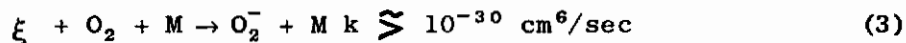
CONVERSION OF CONTAMINANTS TO MOLECULE IONS

The following paragraphs will consider the imparting of an electric charge to contaminant molecules, thus making an ion. If this can be done successfully, a much more secure "handhold" for the action of electric forces than by use of polar forces will have been achieved. The collection and discharge of gaseous ions on electrodes using relatively low electric fields is a well-established technique in gaseous electronics. The rate of collection is limited principally by rate of ion generation and by space charge effects. (These will be considered later, along with an estimate of power consumption in a typical case.)

Conversion to Negative Ions

It will be instructive to first consider what is known about the energetics of negative ions that could be formed in uncontaminated atmosphere by electron attachment. The electron affinities (McDaniel, 1964, pp. 368-425) thought to be important are given in Table I. The tendency is for negative charge to accumulate on available molecules of nitrogen dioxide, free radicals, and ozone. This will be advantageous if these are impurities; however, if these species are introduced by the means of ionization used in the purifier, impurities probably will be unable to acquire a negative charge. For example, one undesirable means of ionization would be a simple negative corona, because it is a copious source of ozone, oxides of nitrogen (if nitrogen is present), and hydroxyl and perhydroxyl radicals (if water vapor is present)--all undesirable species.

These considerations suggest that a desirable method of producing negative ions of impurities could be the injection of a current of near-thermal electrons into the atmosphere. Present knowledge and informed speculation suggest that the following typical electron attachment and charge exchange processes could occur:



(Chanin, Phelps, and Biondi, 1962)

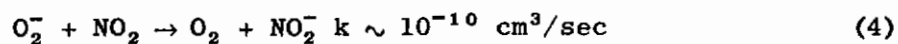
Table I

ELECTRON AFFINITIES OF ATMOSPHERE-DERIVED MOLECULES

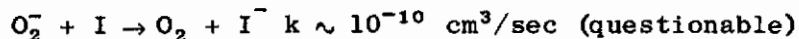
<u>Molecule</u>	<u>Electron affinity (electron volts)</u>	<u>Source reference</u>
NO ₂	3.99	a
HO ₂	3.04	b
O ₃	2.89	b
OH	1.78	c
O	1.465	c
NO	0.89	a
O ₂	0.44	c
N	0.05	c,d
N ₂	-2.3 \approx EA \leftarrow 0 (questionable)	e
N ₂ O	-2.2 (questionable)	e
CO	-1.7 (questionable)	e

-
- a. Farragher, Page, and Wheeler (1964).
 - b. Vedene'ev et al. (1962).
 - c. McDaniel (1964).
 - d. Edlen (1960).
 - e. Biondi (1961, p. 353).

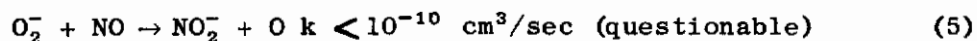
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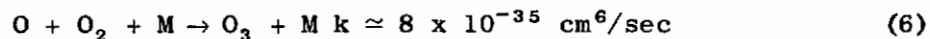
(in analogy with findings of Curran, 1962)



These processes will be accompanied by the slower reactions:



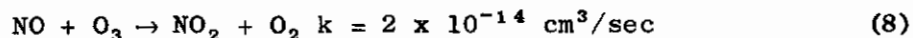
(Branscombe, 1957)



(Benson and Axworthy, 1957)



(Branscombe, 1964)



(Johnson and Yost, 1949, and Ford, Doyle, and Endow, 1957)

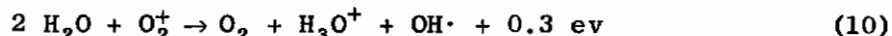
Here I represents an impurity molecule having an electron affinity greater than molecular oxygen. The reactions shown in the second group are slow because they have a low intrinsic rate or because concentration of one of the reactants is small. The impurity molecule may concurrently or subsequently participate in a reaction other than simple charge exchange; a good example is nitric oxide in Eq (6). Possible contaminants energetically capable of participating in reaction (5) include many of the condensed ring aromatic hydrocarbons--halogens, halogen oxides, oxides of nitrogen, and sulfur dioxide (Becker and Wentworth, 1963).

The above considerations apply only for a rather idealized atmosphere. An actual atmosphere may be expected to contain molecular entities clustering on the ions to form such species as CO_4^- , H_2O_3^- , H_2NO_3^- , and so forth (McDaniel, 1964, pp. 426-87; Eiber, 1963; and Fire and Rutherford, 1964). In some instances clustering can be expected to stabilize the negative ions toward charge exchange by something of the order of tenths of an electron volt (Voshell, Page, and Phelps, 1965) and affect the rate of charge exchange (Marcus, 1964). Clustering probably will not affect the general trends implied here for negative ions.

Conversion to Positive Ions

Discussion of positive ion formation is complicated by the occurrence of rapid charge-changing reactions other than electron exchange--most importantly, those involving proton exchange. Table II gives ionization potentials of a number of species of immediate interest; Table III gives known proton affinities for a similar group of molecules.

One criterion for choice of a positive species to be injected into a contaminated atmosphere for reaction by electron exchange with contaminants to form positive molecule ions is: the parent molecule has an ionization potential less than or equal to the atmospheric constituents but greater than as many of the contaminants as possible. This suggests choosing an ion derived from a molecule having an ionization potential very close to 12.5 ev. Probably O_2^+ would be the most innocuous ion fulfilling this specification. However, one can conceive of at least one energetically favorable path leading to degradation of the ionization potential of the positive ion, but this involves more than electron exchange. This path is



which, because of aqueous clustering about the positive oxygen molecule ion, may be faster than one would guess from 3-body considerations. The resulting hydronium ion can be regarded as being derived from a reaction of so low an ionization potential, $7.1 \text{ ev} + \text{H}_2\text{O} + \text{H} \rightarrow \text{H}_3\text{O}^+ + \text{e}$, that it cannot capture an electron from a contaminant molecule (although it could exchange a proton with some contaminants). However, if the reaction of H_2O with O_2^+ is sufficiently slow, then one would hope for rapid electron exchange by O_2^+ with contaminants of lesser ionization potential,

Table II

IONIZATION POTENTIALS OF ATMOSPHERIC CONSTITUENTS AND
OF CLOSELY RELATED MOLECULES

<u>Molecule</u>	<u>Ionization potential (electron volts)</u>	<u>Source Reference</u>
NO	9.5	a,b,c
NO ₂	11.0	a,b,c
HO ₂	11.53	d
O ₂	12.5	a,b,c
H ₂ O	12.6	a,b,c
O ₃	12.8	e
N ₂ O	12.9	a,b,c
OH	13.18	f
H	13.60	a
O	13.614	a,g
CO	14.1	a,b,c
CO ₂	14.4	a,b,c
N	14.54	a,g
N ₂	15.5	a,b,c
H ₂	15.6	a

-
- a. McDaniel (1964).
b. Brown and Allis (1958).
c. Herzberg (1950).
d. Foner and Hudson (1962).
e. Herron and Schiff (1956).
f. Vedene'ev et al. (1962).
g. Finkelberg and Hambach (1955).

Table III

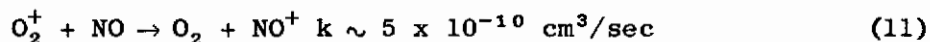
KNOWN PROTON AFFINITIES FOR ATMOSPHERIC CONSTITUENTS
AND RELATED MOLECULES

<u>Molecule</u>	<u>Proton affinity (electron volts)</u>	<u>Source reference</u>
O ₂	4.3	a
O	4.9	b
HO ₂	6.5	c
H ₂ O	6.5, 7.3	b,d
CO	<Value for water	e,f

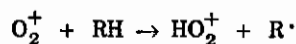
-
- a. Foner and Hudson (1962a).
b. Vedene'ev et al. (1962).
c. Foner and Hudson (1962b).
d. von Raalte and Harrison (1963).
e. Fontijn and Baughman (1963).
f. Hand and von Weyssenhoff (1964).

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to produce collectible positive ions. Inspection of a number of compilations of molecular ionization potentials (Watanabe, 1957, and Watanabe, Nakayama, and Mottl, 1959) reveals that a great many organic molecules and quite a few inorganic molecules have ionization potentials less than molecular oxygens. Important exceptions are carbon monoxide, hydrogen halides, carbon dioxide, sulfur dioxide, nitrous oxide, some saturated hydrocarbons, and halogens (except iodine). Electron exchange reactions with O_2^+ have been observed to be fast in the few instances that have been studied, for example (Fite et al., 1962),



and it is likely that the reaction rate would be comparable for a large number of the energetically eligible molecules. However, there is yet another possibility (among a host of possibilities) for an alternative reaction:

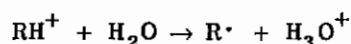


followed by



and subsequent reactions involving the free radical. This is a good example of initiation of oxidative attack by ions in an oxygen-containing atmosphere. For this reaction to be energetically feasible, the R—H bond must be weaker than about 3 ev (69 kcal). Such a weak hydrogen bond indicates that only a few molecular types, such as aldehydes and some hydrogen-containing radicals, will be open to such attack at an appreciable rate (Cottrell, 1958).

Assuming a smooth transfer of positive charge from molecular oxygen to contaminant molecules of lesser ionization potential (electron capture by oxygen ion), the next difficulty to be considered is the possible occurrence of subsequent rapid charge-changing reactions by these ions with normal atmospheric constituents. For example, present limited experimental data indicate that many organic radicals have a lesser proton affinity than does water (Vedene'ev et al., 1962). In the presence of water vapor, then, subsequent reactions of the type



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followed by



will be energetically possible for many radicals, $R\cdot$, and, if energetically possible, will probably be very fast (Munson, Field, and Franklin, 1965; Tal'roze and Frankevitch, 1960; Moran and Hamill, 1963; McLafferty, 1963). Contaminants such as alcohols and amines can take the part of water in a similar reaction but with less distressing consequences for the present purpose. The water reaction could result in a nearly complete conversion of positive charge to hydrated protons; hence, to charge contaminants positively, it might be necessary to inject more than enough positive charge to convert all water molecules to hydrated protons--an impracticable course except for atmospheres having very low water concentration (for example, of the order of parts per million by volume).

Summarizing the above, it is concluded that conversion of some contaminants to ions by injecting a reactant ion into the atmosphere can probably be done using oxygen molecular ions (either positive or negative) as reagents. Negative oxygen molecular ions can be formed by injecting thermal electrons. Whether or not the contaminant molecular ions so formed will have a life long enough for collection depends on the possible occurrence and speed of subsequent reactions.

Section V

CHARGE-EXCHANGE REACTOR AND POWER CONSUMPTION

Three extreme sets of conditions or modes can be envisioned for the reaction of ions with contaminant molecules: (1) a dilute plasma with external collecting field, (2) a monopolar space charge with no appreciable external field, and (3) a monopolar space charge under the influence of an external collecting field.

