PHYSICS OF AIR IONS

Most matter in the universe is "ionized". In the high vacuum of space, atoms and molecules are present in excited energized states and possess electrical charges. By contrast, most matter on earth (and in the earth's atmosphere) is un-ionized. A source of sufficiently high energy is required to induce ionization and separation of charge. Energy can be supplied by either natural or artificial (anthropogenic) sources, as derived from nuclear, thermal, electrical, or chemical processes. Specific energy sources include: cosmic radiation; ionizing (nuclear) radiation from earth sources, UV light, frictional charging by wind, water droplet breakup (waterfalls, showers), electrical discharge (lightning), combustion (fire, burning gas jets, engines), and strong electrical fields (corona).

Human additions and subtractions of ions in air environments include:

- Combustion processes: simultaneous generation of both ions and particles, the latter also tend to scavenge ions, e.g. smoking, candles.

- Indoor environments: synthetic décor and artificial ventilation can deplete space charge.

- Other situations: transmission lines produce ion plumes; video displays deplete local charges.

- Specific devices: produce air ions for air cleaning or charge neutralization.

Engineered devices for artificial air ionization are more controllable than natural processes. Recent developments in large ion generator design and operation have led to the commercial availability of energy-efficient units which can now produce controlled outputs of specific ions on demand, while minimizing the formation of undesirable byproducts, such as ozone. Ion generators have been used in a number of applications to control surface static charges. Air ionizers (ion generators) are being used more extensively to clean air in indoor environments.

Ionization is the process or result of a process whereby an electrically neutral atom or molecule acquires either a positive or negative electrical charge. Ionization occurs when energy in excess of the electron potential is absorbed by an atom yielding a free electron and a positive atom. The ions of the atmosphere have been of scientific interest for more than a century (10). The term "air ions" refers broadly to all airborne particles which possess electrical charge and whose movement is influenced by electric fields (11).

The chemical evolution of air ions, whether created naturally outdoors, or artificially indoors, depends on the composition of each environment, and especially on the types and concentrations of trace species. Specific reactions depend upon the physical properties of individual atoms and molecules, e.g. ionization potential, electron affinity, proton affinity, dipole moment, polarizability, and chemical reactivity. The primary positive ions, N_2^+, O_2^+, N^+, and O^+, are very rapidly converted (microseconds) to protonated hydrates, $H^+ \cdot (H_2O)^n$ (n < 10), while the free electrons quickly attach to oxygen to form the superoxide radical anion, $^3O_2^-$, which also can form hydrates (12). These intermediate species are collectively called "cluster ions".

Cluster ions can react further with trace volatile and particulate constituents. A cluster ion may collide with as many as 1,000,000,000,000 (10^{12}) molecules in air at ground level during its brief (~ one min) lifetime (11). Chemical-, nuclear-, photo-, and electro-ionization processes are used to separate and identify chemical spectra. Molecular disassociations and reactions in the gas phase and on particulate surfaces greatly complicate overall reaction schemes in real-world atmospheres. Ion chemistry continually changes through chemical reactions, molecular rearrangements, and growth of molecular ion "clusters" and ionically charged particulates. The protonated hydrates may be about 1 nm (0.001 um) in diameter and have electrical mobilities of 1-2 cm^2/V-s. The ion clusters may be about 0.01 - 0.1 um, with mobilities of 0.3 - 1 x 10^{-6} m^2/Vs. The later are larger in physical size, but orders of magnitude less electronically mobile. By comparison, common fog droplets or dust particles may range up to 10um in size.

The combined presence of ions and electrons results in space charge, i.e. the total free unbalanced charge existing in the atmosphere. Both unipolar positive or negative space charge densities can be measured. Fair weather values for air ions at sea level are ~200-3,000 $ions/cm^3$ of both polarities. Small ions increase significantly during rainfall & thunderstorms due to natural activation: negative ions may increase to 14,000 $ions/cm^3$, while positive ions may increase to 7,000 $ions/cm^3$. The ratio of positive to negative air ions at ground level normally is about 1.1-1.3, decreasing to about 0.9 following certain weather events. Smoking one cigarette can reduce air ions in a room to ~10-100 $ions/cm^3$.

Small ions and ion clusters have numerous opportunities for collision and reaction with any air impurity, i.e. essentially any and all constituents in the atmosphere. They are removed from the atmosphere through reaction with other volatile constituents, or through attachment to larger particles by diffusional charging and field charging. Lifetimes of ions are shorter, the higher their concentrations (or conversely, lifetimes are longer, the lower their concentrations, i.e. less chance of hitting something). The lifetimes of air ions are strongly dependent on humidity and temperature, and the relative concentrations of trace volatile and particulate species. Typical lifetime of a naturally generated small air ion in clean air is ~100-1000 s.