In the case of reactions in a dilute plasma,¹ there are two difficulties: (1) a suitable mode of generation and (2) the effect of the recombination reactions on the efficacy of contaminant collection. An offsetting advantage is that there is a lesser space-charge limitation on the current density than there is for monopolar space charges. Assuming an effective method of generating O_2^- and O_2^+ ions either at the electrodes or homogeneously (for example, by irradiation with ultraviolet in the oxygen ionization continuum), there remains the problem of the recombination effect. Such reaction rates are extremely rapid, particularly for molecular ions, and there is no energy restriction, that is, the reactions are all exoenergetic (Hasted, 1964, pp. 272-74; McDaniel, 1964, pp. 563-626; Brueciener, 1964; and Mahan and Person, 1964). Any third body requirement will be amply satisfied at the probable pressures employed.

The reaction rate ranges from 10^{-7} to 10^{-6} cm³/sec at hundreds of torr pressures, which may be compared with charge-changing reaction rates of 10^{-11} - 10^{-10} cm³/sec. Assuming a steady and copious supply of reagent O_2^- and O_2^+ ions and no oxidative attack on the contaminant, the ionic form of a contaminant cannot exist at more than 0.001 of the concentration of the neutral form in the plasma, which means that only a small fraction--of the order of 0.1% of the contaminant molecules--is being directly affected by the electric field. This process appears even less efficient if one recalls that oxygen molecular ions would also be recombining rapidly,

-
1. In this discussion, plasma means an ionized gas containing very nearly equal concentrations of positive and negative ions. The question of Debye screening length is not considered in this discussion, that is, a dilute plasma has few electrons and ions per cubic centimeter and the Debye screening length is so large that cooperative effects can be neglected (see McDaniel, 1964, pp. 693-700).

thus requiring a much larger rate of ion generation than that collected as a current, which, in turn, will consist mainly of oxygen molecule ions. Therefore, using a dilute plasma as a reaction medium appears to be impracticable.

If ions are reacted as a monopolar cloud with no external field and then piped into a collecting electrode system, as in a conventional chemical reactor, the rates of ionic reaction must compete with the combined rates of diffusion and dispersion due to mutual repulsion. The half-life of such ion clouds due to dispersion is of the order of $1/4 \pi K \rho_0$, where K = ionic mobility and ρ_0 = initial charge density (McDaniel, 1964, pp. 518-21; Townsend, 1898) by Townsend's simple theory. The half-life for a charge-changing reaction is greater than $0.69 \xi/k\rho_0$, where k is the specific rate of the reaction and ϵ = electronic charge. Comparison of the two half-lives leads to the conclusion that $k \gtrsim 8.7 \epsilon K \sim 10^{-6}$ cm³/sec for appreciable reaction in a transient situation. The only rates approaching this at ordinary temperatures are recombination rates. Analysis of a steady-state situation was not attempted; reactions that are too slow by a factor of 10^5 for the transient situation would probably also be too slow for a steady-state situation.

Since the third mode of operation--a monopolar space charge under the influence of an external field--shows more promise than the other two, it was analyzed in greater detail. A one-dimensional case was considered--planar electrodes of lateral dimensions that were large compared to their separation. A slow² flow at v cm/sec of contaminated atmosphere is assumed between the electrodes. A contaminant having an entering concentration of c_0 cm⁻³ is thought of as reacting with a positive ion of current density j and concentration $p(x)$ (x = coordinate vertical to plane of electrodes) to yield a product ion of concentration $s(x)$. Both ions are considered to be near thermal equilibrium with the atmosphere and to have the same mobility, K , independent of field strength. Hence, reaction does not disturb the charge density distribution between the electrodes $\rho(x)$ and the field $E(x)$. If the molecular balance within a small slice parallel to the electrodes is considered, one can then write

$$K \frac{d}{dx}(pE) + kpc = 0$$

2. Relative to ionic velocities.

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$$K \frac{d}{dx}(sE) - kpc = 0 \quad (14)$$

$$v \frac{dc}{dx} + kpc = 0$$

where $k \text{ cm}^3/\text{sec}$ is the specific rate of the reaction taken as effectively second order at the prevailing pressure of the atmosphere. From the last two of these equations, one obtains $v(c-c_0) = -K(sE - s_0E_0)$. If at $x = 0$ the boundary condition $s_0 = s(0) = 0$ is imposed, and using the relationship $\rho = \epsilon(p + s)$ (which use, incidentally, makes the first of the above differential equations redundant), $\rho =$ charge density, a function of x , and $\epsilon =$ electronic charge (absolute value), the result is

$$p = \frac{\rho}{\epsilon} - s = \frac{\rho}{\epsilon} - \frac{v}{KE} (c_0 - c) \quad (15)$$

Substituting this into the last of the above set of differential equations yields an ordinary differential equation of the Bernoulli type (Ince, 1944, p. 22) for c as a function of x :

$$\frac{dc}{dx} + \frac{k}{v} \frac{j - \epsilon v c}{\epsilon j} \rho c = \frac{k\rho}{j} c^2 \quad (16)$$

where $j = KE(p+s)\epsilon = KE\rho$, the current density, independent of x under steady-state conditions. Using the canonical method of solution yields

$$\frac{1}{c} = A \exp\left[-\int_0^x \phi(s) ds\right] + \exp\left[-\int_0^x \phi(s) ds\right] \int_0^x \psi(s) \exp\left[\int_0^s \phi(t) dt\right] ds$$

$$\phi(s) = -\frac{k}{v} \frac{j - \epsilon v c}{\epsilon j} \rho(s) \quad (17)$$

$$\psi(s) = \frac{k}{j} \rho(s)$$

Contrails

Evaluating the integrals by the expedient of introducing ρ as a new independent variable yields

$$\frac{1}{c} = \frac{k}{4\pi k \alpha \rho_0} + \left(\frac{1}{c_0} - \frac{k}{4\pi k \alpha \rho_0} \right) \exp \left[-\alpha \left(\frac{\rho_0}{\rho} - 1 \right) \right] \quad (18)$$

where α is a composite parameter,

$$\alpha = \frac{k(\epsilon v c_0 - j)}{4\pi K \epsilon v \rho_0} = \frac{k c_0 \left(1 - \frac{j}{\epsilon v c_0} \right)}{4\pi K \rho_0}$$

and ρ_0 and c_0 are the values of these variables for $x = 0$. If one appends to these relationships the space-charge dependence on x for one-dimensional space-charge-limited currents of monopolar ions in a relatively dense gas (White, 1963, pp. 90-100, and Loeb, 1961, pp. 634-46), derived using Poisson's equation,

$$\frac{\rho_0}{\rho} = \frac{\left(\frac{dE}{dx} \right)_{x=0}}{\left(\frac{dE}{dx} \right)} = \left[1 + \frac{8\pi K \rho_0^2}{j} x \right]^{\frac{1}{2}} \quad (19)$$

then it is apparent that the trend of c with x depends on the value of $j/\epsilon v c_0$ relative to 1. If reagent ion current exceeds and hypothetical current equivalent to the inflow of contaminant molecules, then $j/\epsilon v c_0 > 1$ and $c_0/c \rightarrow \infty$ with increasing x (increasing ρ_0/ρ). If the ion current is deficient, then $j/\epsilon v c_0 < 1$ and $c/c_0 \rightarrow 1/1 - (j/\epsilon v c_0)$ with increasing x . This is in accordance with expectations based on a priori considerations.

These equations can be used to estimate power consumed to maintain these currents under conditions favorable to appreciable reaction between reagent ion and contaminant (in an actual purifier, additional power will be consumed to generate the reagent ions):

$$p = j \int_0^{\ell} E dx = \text{power density per unit electrode area.} \quad (20)$$

Contrails

Inserting $E^2 = (8\pi jx/K) + E_0^2$, one obtains

$$p = (K/4\pi) (E_\ell^3 - E_0^3) = P/A \quad (21)$$

Here E_ℓ = field strength at second electrode, which is a distance ℓ from the first electrode, where $E = E_0$, P = total power to drive current, and A = electrode area. This can be expressed in terms of E_ℓ only:

$$(P/A) = (K/12\pi) \left\{ E_1^3 - \left[E_\ell^2 - (8\pi j\ell/K) \right] \right\} \quad (22)$$

which is a useful expression because E_1 is the maximum field strength when $(j/K) > 0$ (which we are assuming). We also assumed that: (1) there is an excess of reagent ion inflow rate over contaminant inflow rate

$$\frac{j}{\epsilon v c_0} = \frac{Aj}{\epsilon Av c_0} = 1 + \delta, \delta \geq 0 \quad (23)$$

and (2) this contaminant will not be completely converted to collectible ions

$$r = \frac{c_0 - c_\ell}{c_0}, r \leq 1 \quad (24)$$

To maintain the influent concentration at c_0 , the rate of conversion must balance the emission rate ξ

$$Avrc_0 = \xi \quad (25)$$

giving

$$j = \frac{(1 + \delta)\epsilon\xi}{rA} \quad (25)$$

Contrails

for the required current density of reagent ions. Substituting r and δ into the solution of the differential equation for the dependence of concentration on charge density gives

$$\frac{1}{\rho_o} \left(\frac{\rho_o}{\rho_o} - 1 \right) = \frac{4\pi K}{kc_o \delta} \ln \left[\frac{\delta}{(1-r)(1+\delta)} + \frac{1}{(1+\delta)} \right] \quad (26)$$

which is a prescribed constant if r and δ are specified. The resulting equations determining power expenditure for a prescribed conversion are

$$P = \frac{I^3}{12\pi K^2 A^2} \left[\frac{1}{\rho_l^3} - \frac{1}{\rho_o^3} \right] \quad (27)$$

$$\frac{\rho_o}{\rho_l} = \frac{E_l}{E_o} = \left[1 + \frac{\delta \pi K \rho_o^2 A l}{I} \right]^{\frac{1}{2}} \quad (28)$$

$$\beta = \left(\frac{1}{\rho_l} - \frac{1}{\rho_o} \right) = \frac{4\pi K}{kc_o \delta} \ln \left[\frac{\delta}{(1-r)(1-\delta)} + \frac{1}{1+\delta} \right] \quad (29)$$

A prescribed value of β leads to a quadratic dependence of power, P , on $(1/\rho_l)$ or $(1/\beta\rho_l)$:

$$\begin{aligned} P &= \frac{I^3}{12\pi K^2 A^2} \left[\frac{3\beta}{\rho_l^2} - \frac{3\beta^2}{\rho_l} + \beta^3 \right] \\ &= \frac{I^3 \beta^3}{12\pi K^2 A^2} \left[\frac{3}{(\beta\rho_l)^2} - \frac{3}{\beta\rho_l} + 1 \right] \end{aligned} \quad (30)$$

and we can derive a second relationship

$$\frac{1}{\beta \rho \ell} = \frac{1}{2} + \frac{4\pi K A \ell}{\beta^2 I} \quad (31)$$

showing that $1/\beta \rho \ell$ depends linearly on the interelectrode volume $A\ell$. The power is a minimum for maximum attainable electrode area A and for $1/\beta \rho \ell = 1/2$. The second of the above relationships shows that this power minimum can only be approached but not attained for minimum attainable interelectrode separation ℓ . The minimum power is given by

$$P_{\min} = \frac{1^3 \beta^3}{48\pi K^2 A^2} \quad (32)$$

The important parameters determining power for a single contaminant are rate constant, k , emission rate, ξ , and maximum allowable concentration, c_0 . The specific rate constant for energetically favored charge-changing reactions ranges from 10^{-11} to 10^{-9} cm^3/sec for those instances that have been studied. The slower rates in this range tend to belong to charge-exchange reactions, the faster rates to reactions where an atom or group of atoms are exchanged as well as charge, e.g., proton exchange (Hasted, 1964). For sake of illustration, let us assume a maximum allowable concentration of 10 ppm ($c_0 = 2.5 \times 10^{14} \text{ cm}^{-3}$), an emission rate³ of 0.1 mole/day ($7.0 \times 10^{17} \text{ sec}^{-1}$), and a mobility of $K = 300$ esu. Further, let us impose the conditions that 50% excess reagent ions be produced ($\delta = 0.5$) and that the purifier be 90% efficient ($r = 0.9$). Using these figures for the lowest specific rate of 10^{-11} shows that a reactor volume of $1.3 \times 10^5 \text{ cm}^3$ will be sufficient and a power expenditure of hundreds of watts will be required for electrode separation of a few tenths of a centimeter. Maintaining the same electrode dimensions and varying the specific rate through its estimated range will demonstrate no great variation in power required. Because of the order of magnitude nature of our present knowledge of the proposed system, there is no advantage in devoting more effort to numerical calculations once conditions for a practical power level have been established. It will probably be expedient to satisfy the

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3. Derived from a rough unofficial estimate of emission rate of trace contaminants (excluding hydrogen and methane) for the Apollo space craft, assuming an average molecular weight of 65.

Contrails

requirements by using large cross-sectional areas and small electrode separations, thereby reducing both the power required and the terminal field strength E_{ℓ} . The latter will have to be kept below some upper limit depending on atmosphere composition and pressure to avoid ionization and dissociation by collision and the consequent appearance of charge-trapping molecular species.

In summary, the apparently best chance of imparting a charge to contaminant molecules and of collecting them is by reaction with positive and negative oxygen molecular ions generated at energies near thermal equilibrium by some very specific process. This reaction should take place in narrow gaps between electrodes of large area in a space-charge-limited monopolar current of ions. At least two stages are indicated--reaction with O_2^- to produce and collect negative ions and reaction with O_2^+ to produce and collect positive ions. The dangers are that all possible charge-changing reactions may not be fast enough, that potentially rapid reaction with such harmless constituents as water vapor will trap the charges, and that incidental and undesired generation of charge-trapping species will occur.

Section VI

CLUSTERING

If the direct attack outlined and discussed in Section V fails or is only partially successful (which is very likely because of the many unknown factors), another expedient can be investigated. This would be to exploit the intense inhomogeneous fields in the neighborhood of stable gaseous ions in order to entrap polar contaminants. Such an interaction is very attractive because of its potential universality. There are two extreme cases of this interaction: (1) extremely labile interaction, amounting to little more than a strong preference for the neighborhood of an ion by a molecule, or Loeb's statistical clustering process (Loeb, 1961, p. 118), and (2) very strong interaction resulting in bonds of energy many times greater than average thermal energy, that is, stable clustering.⁴ The first case will be discussed briefly, the second discussed at some length because of its greater promise. The intermediate case of labile clustering (Overhauser, 1949) will be implicitly included in the discussion of strong interaction under the assumption that sweeping electric fields used in an electrostatic purifier would not be intense enough to greatly disturb the internal energy of the ionic complexes.

Use of Statistical Clustering To Concentrate Impurities

Overhauser (1949) has shown that the effect of statistical clustering in Loeb's sense is implicitly included in Blanc's law for the mobility of a specific ion in gaseous mixtures. His demonstration depends on some idealized assumptions regarding ion-gas and gas-gas interactions and should not be accepted unreservedly. However, for gases having the composition of a breathable atmosphere at atmospheric and subatmospheric pressures and at a temperature around 25°C, Overhauser's demonstration is probably approximately correct. Consider a uniform current density, j , of ions flowing through an atmosphere. The dependence of the reduced mobility of ions in a mixture on its composition can be expressed in the form of Blanc's law:

$$\frac{1}{K} = \sum_i x_i / K_i \quad (33)$$

4. Or hydration, solvation, and so forth.

Contrails

where x_i is the mole fraction of component i in which the ion would have a reduced mobility K_i . Equating rate of change of momentum of the ion to that of the gas yields for the electric force per unit volume

$$f = j \sum \frac{x_i}{K_i} \quad (34)$$

at 1 atm and 0°C. By the same type of idealized reasoning exhibited by Overhauser, we can conclude that the force per unit volume acting on the i th component is $f_i = jx_i/K_i$. Removing the restrictions of standard conditions results in an expression for the average force ϕ_i exerted on a molecule of component i at temperature T in °K and pressure p in dynes/cm², as follows: $\phi_i = j\delta kT/K_i p$, where δ is the relative density of the mixture referred to standard conditions. This implies that a drift velocity v_i is imparted to the molecule that is proportional to this force through the molecular mobility u_i

$$v_i = (u_i \delta kT/K_i p) \quad j = \beta_i j \quad (35)$$

which defines the parameter β_i . Consider one-dimensional diffusion of a trace component in an atmosphere in the presence of such an ionic current (Jost, 1960, pp. 47-56). A partial differential equation (approximate) can be written

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \beta_i j \frac{\partial c_i}{\partial x} \quad (36)$$

where c_i = number concentration of i th trace component. Assuming steady state ($\frac{\partial c_i}{\partial t} = 0$) and a finite gap of length l in which the steady state is established yields a solution

$$c_i = \frac{c_i^l \left(-\frac{\beta_i j x}{D_i} \right) + c_i^0 \left(-\frac{\beta_i j x}{D_i} - \frac{\beta_i j l}{D_i} \right)}{1 - e^{-\frac{\beta_i j l}{D_i}}} \quad (37)$$

Contrails

From this one can compute the molecular flux density J_i of component i at steady state:

$$J_i = \frac{\beta_i j (c_o - c_i e^Y)}{e^Y - 1}, \quad Y = \beta_i j \ell / D_i \quad (38)$$

Comparison with diffusion driven only by a concentration gradient $(c_i - c_o) / \ell$ gives the ratio of electric wind-driven transport to diffusional transport of $Y / (1 - e^{-Y})$, provided $c_o \ll c_i$. This function is appreciably greater than one for $Y \gtrsim 1$ and asymptotically approaches Y for Y large. The parameter Y contains one unknown quantity--the molecular mobility u_i . This may be evaluated either by use of Einstein's relationship between mobility and diffusion constant (Chandrasekhar, 1943) or by comparing the steady-state-driven diffusion distribution when $j = 0$, with the result of considering the average force per molecule due to the ionic current as derived from a pseudopotential. The mobility is thus identified as $u_i = D_i / kT$. This, in turn, yields $\beta_i = \delta D_i / K_i p$ and $Y = \delta \ell j / K_i p$. Taking $\delta \approx 1$, one finds that $j \ell \gtrsim 10^8$ for $x \gtrsim \ell$ at near atmospheric pressures. Much lower pressures would proportionally reduce the required value of $j \ell$. At ordinary pressures, a large current density j and a fairly large length ℓ would be required; for example, $\ell = 100$ cm and $j = 10^6$ statamperes/cm², or 0.33 ma/cm². Such currents could not be maintained without exceeding breakdown potentials. Application of this method would conceivably require reduced pressures, as in the usual cataphoretic purification process, but this would decrease the breakdown field strength proportionately to quite low pressures. Cataphoresis works very well for noble gases which cannot be converted to other compounds by the discharge in the presence of the usual impurities.

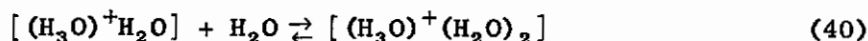
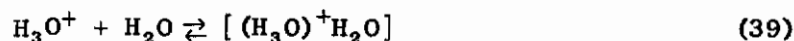
Use of Stable Clusters To Concentrate Impurities

Two circumstances suggest the use of protons as the model stable ion for formation of stable clusters of polar ions: (1) the earlier discussion on converting impurities to positive ions shows that hydrated protons are one of the stable positive ions and (2) the proton is a small ion and is therefore efficient for clustering. (This circumstance is considerably restricted by the formation of hydrated protons in atmospheres containing water vapor.) Another choice, such as an alkali metal ion (Li^+), possibly would be better, especially if the conversion of some impurities to positive ions is attended by complications.

Contrails

Because of the large specific rates⁵ estimated for clustering reactions at total pressures of hundreds of torr, the effectiveness of this mechanism for collection of particular contaminants is considered to be determined primarily by equilibrium constants for clustering reactions. Initially, we considered the clustering of water molecules around a hydronium ion. This example is classical in the sense that the hydration or solvation of protons is important in many fields of chemistry and has been considered from many points of view.

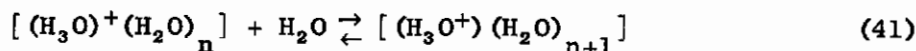
The clustering of water molecules around a hydronium ion can be described by writing a series of equilibrium equations:



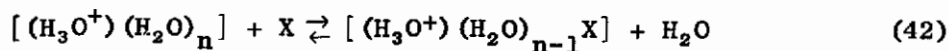
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At any step in the sequence, the reaction of a contaminant molecule X, with the ion cluster of water molecules around a central hydronium ion can be written as



In view of the fact that water is present in large concentrations in space-cabin atmospheres, the relative probability of incorporating contaminant molecules into ion clusters (relative to incorporating water molecules into the same ion clusters) should suffice to indicate the feasibility of collecting contaminant molecules by this means. Experimentally, clusters of water molecules form around a hydronium ion

5. Estimated by classical reasoning analogous to that used in estimating ion-recombination rates. See Hasted (1964) and Magee and Funabashi (1959); see also Thompson (1924).

Contrails

(Knewstubb, and Tickner, 1963, and Kebarle and Hogg, 1965); therefore, the possibility of collecting contaminant molecules in ion clusters can be considered in terms of the relative probability of incorporating contaminant molecules or water molecules into the clusters.

For convenience in the following discussions and in order to generalize regarding the treatment for other applications, the clustering reaction represented by Eq (42) is rewritten as



where, for the present case of interest,

$$A = (H_3O^+) (H_2O)_{n-1}$$

$$B = X, \text{ a contaminant molecule}$$

$$C = H_2O$$

$$AB = (H_3O^+) (H_2O)_{n-1} \cdot X$$

$$AC = (H_3O^+) (H_2O)_n$$

The equilibrium constant for the reaction is

$$K = \frac{[AB] [C]}{[AC] [B]} \quad (44)$$

where the brackets denote concentrations, and the relative probability of incorporating a molecule of B (relative to incorporating a molecule of C) into the cluster is given by

$$P = \frac{[AB]}{[AC]} = \frac{[B]}{[C]} K \quad (45)$$

Thus, if the equilibrium constant, K, can be estimated, the probability of a contaminant molecule successfully competing with water molecules in clustering reactions can also be estimated.