CHEMISTRY OF AIR IONS.

"Oxygen" is required by most life forms. There is a dynamic balance, however, between generation of any oxygen species necessary for life on one hand and protection against its toxic effects on the other (13, 14). Four oxidation states of molecular dioxygen are known: $[O_2]^n$, where n = 0, +1, -1, and -2, resp., for dioxygen, dioxygen cation, superoxide anion, and peroxide dianion (symbolically expressed as $^3O_2$, $^3O_2^+$, $^3O_2^-$, and $^3O_2^{-2}$. In addition, "common" oxygen in air, $^3O_2$, is in a "ground" (not energetically excited) state. It is a free "diradical" having two unpaired electrons. The two outermost pair of electrons in oxygen have parallel spins indicating the "triplet" state (the preceding superscript "3", usually omitted for simplicity). Oxygen itself is a common terminal electron acceptor in biochemical processes. It is not particularly reactive, and by itself does not cause much oxidative damage in biological systems. It is a precursor, however, to other oxygen species that can be toxic, including: superoxide anion radical, hydroxyl radical, peroxy radical, alkoxy radical, and hydrogen peroxide. Other highly reactive molecules include: singlet oxygen, $^1O_2$, and ozone, O_3.

Ordinary oxygen does not react well with most molecules, but it can be "activated" by the addition of energy (naturally or artificially derived; electrical, thermal, photochemical, or nuclear), and transformed into reactive oxygen species (ROS). Transformation of oxygen into a reactive state upon addition of a single electron is called reduction (Eqn. 1). The donor molecule that gave up the electron is oxidized. The result of this monovalent reduction of triplet oxygen is superoxide, $O_2^{\cdot-}$. It is both a radical ($\cdot$, dot sign) and an anion (charge of -1).

$$O_2 + e^- \rightarrow O_2^{\cdot-} \tag{1}$$

The superoxide radical anion is quantitatively the most important radical formed in humans – a 70 kg adult synthesizes at least 10 kg(!) per year (15). Approximately 98% of the oxygen consumed by respiring mitochondria is converted to water; the remaining 2 % results in superoxide formation through side reactions in the respiratory chain (16). Human cells constantly produce superoxide (and the reactive molecules derived from it) as an "antibiotic" against invading microorganisms. The biology of small air ions and oxygen radicals has been reviewed (Krueger and Reed, 1976). Superoxide also acts as a signaling molecule, along with $NO^{\cdot}$, to regulate many cellular processes. Under biological conditions, it reacts with itself to produce hydrogen peroxide and oxygen through a reaction (Eqn. 2) known as "dismutation", which can be spontaneous, or catalyzed by superoxide dismutase ("SOD").

$$2\,O_2^{\cdot-} + 2\,H^+ \rightarrow H_2O_2 + O_2 \tag{2}$$
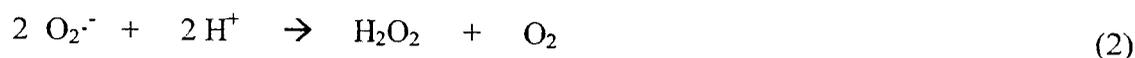
Superoxide is both an oxidant (electron acceptor) and a reductant (electron donor). It is important in the production of the highly reactive hydroxyl radical ($HO\cdot$), as catalyzed by metallic ions and/or by sunlight. Superoxide reacts with nitric oxide radical ($NO\cdot$) in vivo producing peroxynitrate ($OONO\cdot$), another highly reactive oxidizing molecule. Superoxide can undergo further reduction to peroxide (O_2^{-2}), an activated form of oxygen, usually described as "hydrogen peroxide" (H_2O_2), in aqueous systems, where it is also necessary for health.

Superoxide is the dissociated form of a weak acid, the hydroperoxyl radical, $HO_2\cdot$. In aqueous systems, the relative proportions of these two species depend upon pH, and the appropriate equilibrium constant. Superoxide also can be formed by negative air ionization (17). The generation of low concentrations of hydrogen peroxide in wet air subjected to negative air ionization also has been confirmed (18, 19).

In the absence of metallic impurities, a solution of superoxide in strong alkali can be kept in the refrigerator overnight. By contrast, superoxide ion clusters in air react rapidly with airborne particulates and volatile organic species. While hydrogen peroxide is an oxidizing agent, the combination of hydrogen peroxide and superoxide (Eqn. 3) yields a much more reactive species, the hydroxyl radical, one of the strongest known oxidants.