Contrails

The equilibrium constant can be written in terms of statistical thermodynamic quantities as

$$K = \frac{Q_{AB} Q_C}{Q_{AC} Q_B} \exp\left(-\frac{\Delta E}{RT}\right) \quad (46)$$

Here, the Q 's are thermodynamic partition functions for the different molecular species, and ΔE is the molar zero-point energy change for the reaction.

To derive an expression for practical applications, a number of simplifications and assumptions must be made because of lack of knowledge and data concerning the processes and molecules of interest. These assumptions and simplifications are enumerated in the following discussion.

For simplicity, and since there are numerous constants in the partition coefficients that cancel in the expression involving ratios of partition coefficients (Eq 46), the derivation of the equation to be used for estimating equilibrium constants is carried out in terms of ratios of partition functions for similar types of molecules. The ratios to be treated are Q_{AB}/Q_{AC} and Q_C/Q_B .

The molecular partition functions can be written as a product of translational, rotational, and vibrational partition functions, $Q = Q_T Q_R Q_V$. We first consider the partition function ratio Q_{AB}/Q_{AC} . From standard formulas, the translational factor can be shown to be

$$\left(\frac{Q_{AB}}{Q_{AC}}\right)_T = \left(\frac{M_A + M_B}{M_A + M_C}\right)^{\frac{3}{2}} \quad (47)$$

where M_A is the mass of molecule A and M_B is the mass of molecule B.

The rotational partition function ratio can be written as a product of functions related to external and internal rotations in the molecules.

$$\left(\frac{Q_{AB}}{Q_{AC}}\right)_R = \left(\frac{Q_{AB}}{Q_{AC}}\right)_{R(\text{ext})} \left(\frac{Q_{AB}}{Q_{AC}}\right)_{R(\text{int})} \quad (48)$$

Contrails

To gain an approximate expression for the external rotational function, AB and AC are considered as diatomic molecules.⁶ This leads to

$$\left(\frac{Q_{AB}}{Q_{AC}}\right)_{R(\text{ext})} = \frac{M_B(M_A + M_C)}{M_C(M_A + M_B)} \cdot \left(\frac{r_{AB}}{r_{AC}}\right)^2 \quad (49)$$

where r_{AB} and r_{AC} are the distances between the center of masses of A and B in the molecule AB, and A and C in the molecule AC, respectively.

The internal rotation function can be written

$$\left(\frac{Q_{AB}}{Q_{AC}}\right)_{R(\text{int})} = \left(\frac{Q'_{AB}}{Q'_{AC}}\right)_{R(\text{int})} \cdot \left(\frac{I_{Bi}}{I_{Ci}}\right)^{\frac{1}{2}} \frac{\sigma_{Ci}}{\sigma_{Bi}} \quad (50)$$

where the Q primes include all internal rotations except those around the A—B and A—C bonds. I_{Bi} and I_{Ci} are the reduced moments of inertia for the rotations of B and C in the molecules AB and AC. The I_{Bi} and I_{Ci} are approximated by expressions of the form

$$I_{Bi} = \frac{I_A I_B}{I_A + I_B} \quad (51)$$

where I_A and I_B are moments of inertia for the rotation of A and B around the axis of the bonds A—B for symmetrical coaxial molecules. σ_{Ci} and σ_{Bi} are symmetry numbers for the inner rotations of C and B in the AC and AB complexes respectively.

6. See Hirshfelder et al., 1954, pp. 1097-98, and references cited therein for a related treatment.

Contrails

Considering the vibrations of the A—C and A—B bonds to be harmonic oscillations, the vibrational partition function ratio can be written as

$$\left(\frac{Q_{AB}}{Q_{AC}}\right)_v = \left(\frac{Q'_{AB}}{Q'_{AC}}\right) \frac{\sinh\left(\frac{h\nu_{AC}}{2kT}\right)}{\sinh\left(\frac{h\nu_{AB}}{2kT}\right)} \quad (52)$$

Here, the Q primes refer to all vibrational modes except that of A—C and A—B bonds, ν_{AC} and ν_{AB} are the fundamental vibrational frequencies of the A—C and A—B bonds in the clusters, h is Planck's constant, k is Boltzman's constant, and T is the absolute temperature.

In a similar manner, the ratio Q_C/Q_B was estimated. We find that

$$\left(\frac{Q_C}{Q_B}\right)_T = \left(\frac{M_C}{M_B}\right)^{\frac{3}{2}} \quad (53)$$

and

$$\left(\frac{Q_C}{Q_B}\right)_R = \left(\frac{Q_C}{Q_B}\right)_{R(int)} \left[\frac{(I_x I_y I_z)_C}{(I_x I_y I_z)_B} \right]^{\frac{1}{2}} \frac{\sigma_B}{\sigma_C} \quad (54)$$

Here $(I_x I_y I_z)_C$ is the product of the principal moments of inertia for molecule C, and σ_C is the symmetry number for the rotations of molecule C. (Similar definitions apply for the terms with subscript B.)

Several further assumptions were made in order to get a reasonable expression for the complete ratio, $Q_{AB}Q_C/Q_{AC}Q_B$.

$$\text{Writing } \left(\frac{Q'_{AB}}{Q'_{AC}}\right)_{R(int)} = \left(\frac{Q'_A Q'_B}{Q'_A Q'_C}\right)_{R(int)} = \left(\frac{Q_B}{Q_C}\right)_{R(int)} \quad (55)$$

Contrails

the factors involving internal rotation, with the exception of internal rotation around the A—C and A—B bonds, drop out of the complete expression. Further, since data are not available concerning the vibrational modes of the complex, it is expedient to assume that

$$\left(\frac{Q'_{AB}}{Q'_{AC}} \right)_v \approx \left(\frac{Q'_A Q'_B}{Q'_A Q'_C} \right)_v = \left(\frac{Q_B}{Q_C} \right)_v \quad (56)$$

This means we assume that, except for the new vibration of A—C and A—B bonds in the cluster, the vibrational modes of the C and B molecules are approximately the same in the cluster as in the free molecules. In view of the lack of knowledge of the vibrational modes in the ion cluster, this assumption appears to be reasonable and allows considerable simplification of the treatment.

Using the expressions derived above, together with the given assumptions, the complete ratio of partition functions can then be written

$$\frac{Q_{AB} Q_C}{Q_{AC} Q_B} \approx SRMVD \quad (57)$$

where

$$S = \frac{\sigma_B \sigma_{Ci}}{\sigma_{Bi} \sigma_C} \quad (58)$$

$$R = \left[\frac{I_{Bi}}{I_{Ci}} \cdot \frac{\left(\begin{smallmatrix} I & I & I \\ x & y & z \end{smallmatrix} \right)_C}{\left(\begin{smallmatrix} I & I & I \\ x & y & z \end{smallmatrix} \right)_B} \right]^{\frac{1}{2}} \quad (59)$$

$$M = \frac{\left[\frac{M_C (M_A + M_B)}{M_B (M_A + M_C)} \right]^{\frac{1}{2}}}{\dots} \quad (60)$$

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$$V = \frac{\text{Sinh} \left(\frac{h\nu_{AC}}{2kT} \right)}{\text{Sinh} \left(\frac{h\nu_{AB}}{2kT} \right)} \quad (61)$$

and

$$D = \left(\frac{r_{AB}}{r_{AC}} \right)^2 \quad (62)$$

Some further simplifications are possible for special cases, and these apply to the conditions of present interest. The fundamental vibration frequencies ν_{AB} are expected to be quite low, and the hyperbolic sine functions can be approximated quite well using only the first terms in a power expansion of the functions. Equation (61) then becomes

$$V = \frac{\nu_{AC}}{\nu_{AB}} \quad (63)$$

From the usual relationship between vibration frequencies and force constants, we have

$$\nu_{AC} = \frac{1}{2\pi} \left(\frac{k_{AC}}{\mu_{AB}} \right)^{\frac{1}{2}} \quad (64)$$

where k_{AC} is the force constant for A—C bond vibration and μ_{AC} is the reduced mass of the system A—C with similar definitions for k_{AB} and μ_{AB} . We have, then,

$$V = \frac{\nu_{AC}}{\nu_{AB}} = \left(\frac{k_{AC}}{k_{AB}} \cdot \frac{\mu_{AB}}{\mu_{AC}} \right)^{\frac{1}{2}} \quad (65)$$

But

$$\left(\frac{\mu_{AB}}{\mu_{AC}} \right)^{\frac{1}{2}} = \left[\frac{M_B(M_A + M_C)}{M_C(M_A + M_B)} \right]^{\frac{1}{2}} = M^{-1} \quad (66)$$

Contrails

Therefore, from Eqs (60), (65), and (66), we have

$$VM = \left(\frac{k_{AC}}{k_{AB}} \right)^{\frac{1}{2}} \equiv K \quad (67)$$

and, finally,

$$\frac{Q_{AB} Q_C}{Q_{AC} Q_B} = SRDK \quad (68)$$

This can be shown more explicitly as follows:

$$\frac{Q_{AB} Q_C}{Q_{AC} Q_B} \approx S \left[\frac{I_{Bi}}{I_{Ci}} \cdot \frac{\begin{pmatrix} I & I & I \\ x & y & z \end{pmatrix} C}{\begin{pmatrix} I & I & I \\ x & y & z \end{pmatrix} B} \right]^{\frac{1}{2}} \left(\frac{r_{AB}}{r_{AC}} \right)^2 \left(\frac{k_{AC}}{k_{AB}} \right)^{\frac{1}{2}} \quad (69)$$

This is the final approximate expression that will be used for the discussion that follows. Although the validity of this expression is limited by the simplifications and assumptions discussed above, it is believed that the more important factors relative to competitive cluster formation are at least partially included in the equation and that use of the equation will result in a definite improvement over the usual treatment, where it is assumed that the clustered molecules are not oriented and rotate freely around all axes in the cluster.

The role and importance of the various terms in Eq (69) will be discussed below after specific examples have been considered.

The Hydronium Ion Model

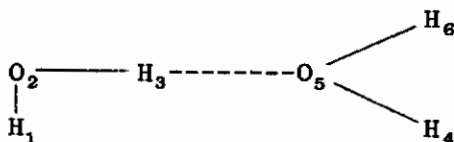
In order to estimate the energy of binding molecules to hydronium ions in clusters, it is necessary to adopt a specific geometrical model for the hydronium ion and to estimate the electronic charge distribution in the ion. The model should reflect the asymmetric nature of the charge distribution in the ion and yet be simple enough to allow tractable calculations to be made.

Contraails

To develop a model of the hydronium ion, the water molecule was considered first. Its geometry is, of course, well known, as are its physical properties. It remained to adopt a charge distribution consistent with its properties and appropriate for the present calculation. Since the energy of interaction between water molecules is important in the present work, this was taken as a criterion for calibrating the present calculations.

Since the major part of the energy of a hydrogen bond is known to be due to electrostatic interactions (and electrostatic contributions are especially important in the present work), it was decided to calculate the electrostatic interaction directly. It did not appear reasonable to use the usual approximations since, in the close approach of hydronium ions and molecules, the assumption of spherically symmetrical ions and point dipoles might be too drastic. Additional difficulties are met in assigning meaningful distances between point charges and point dipoles. Furthermore, Buckingham (1957) has established that, in addition to ion-dipole interactions, ion-quadrupole interactions contribute significantly to the energy of ion-solvent interactions.

Ideally, the interactions of charge distributions in the water molecules should be calculated quantum-mechanically, using proper wave functions. However, for the present purpose, a simpler procedure is dictated. We assume electronic charges to be centered on the atomic nuclei of the atoms in the molecules. The energy of electrostatic interaction between two water molecules in the configuration



was calculated using the expression

$$E_e = \sum_{r=1}^3 \sum_{s=4}^6 \frac{Q_r Q_s}{R_{rs}} \quad (70)$$

Here Q_r and Q_s are the electronic charges on the r th and s th atoms, and R_{rs} is the distance between the atoms r and s .

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Rosenfeld (1964) has recently carried out an electron population analysis of self-consistent-field molecular orbital calculations on an isoelectronic series of oxygen hydrides. His values for the gross electronic charges on the hydrogen and oxygen atoms in water were used, along with the interatomic distances R_{RS} , to calculate the electrostatic interaction of two water molecules. The gross electronic charges on the hydrogen atoms and the oxygen atoms were $Q_H = 0.1329$ and $Q_O = -0.2658$ in units of electronic charge.

For this calculation, and for many of the calculations described below, molecular models of the molecules (and later ions) were constructed. For convenience, the various valence angles were considered to be purely tetrahedral or trigonal; the bond lengths concerned were constructed to scale. When different molecular configurations were possible, a reasonable assumption of an average position was made, and the inter-atomic distances were measured with a ruler. Using Rosenfeld's values, the electrostatic energy calculated from Eq (70) was found to be only -0.90 kcal/mole. This value is too low, probably by a factor > 5 , and was therefore unsatisfactory for our purposes.

To develop a satisfactory model, the work of Duncan and Pople (1953), Rowlinson (1951), and others was considered. Rowlinson's model was finally chosen (modified to place the negative electronic charges on the oxygen nucleus) because it had been used successfully to account for the heat of sublimation of ice at 0°K , for the predicted value of the distance between nearest neighbors, and for our calculation of H-bond energy. The values of electronic charges in water molecules were $Q_H = 0.32$ and $Q_O = -0.64$ electronic charges. The electrostatic energy calculated from Eq (70) was found to be -5.24 kcal/mole.

In order to estimate the energy of the H-bond, dipole-induced polarization and London dispersion energies were calculated for the molecular configuration. These energies were calculated using the formulas

$$E_p = - \frac{\alpha \mu^2}{R^6} (1+3 \cos^2 \theta) \quad (71)$$

(Moelwyn-Hughes, 1961, pp. 303-310) where α is the molecular polarizability of a water molecule, μ is the dipole moment of the water molecule, R is the distance between the molecules, θ is the angle between the dipole moments of the two molecules, and

$$E_o = - \frac{3}{4} \frac{\alpha^2 I}{R^6} \quad (72)$$

Here α is the polarizability of a water molecule and I is the ionization potential of a water molecule.

The total binding energy for a hydrogen bond calculated from Eqs (70, 71, 72) was found to be -6.4 kcal/mole, a value in satisfactory agreement with those found in previous experiments (Pimentel and McClellan, 1960, Chapter 7). Although much more sophisticated treatments have been given, the simplified approach is much more tractable for dealing with complex molecular configurations in ion clusters.

To estimate electronic charges on the atoms of a hydronium ion, as well as for other types of molecules, some systematic approach should be used for all the molecules. An approximate method was thus adopted using the following considerations: Bond dipole moments may be used to estimate charges on the atoms of the bond. Although bond dipole moments are actually quite complex quantities containing contributions from a number of factors, they still indicate the general disposition of electronic charge in bonds. From the definition of dipole moment, $\mu = QR$, where μ is now a bond dipole moment, Q the electronic charge on each atom of the bond, and R the bond distance, Q can be estimated for known μ and R .

Assuming as a first approximation that the charges calculated from bond dipole moments are additive in a molecule, the electronic charges on the atoms in a molecule can then be found. For the water molecule, using $\mu_{\text{O-H}} = 1.53\text{D}$, $R = 0.97\text{\AA}$, we find that $Q_{\text{H}} = +0.328$ and $Q_{\text{O}} = -0.656$. These values are very close to those used above ($Q_{\text{H}} = +0.32$ and $Q_{\text{O}} = -0.64$), which suggests that reasonable estimates of electronic charges can be made in this way.

Quantum chemical calculations have been carried out by Grahn (1962) for a planar model of H_3O^+ , and an electronic population analysis has been made by Rosenfeld (1964). However, it was believed necessary to choose the more generally accepted tetrahedral model rather than the planar one used in the works cited above and to estimate the charges as described in the preceding paragraphs. Rosenfeld found that the oxygen atom was more negative in the H_3O^+ ion than in the H_2O molecule and that the electronic charge on the hydrogen atom was increased by approximately $\frac{1}{3}$ of an electronic charge in the H_3O^+ ion, as compared to that in the H_2O molecule. Using the method outlined above, the charges in the hypothetical molecule H_3O were obtained. Electronic charges of $+\frac{1}{3}$ for each proton were superimposed on the charge distribution for neutral H_3O . The estimated electronic charges are $Q_{\text{H}} = +0.65$ and $Q_{\text{O}} = -0.95$.

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We cannot expect to be quantitatively accurate in the present considerations, but we do strive for order-of-magnitude accuracy and attempt, even in a rough manner, to include factors that appear important. The electric field around an H_3O^+ ion using the above charge distribution is quite different from that of a spherically symmetrical model or from that of a model bearing only $+\frac{1}{3}$ charges on the hydrogen atoms.

Because of lack of pertinent data, O-H distances were assumed to be the same in H_3O^+ as in H_2O . This is certainly not correct, but no large error will be introduced by this assumption. With these assumptions, and that of a tetrahedral H_3O^+ configuration, molecular models were constructed for estimating interatomic distances.

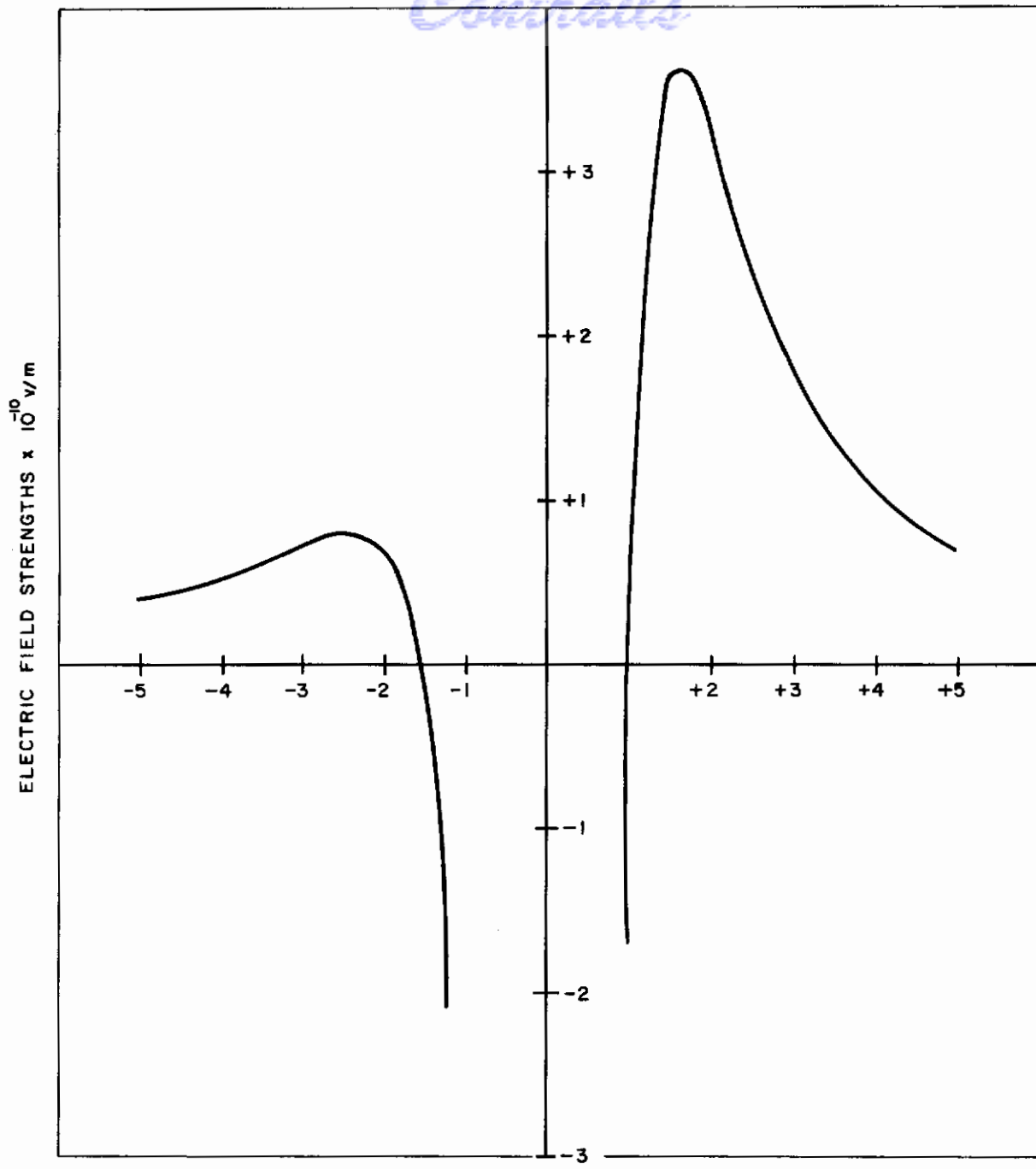
It is a straightforward matter to calculate the electric field strength at some point in space when the distances from the atoms in the H_3O^+ ion are known. A simple but important example concerns the electric field strength along the axis of symmetry of the H_3O^+ ion. With our model, this field strength is found to be

$$F_{\pm} = 1.95 \frac{d \pm 0.333}{(d^2 \pm 0.333d + 1)^{\frac{3}{2}}} - \frac{0.95}{d^2} \quad (73)$$

Here the plus part of the \pm sign refers to the apex oxygen side of the ion; the minus part refers to the hydrogen atom side of the ion; d is the distance in \AA from the oxygen atom along the symmetry axis; and the field strength is given in units of $e/\text{\AA}^2$. Multiplying the value of F found in this way by 1.44×10^{11} gives the field strength in MKS units v/m.

A plot of the field strength along the symmetry axis of the H_3O^+ ion is shown in Fig. 1. The asymmetry around the H_3O^+ ion can be clearly seen in the figure. Due to the asymmetry and the inhomogeneity of the field around the ion, the approximation of using point dipoles for electrostatic calculations would clearly be inaccurate, and our approach of resolving dipoles into atomic charges much more reasonable. Polarization energies using molecular polarizabilities in the calculations would also be open to question. To partially account for this uncertainty, the calculations that are discussed below utilize atomic polarizabilities and the value of the field strength at each atomic position.

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DISTANCE FROM OXYGEN ATOM ALONG SYMMETRY AXIS IN Å UNITS
(+ DIRECTION IS ON H ATOM SIDE OF ION; - DIRECTION ON O ATOM APEX)

Figure 1

ELECTRIC FIELD STRENGTHS ALONG SYMMETRY AXIS OF HYDRONIUM ION
FOR ESTIMATED CHARGE MODEL OF ION

The large value of the field strengths introduces another uncertainty. At field strengths of the order 3×10^{10} v/m, it is not expected that small-field polarizabilities, α , will be accurate; some correction should be included in the calculation. From Coulson's work (1952) it may be inferred that the polarization terms might be multiplied by a factor greater than two. However, in view of the lack of knowledge concerning this situation, no specific correction has been included.

Normal O-----H distances for hydrogen bonds are around 1.8\AA . Placing an O atom 1.8\AA along the symmetry axis gives a $d \approx 1.9\text{\AA}$. Since this distance might be slightly shorter in the ion, we have taken $d = 1.8\text{\AA}$ as a lower limit for our calculations. For typical Van der Waals' radii and with an allowance for using our point atomic charge approximations (discussed below), we have taken 3.4\AA as the upper limit for the distance of closest atomic approach.

While we do not explicitly use point dipoles in our calculations, it is instructive to write down the energy expressions that would result. For a point dipole at 3.4\AA , using the usual expressions for field-dipole interactions and for molecular polarization energies, the following expressions can be derived:

$$E_+ = -3.1\mu - 0.35\alpha \text{ kcal/mole} \quad (74)$$

$$E_- = -6.8\mu - 1.63\alpha \text{ kcal/mole} \quad (75)$$

where μ is to be used in D units and α in units of \AA^3 . It should be remembered that only the portion of the molecular polarizability due to atoms in the vicinity of the ion will be important.

It is immediately obvious that a large dipole moment is of overriding importance if a molecule is to successfully compete with a water molecule for clustering around an H_3O^+ ion. This statement will be elaborated in the discussion below.

The Energy of Clustering Reactions

To estimate the energy change in the clustering of contaminant molecules around an H_3O^+ ion, some new difficulties arise. The energy of interaction of the ion and the molecule can be written as a sum of

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electrostatic, polarization, dispersion, and Van der Waals' repulsive energy terms. The last two types of interaction energy are difficult to estimate. The dispersion energy term, however, would be much smaller than the electrostatic and polarization terms. The ionization potential (or some mean excitation energy) necessary to calculate the dispersion energies is not known and would be difficult to estimate. There does, however, appear to be a reasonable approximate means to get around this difficulty.

As seen in Fig. 1, the field strengths around the H_3O^+ are extremely high. In view of the large field strengths involved, the molecules may be considered to be preferentially oriented in their most favorable positions. For the examples chosen for study (with the exception of the benzene molecule), the most favored position involves the closest approach of one atom in the molecule. Now, we are actually concerned with energy differences between interaction energies of the ions and the contaminant molecules and of the ions and water molecules in Eq (70). Since the energies are small, and since the same number of atoms are involved in the closest-approach part of the interactions, a partial cancellation of these dispersion and repulsion terms is expected when the energy differences are calculated. In the remaining calculations, then, only electrostatic and polarization terms in the interaction energies are considered.

The hydration of hydronium ions is considered first, since there are experimental data available for comparison with the calculated results. The addition of the first water molecule, the completion of the primary solvation shell, and the addition of H_2O to the secondary shell are considered. Then, as an example of the addition of a contaminant molecule, formaldehyde is investigated with respect to addition to H_3O^+ alone, addition to the primary shell, and to the secondary shell.

For the calculation of the partition coefficient terms in Eq (70) it is of great advantage to use a model with the contaminant molecules aligned on the symmetry axis of the H_3O^+ ion. This allows the reduced moments of inertia related to the rotation of the contaminant molecules relative to H_3O^+ to be more easily estimated. The remaining calculations are then concerned with the symmetrical clustering of water, formaldehyde, acetone, methyl chloride, carbon dioxide, carbon disulfide, and benzene.

Clustering of Water Molecules Around Hydronium Ions

The primary solvation shell of hydronium ions in water is now considered to consist of three water molecules hydrogen bonded to the hydronium ion hydrogen atoms (see, for example, Eigen and DeMaeyer, 1959, pp. 64-85). The water molecules are aligned on the tetrahedral axes of the ion. This species appears to be stable enough to be classified as a complex ion, $H_3O_4^+$. Further hydration in the secondary and higher solvation sheaths is more labile. This model was adopted for calculations of the binding energy of water molecules to hydronium ions.

Qualitative considerations suggest that the most stable configuration for $(H_3O^+)(H_2O)$ will have the water molecule aligned along the symmetry axis of the H_3O^+ ion and not along a tetrahedral axis of the ion. However, we first consider tetrahedral alignment in hypothetical complexes in order to facilitate the treatment of the complete primary hydration shell and later consider the model with a water molecule on the symmetry axis of the ion.

The water molecules were assumed to be positioned at the normal hydrogen-bonding distance for water: 1.8\AA for the O-----H distance, 2.8\AA for the O-----O distance, and O-----H-----O was taken as linear. Molecular models were constructed to allow the estimation of all the interatomic distances in the complexes $(H_3O^+)(H_2O)$, $(H_3O^+)(H_2O)_2$, $(H_3O^+)(H_2O)_3$, and $(H_3O^+)(H_2O)_4$. The molecular models were adjusted to give reasonable average positions of the water molecules within the complexes.

The electrostatic interaction between the ion and the water molecules was calculated from

$$E_e = \sum_r \sum_s \frac{Q_r Q_s}{R_{rs}} \quad (76)$$

where the symbols have the same meaning as in Eq (70), the index "r" runs over the atoms of the ion, and the index "s" runs over all the atoms in the water molecules.

The polarization energy was calculated from the following formula:

$$E_p = -\frac{1}{2} \sum_r \alpha_r F_r^2 \quad (77)$$

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Here α_r is the atomic polarizability of the r th atom and F_r is the field strength at the r th atomic nucleus. While some new approximations are introduced by the use of this equation, some difficulties associated with the use of point molecular polarizabilities are avoided. Since the field around the ion is so inhomogeneous, the field strengths at the various atomic positions within the clustered molecules will be quite different, and molecular polarizabilities as such are not applicable. The present approach eliminates this difficulty; however, inherent in the use of this equation is the assumption of point atomic polarizabilities for the atoms within the clustered molecules. Since the field strengths are also inhomogeneous over distances corresponding to atomic diameters, the equation still must be regarded as related to some "average" polarization. The use of the equation, however, should yield distinctly improved results over those that would be found using point molecular polarizabilities.

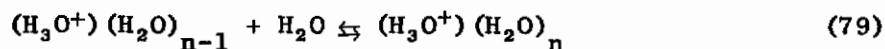
The field strengths, F_r , at the position of atom r , were calculated from the formula

$$F_r = \sum_s \frac{Q_s}{R_{rs}^2} \quad (78)$$

where the index "s" runs over the atoms of the ion. The atomic polarizabilities were taken from the tabulation of atomic refractive indexes listed in Advances in Chemistry Series No. 15 (American Chemical Society, 1955).

For the configuration assumed, the electrostatic interaction between an H_3O^+ ion and an H_2O molecule was calculated to be -20.6 kcal/mole, and the polarization energy was calculated to be -5.7 kcal/mole. This corresponds to an interaction energy of -26.3 kcal/mole (disregarding dispersion and Van der Waals' repulsion energies, as discussed above).

The remaining calculations concerning the hydration of hydronium ions were concerned with the energy of the reactions



where n ranges from 1 to 4. In addition to the interaction of the n th water molecule with the H_3O^+ ion, the interaction of the water molecules in the primary shell was also estimated.

Conclusions

It was calculated that the electrostatic interaction between two water molecules in the primary shell was +0.84 kcal/mole. That is, there is a net electrostatic repulsion between two bound water molecules due to the similar alignment of the molecular dipoles toward the central ion. London dispersion energies were expected to be small and were calculated to amount to only ~ 0.04 kcal/mole. Thus the binding energies accompanying the addition of three water molecules to the hydronium ion to form the primary hydration shell were estimated to be:

<u>n</u>	<u>Energy of adding nth H₂O</u>
1	-26.3 kcal/mole
2	-25.5 kcal/mole
3	-24.7 kcal/mole

The first water molecule added to the secondary shell was assumed to be hydrogen-bonded to one of the molecules in the primary shell. The energies of interaction considered included interaction of the fourth water molecule with the water molecule to which it is hydrogen-bonded (-6.4 kcal/mole), electrostatic interaction with the H₃O⁺ ion (-3.7 kcal/mole), electrostatic interaction with the two other molecules in the primary shell (+0.17 kcal/mole), polarization by the H₃O⁺ ion (-0.36 kcal/mole), and dispersion interaction with the two other water molecules in the primary shell (-0.02 kcal/mole). The total energy of interaction of H₂O with (H₃O⁺)(H₂O)₃ is found to be -10.3 kcal/mole; thus, the energy of binding a water molecule to the ion cluster after the primary shell is filled is significantly lower than binding energies in the primary shell.

It is again pointed out that these energies correspond with a hypothetical set of equilibria in which the water molecules are added to the hydronium ion along the tetrahedral axes of the ion. In actuality, the first water molecule probably adds to the ion along the symmetry axis of the ion. This is expected to be energetically more favorable (see below). The addition of the second and third molecules of water causes a rearrangement of the cluster to new configurations that are energetically more favorable for the complex as a whole, although less energetically favorable for the interaction of any one particular molecule.

From this discussion it can be inferred that, in the actual equilibria, the energy of addition of the first water molecule will be greater than that calculated here, and the energies of addition of the second and third molecules will be less than that calculated here. However, the total

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binding energy of the tetrahedral complex $H_9O_4^+$ should be the same as that calculated here for the hypothetical models, since the final binding energy is independent of the path of reaching the final equilibrium configuration--which is the same in both cases.

The addition of one molecule of water to an H_3O^+ ion along the ion's symmetry axis was treated in a slightly different manner to facilitate comparison with calculations on other kinds of molecules, discussed below. The molecules are assumed to be aligned so that the negatively charged atoms are adjacent to the ion and the positively charged atoms are on the side away from the ion. The molecules considered are also symmetrical with respect to the ion's symmetry axis. At the level of approximation used here, it does not introduce significant error to project the positive charges on the positively charged atoms to a point of "center of positive charge." This center of positive charge is found by taking a charge-weighted average of the positions of positive charge. That is,

$$\bar{X} = \frac{\sum_r Q_r X_r}{\sum_r Q_r} \quad (80)$$

where X_r is the distance of the r th positive charge, Q_r , projected on the symmetry axis. The electrostatic energy is then calculated according to Eq (76) using R_{rs} values calculated in the manner just described.

Assuming a water molecule to be aligned along the symmetry axis of a hydronium ion, on the hydrogen atom side, it was calculated that the electrostatic energy was increased to -25.2 kcal/mole and the polarization energy was increased to -11.5 kcal/mole. The sum of electrostatic and polarization energy for the interaction of one water molecule with a hydronium ion for this configuration was -36.7 kcal/mole. This confirms the qualitative considerations mentioned above that the first water molecule is more firmly bound than are subsequent water molecules added to the cluster.

The results discussed above are in good accord with experimental data in the technical literature. Kebarle and Hogg (1965) and Knewstubb and Tickner (1963) have recently studied the clustering of water molecules around hydronium ions by mass spectrometry. Knewstubb and Tickner used d-c glow discharges in water vapor to generate hydronium ions by the

process



This reaction has been shown to proceed very rapidly (Lampe, Field, and Franklin, 1957). Under their experimental conditions, hydrates of hydronium ions were found up to a size of $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_5$, although Beckey (1960), using field emission techniques, has detected ion clusters up to a size $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_9$.

Knewstubb and Tickner found that the heats of reaction decrease for successive steps of the hydration sequence and drop sharply for the reaction stages beyond H_3O_4^+ , $[\text{H}_2\text{O}^+(\text{H}_2\text{O})_3]$. For thermal ions, or for ions in regions of low field, the equilibrium was well to the side for the completion of the primary hydration shell but probably not for further hydration steps. Increasing the field strengths decreased the stability of the larger clusters and, as the field strengths increased, the water molecules of hydration disappeared in sequence. Under their conditions, at fields of 10^4 v/m, only H_3O^+ was sufficiently stable to be detected.

Knewstubb and Tickner also concluded that the rate constants for the hydration reactions probably increase with successive additions of water molecules, at least up to $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_3$. It was suggested that the requirement for 3-body collisions was most strict for the addition of the first molecule and that the requirement is eased as the reactant ion becomes larger.

Kebarle and Hogg observed a complete set of hydrates, $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$, from $n = 1$ to $n = 8$. Ion intensities had a bell-shaped distribution around a maximum which shifted from $n = 6$ to $n = 4$ as the temperature was raised from 20°C to 45°C . They were able to estimate the heats of hydration for the first three water molecules in the secondary shell to be -20, -24, and -13 kcal/mole. These values are somewhat higher than those we have estimated by calculation. However, they have refined the experimental technique and, using a more elaborate procedure, they have been able to find lower values (private communication, P. Kebarle).

In some similar work on the ammoniation of ammonium ions Hogg and Kebarle (1965) found that the cluster distributions obtained under molecular flow conditions shifted toward lower mass. The higher masses observed under nonmolecular flow conditions appeared to be due to adiabatic cooling of the gas jet.

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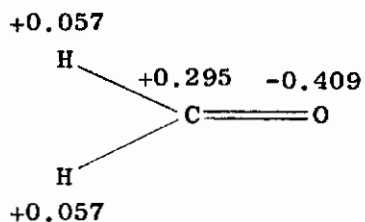
Our calculated results are in qualitative accord with these experimental studies, and the numerical values are probably of the right order. The energies involved in the bonding of molecules other than water into the ion clusters were then considered and are discussed below.

The Energy of Binding Molecules Other Than Water in Hydronium Ion Clusters

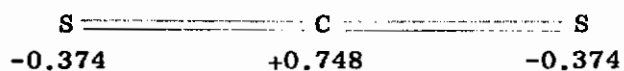
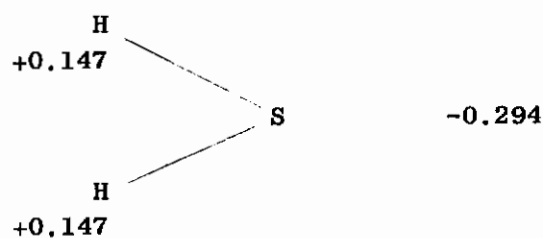
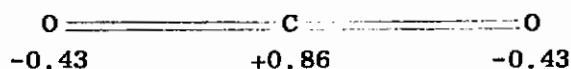
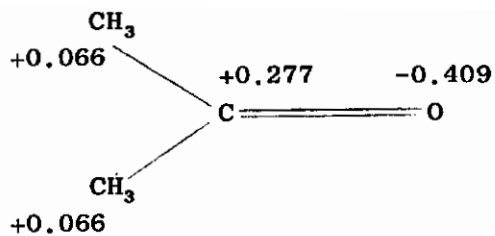
As mentioned above, the calculation of the rotational contributions in Eq (69) is greatly simplified for systems in which the internal rotation is that of two symmetrical coaxial tops rotating relative to each other. For purposes of comparing the relative ability of a series of molecular types to cluster with an H_3O^+ ion, we have chosen molecules that satisfy this criterion of symmetrical rotation. This further requires that we consider only binding with the molecules aligned on the symmetry axis of the H_3O^+ ion. (This was the position of strongest binding, as discussed above, for the interaction of one molecule of water with an H_3O^+ ion.) For comparison with the discussion of different configurations and sizes of ion-water clusters, however, we have also considered several different configurations for the interaction of formaldehyde molecules with H_3O^+ ions.

For the calculation of the strongest bonding of a water molecule to an H_3O^+ ion, the distance of closest approach was assumed to be 1.8\AA . As discussed above, this value was adopted as a lower limit. To gain a general idea of the significance of the present treatment, calculations were also carried out for a distance of closest approach of 3.4\AA . If the same conclusions hold for both sets of calculations, the exact geometry chosen is not too important, and some confidence can be placed on the results.

When the atom most closely approaching the H_3O^+ ion is not an oxygen atom, the distance of closest approach was taken to be 1.8\AA plus the difference between the covalent radius of the atom and that of an oxygen atom. As discussed above, the electronic charges on the atoms in the various molecules were calculated from bond dipole moments and known interatomic distances. The benzene molecule was treated in a different way and is discussed below. The charge values adopted for these molecules were the following:



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As in the calculations on the symmetrical ion-water cluster described above, the positive charges were projected to a center of positive charge on the symmetry axis of the clusters.

For a formaldehyde molecule aligned on the hydrogen atom side of the symmetry axis of the ion at a closest approach distance 1.8Å, the electrostatic energy of interaction was calculated to be -32.8 kcal/mole and the polarization energy to be -11.7 kcal/mole. This gives a total of -44.5 kcal/mole, as compared with the value of -36.3 kcal/mole found above for water. The difference--8.2 kcal/mole when substituted into the exponential factor in Eq (46)--leads to a factor of $\sim 10^6$ in favor of successful

competition of formaldehyde with water for reaction with H_3O^+ . Similar calculations were carried out for an upper limit of atomic approach of 3.4\AA . These calculations lead to electrostatic and polarization energies of -14.4 kcal/mole and an exponential factor of 80. These values will be discussed further below.

For comparison with calculations concerning water molecules, calculations were carried out for interaction of formaldehyde in a tetrahedral configuration with the ion and for attachment in the secondary shell of the cluster. To estimate the many interatomic distances necessary for these calculations, measurements were made on scale molecular models constructed for this purpose.

For the tetrahedral configuration, the electrostatic and polarization energies were calculated to be -20.6 kcal/mole and -6.2 kcal/mole, respectively. The total energy of interaction (-26.8 kcal/mole), compared to the value for the tetrahedral water interaction (-26.3 kcal/mole), leads to an exponential factor somewhat greater than two.

The electrostatic and polarization energies for the interaction of a formaldehyde molecule with an ion cluster with completed primary shell was calculated to be -8.8 kcal/mole. The corresponding value for water was -10.3 kcal. The exponential factor for Eq (46) is about 5×10^{-2} and is unfavorable for successful competition of formaldehyde for attachment in the secondary shell of the ion cluster.

In view of the many assumptions and approximations made, not much importance can be ascribed to the exact numbers obtained. However, it seems reasonable to state that, if formaldehyde is to successfully compete with water for attachment to an H_3O^+ ion cluster, the successful competition must be in the primary shell. Within the primary shell, the smaller the cluster, the more probable the successful competition of formaldehyde with water. This will be discussed further below.

Similar calculations were carried out on acetone, methyl chloride, carbon dioxide, carbon disulfide, hydrogen sulfide, and benzene; the results are shown in Table IV. These molecules were chosen not only to meet the criteria mentioned above but to include a variety of molecular types.

On all molecules but benzene, the calculations were carried out using the methods and approximations described above. Only polarization energy was calculated for the benzene molecule, and it was necessary to use a specific model for the complex. A molecular model was constructed with the hydronium ion on the symmetry axis through the center of the

Table IV

ENERGY OF INTERACTION OF MOLECULES ON SYMMETRY AXIS
OF HYDRONIUM IONS

Molecule	Closest approach 1.8 $\overset{\circ}{\text{A}}$ (kcal/mole)		Closest approach 3.4 $\overset{\circ}{\text{A}}$ (kcal/mole)	
	Electrostatic	Polarization	Electrostatic	Polarization
H ₂ O	-25.2	-10.1 = -35.3	- 9.7	-1.8 = -11.5
H ₂ C=O	-32.8	-11.7 = -44.5	-12.3	-2.1 = -14.4
Me ₂ C=O	-33.6	-16.9 = -50.5	-12.9	-3.6 = -16.5
H ₂ S*	-14.3	-26.1 = -40.4	- 6.7	-6.3 = -13.0
CH ₃ Cl*	-16.3	-17.5 = -33.8	- 8.5	-4.6 = -13.1
CO ₂	-17.2	-11.0 = -28.2	- 4.9	-2.0 = - 6.9
CS ₂ *	-15.0	-26.6 = -41.6	- 6.2	-7.0 = -13.2
Benzene	--	--	--	-2.8

-- means not calculated.

* Corrected for increased size of atom most closely approaching ion
over size of oxygen atom in water.

Contraails

benzene ring. The three hydrogen atoms of the ion were aligned with three (alternate) carbon atoms of the benzene ring. The distance from the benzene molecular plane to the oxygen atom of the ion was assumed to be 3.4Å. All interatomic distances were then directly measured.

There are essentially two different kinds of carbon atoms in this model: the carbon atoms to which the O—H bonds of the ion are pointing, and those atoms remaining to which the O—H bonds do not point. The field strengths were calculated at the nuclear positions of the two different kinds of carbon atoms, and an average value was taken for the molecule as a whole. Using the molecular polarizability for the molecule, the polarization energy was then calculated from $E_p = -\frac{1}{2} \alpha F^2$ to be -2.8 kcal/mole. Alternatively, using $\frac{1}{6}$ of the molecular polarizability as the polarizability of each H—C group, together with the calculated field strengths, the result from our usual method of calculation is again -2.8 kcal/mole.

Because of the anisotropy of the molecular polarizability of benzene, this is not expected to be a numerically accurate result; however, the point can be made that the polarization energy is very small compared to the total energy of interaction of the other molecules considered, and it is very improbable that benzene could compete successfully. In actuality, this may not be the most stable cluster configuration, but the general conclusion is not expected to change.

The use of the detailed model leads to smaller values for the benzene molecule's polarization energy than are found if a point-polarizable-molecule model is used--or, alternatively, if the field is considered uniform and the same as that on the symmetry axis of the H_3O^+ ion. This energy is found by substituting the polarizability component perpendicular to the benzene ring into Eq (75). This is found to be -10.3 kcal/mole. Thus, the use of a detailed model considerably modifies the results obtained from more simplified models and reemphasizes the importance of electrostatic interactions in clustering reactions.

Data in Table IV indicate that particularly polar and/or polarizable molecules can be energetically favored to compete favorably for clustering around an H_3O^+ ion. Nonpolar molecules such as CO_2 or CS_2 , although they exhibit no overall dipole moment, still have large electrostatic interaction energies. CO_2 is predicted to be less energetically favored than water for clustering with an H_3O^+ ion, and CS_2 to be more energetically favored. The important difference between these two cases is due to the fact that the S atoms of CS_2 are much more polarizable than the O atoms in CO_2 . Neutral molecules with no large electrostatic interactions such as benzene, are not expected to compete at all in clustering reactions.

From Table IV it can also be seen that the general conclusions drawn from the calculations for a distance of closest approach of 1.8Å are still maintained at a distance of closest approach of 3.4Å. Thus, the exact geometry assumed is not critical, and the general conclusions are expected to be insensitive to the exact geometries assumed and should, thus, hold for geometries other than those of the particular models assumed.

Since consideration of the preexponential terms in Eq (46) is necessary for the more complete discussion of the relative probabilities for competition of various molecules with water molecules in clustering reactions with H_3O^+ ions, further discussion is delayed until the pre-exponential terms in the equation have been discussed in the next section.

The Effect of Non-Energy Terms on the Probability of Clustering of Molecules Around Hydronium Ions

In addition to the energy of interaction between a molecule and an ion, it is necessary to consider the preexponential terms in Eq (46) in order to estimate the probability of successful competition of a molecule with water for clustering reactions. The preexponential terms were written in Eq (57) as a product of factors S, R, D, and K in Eq (68), and were defined in Eqs (58), (59), (62), and (67).

For linear molecules, such as carbon dioxide and carbon disulfide, the equations defining S and R must be modified. For linear molecules we find

$$S = \frac{\sigma_{Ci} \sigma_B}{\sigma_C} \quad (82)$$

and

$$R = \frac{(I_x I_y I_z)^{\frac{1}{2}}}{I_B I_{Ci}^{\frac{1}{2}}} \quad (83)$$

The various terms as defined herein were calculated using values for principal moments of inertia quoted in Moelwyn-Hughes (1961), bond lengths, and bond angles from The Chemical Society (1958). The calculated factors (dimensionless) are presented in Table V, and their products for each molecule are also included. The products of factors S, R, D, and K enter directly into the equation for the relative probabilities of successful competition for clustering as a multiplicative factor.

Table V

PREEXPONENTIAL FACTORS RELATED TO RELATIVE PROBABILITY
OF CLUSTERING OF CONTAMINANT MOLECULES

<u>Molecule</u>	<u>S</u>	<u>R</u>	<u>D</u>	<u>K</u>	<u>SRDK</u>
H ₂ O	1	1	1	1	1
H ₂ C=O	1	6.6 x 10 ⁻²	1.4	1	9 x 10 ⁻²
Me ₂ C=O	1	4.2 x 10 ⁻³	2.9	1	1 x 10 ⁻²
H ₂ S	1	0.38	1.4	1	5 x 10 ⁻¹
CH ₃ Cl	1	2.1 x 10 ⁻²	2.1	1	4 x 10 ⁻²
CO ₂	2	3.3 x 10 ⁻²	1.1	1	7 x 10 ⁻²
CS ₂	2	3.2 x 10 ⁻³	1.4	1.4	1 x 10 ⁻²
Benzene	2	1.1 x 10 ⁻³	1	1.4	3 x 10 ⁻³

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The factor S related to symmetry numbers for external and internal rotations will usually not contribute an entropy term for most molecules. The only exceptions are molecules such as CO₂, CS₂, and benzene, where rotational degrees of freedom are lost when a molecule is aligned in an ion cluster. In any case, this factor will be small and will not materially affect order-of-magnitude results.

From Table V it can be seen that the factor R, related to rotational partition functions, contributes significantly to Eq (57). It is often considered that, in loose ion clusters, the molecules are loosely bound and still rotate within the cluster with all rotational degrees of freedom. In the present work we have assumed that the added molecules are aligned in the most energetically favorable positions within the cluster, because of the high field strengths and the directional nature of the fields around the hydronium ions. This causes the freezing of some rotational degrees of freedom and results in values of R that are unfavorable for successful competition for molecules larger than the water molecule.

From Eq (59) it is indicated that R can be factored into two components: One relates to internal rotation around the bond binding the molecules to the ion, and the other relates to the free rotation of the isolated molecules. The term relating to internal rotations

$(I_{Bi}/I_{Ci})^{\frac{1}{2}}$ covers a relatively small range of numerical values. For a range of molecular sizes from a water molecule to an infinitely large molecule, this factor ranges only from 1 to somewhat less than 2. This factor thus is not of much numerical importance in determining order-of-magnitude probabilities for successful clustering. The remaining factor in R, however, is of great importance.

The factor $[(I_x I_y I_z)_C / (I_x I_y I_z)_B]^{\frac{1}{2}}$ is the most important in the preexponential term of Eq (46). Since the subscript C refers to the water molecule and B to a competing molecule, the factor will always be less than 1 for molecules larger than water. From Table V it is indicated that, except for the smaller molecules, R is usually less than 10⁻². For larger molecules, this factor can be orders of magnitude smaller and extremely unfavorable for successful competition for clustering.

The factor D is related to the distances between the centers of mass of the added molecules and the ions. For large clusters, this factor approaches 1 as cluster size increases. For smaller clusters, the factor is fairly small and favors successful competition of molecules

larger than water. However, from Table V, it is indicated that this factor is not numerically of order-of-magnitude importance.

The factor K is related to the force constants for the bond binding the added molecules to the ion. Since little is known of actual force constants, we have assumed that the force constants for all hydrogen-bonding molecules are the same and, therefore, $K = 1$. For nonhydrogen-bonding molecules, we have assumed that the force constant is half that for hydrogen-bonding molecules and, therefore, $K \approx 1.4$. This factor is more favorable for successful competition for molecules more loosely bound than water molecules. However, for looser binding, the energy of binding will be less, and the increase in K will be more than offset by the decrease in the exponential factor in Eq (46).

The product of S, R, D, and K factors is also shown in Table V for a series of different molecular species. For successful competition of a molecule for clustering reactions, the exponential energy factor probably must be at least 10^2 in order to outweigh the unfavorable preexponential terms. This means that, for these molecules to successfully compete with water molecules in clustering reactions, they must be more strongly bound than is a water molecule by at least ~ 2.8 kcal/mole.

The preexponential factor decreases strongly with molecular size (moments of inertia) and points out the desirability of breaking down larger molecules to smaller polar fragments if they are to successfully compete in clustering reactions.

Other Considerations Regarding the Clustering of Contaminant Molecules Around Ions

In the foregoing discussion of the factors important in competitive cluster reactions, chemical systems in equilibrium were considered. Under some conditions it appears that small polar molecules can be incorporated into clusters around hydronium ions. In actual dynamic systems with complex chemical composition, some further considerations are necessary.

Due to the relatively large concentration of water expected in manned space-cabin atmospheres and to the large proton affinity of water, the majority of positive ions will be hydronium ions (or clusters). Several classes of compounds, however, have higher proton affinities than water. The collision of such a compound as an alcohol with a $(H_3O^+)(H_2O)_n$ cluster could result in the transfer of a proton or in the rearrangement of the

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cluster to incorporate the alcohol. This could take place as follows: For a stable $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$ cluster, the protons on hydronium ion have been considered fixed. The proton or hydronium ion should, however, behave similarly to a proton in water solution and exhibit a great mobility. The collision of an alcohol molecule with a $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$ cluster could lead to a series of short electron shifts, and a proton or hydronium ion could appear at the position of the alcohol molecule. The proton may be transferred to the alcohol and the cluster could rearrange to effectively incorporate the alcohol into the primary cluster shell.

Because of the many unknowns, it is difficult to assess the role of such reactions in a complex actual situation. Bonding in the secondary shell of $(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_n$ is unlikely for contaminant molecules since hydrogen bonding would probably be the main factor. In order to enter this shell in preference to water, the contaminant molecule would have to have hydrogen bond strengths 2 to 3 kcal/mole greater than water to offset an unfavorable preexponential factor. This is highly unlikely. The effective mobility of the proton in a colliding cluster, as just discussed, could provide a mechanism for incorporating those molecules into the primary shell that are energetically favored even if the primary shell is filled before collision and subsequent rearrangement.

Clustering around other ions in an actual system could also occur. Similar considerations as those discussed above should still apply. The competition of contaminant molecules with water molecules for clustering around ions other than hydronium ions should still be governed by essentially the same factors.

So far, only equilibrium clustering reactions have been considered in the absence of a collecting electric field. In the presence of an electric field, the ion temperatures are increased and equilibrium cluster sizes are smaller than they are in the absence of a field. The temperature increase would also be expected to have an effect on the competition probabilities. Increasing T in the exponential factor of Eq (46) decreases the weight of the exponential factor in the equation. Thus, the molecules energetically favored for cluster formation will be somewhat less favored in the presence of higher fields and/or higher temperatures.

In spite of the fact that many molecules are not expected to compete successfully with water molecules in cluster formation, the large binding energies for some of the compounds listed in Table IV suggest that these molecules might be collectable in the absence of water. From the previous

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discussion, a possible sequence of steps for the electrostatic collection of contaminant molecules may be suggested. Most of the water present should be removed, and then the ions must be injected into the system. In the presence of ions, water, and oxygen, an oxidizing atmosphere would exist. At this step, an attempt should be made to fragment or oxidize those neutral molecular species that could not normally compete in clustering reactions to smaller polar species that could be clustered.

The water remaining in the system might be reduced to a low enough concentration to afford electrostatic collection of contaminant molecules. First, low temperatures and low collecting electric field strengths would favor the formation and collection of larger $(H_3O^+)(H_2O)_n$ clusters. The gas would be cooled to a low temperature (perhaps by adiabatic expansion), and a collecting field of low strength would be used to collect the ions. At this stage, water would be preferentially collected. This procedure should be repeated until the water concentration is reduced to the desired level.

The next step would involve the electrostatic collection of contaminant molecules. Smaller clusters are more likely to collect a contaminant molecule, since addition to the primary shell is more favorable than addition to larger clusters. Increasing the collecting field strength could then decrease the $(H_3O^+)(H_2O)_n$ cluster sizes to an optimum value for the clustering of contaminant molecules.

Section VII

CONCLUSIONS AND RECOMMENDATIONS

From the foregoing considerations the use of clustering to purify cabin atmospheres will probably be applicable to a restricted number of contaminants under specially favorable conditions. The use of charge exchange with reagent ions followed by collection appears far more inclusive, but this course has more uncertainties due to lack of detailed knowledge about ion molecule reactions. Further evaluation of these concepts would best be obtained by direct experiment, which is now recommended.

It is proposed to restrict an ensuing experimental program to semiempirical tests of feasibility. This will require the development of specific ion sources and the choice of compositions of synthetic atmospheres. Tests of any mode of collection will progress in atmospheric composition from the most favorable conditions possible toward an atmosphere of more realistic composition until difficulties are encountered that are regarded as unsolvable within the scope of this research.

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