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + OH\cdot + OH^- \tag{3}$$
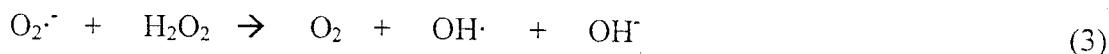
Identifications of the individual chemical species that might be involved in chemical reactions in air environments are not trivial. Modeling of the reaction scheme may involve dozens of homogeneous and heterogeneous reactions amongst species including those mentioned above.

REACTIVE OXYGEN SPECIES.

Oxygen, superoxide, peroxide, and hydroxyl species are all "Reactive Oxygen Species" (ROS), that can participate in a potpourri of oxidation-reduction reactions in both gaseous and aqueous phases (8, 20, 21). These active species are significant in the atmospheric destruction of organics, the removal of particulates, the formation of "smog", and the destruction of ozone (O_3). The hydroxyl radical is key to the tropospheric destruction of volatile organic compounds through a series of complex chemical reactions involving oxidation (abstracting electrons from organic compounds), which in turn can react with other organic molecules in a chain reaction.

The chemistries of reactive oxygen ions are found from "inner" to "outer" space. Solid-state sensors of the SnO_2 type, commonly used to "sense" trace gases, are affected by chemisorption of oxygen and water vapor. At sufficiently high operating temperature, O_2 from air is adsorbed onto crystalline surfaces having negative charges. Donor electrons in the crystals are then transferred to the adsorbed O_2 forming superoxide radicals that react with CO, hydrocarbons, and other trace gases or vapors. The resulting liberation of electrons decreases the surface charge and produces an increase in conductance that is then "sensed". Similar chemistries are encountered in photocatalytic oxidation processes (22, 23), solid oxide fuel cells, and various nonthermal plasma processes.

Space scientists have postulated that the unusual reactivity of the Martian soil and the absence of organic compounds are explained by ultraviolet radiation which causes oxidation of metal atoms and the creation of reactive oxygen species on the soil grains (24). The three radical species most commonly formed by UV in the presence of oxygen are: $O^{\cdot-}$, $O_2^{\cdot-}$, and $O_3^{\cdot-}$, sometimes collectively referred to as Reactive Oxygen Species (ROS). $O_2^{\cdot-}$ is the least reactive, the most stable, and the most likely oxygen radical species to be encountered at ambient temperatures on earth. Its chemistry involves reaction with water to form hydrated cluster ions (25). Two associated species, hydroperoxide and hydroxide, are capable of oxidizing organic molecules. Superoxide reacts with water (Eqn. 4) to produce oxygen, and perhydroxyl and hydroxyl radicals, which are easily capable of oxidizing organic molecules.

$$2\ O_2^{\cdot-}\ +\ 2\ H_2O\ \rightarrow\ O_2\ +\ HO_2^{\cdot-}\ +\ OH^{\cdot-} \tag{4}$$
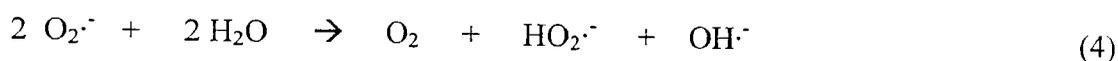
Superoxide may also react directly with ozone to form hydroxyl radicals (Eqn. 5).

$$2\ O_2^{\cdot-}\ +\ O_3\ +\ H_2O\ \rightarrow\ 2\ O_2\ +\ OH^-\ +\ OH^{\cdot} \tag{5}$$
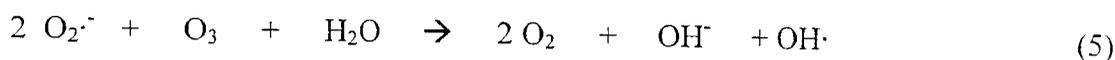
A composite scheme (Eqn. 6) involving several of the reactions described above might be postulated in which superoxide, generated by air ionization, causes the oxidation of volatile organics associated with airborne particulates having metallic inclusions:

$$C_xH_y\ +\ (x + y/4)\ O_2\ \rightarrow\ x\ CO_2\ +\ (y/2)\ H_2O \tag{6}$$
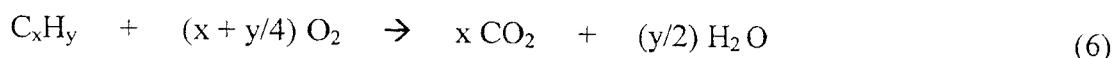
This is a simplistic representation. For any given reactive oxygen species (ROS), there exists some confirmed or postulated reaction scheme for interconversion to any of the other species.

The speciation of individual VOCs, both before and after air ionization, i.e. the disappearance of parent species and the formation of byproduct species, other than carbon dioxide and water, has been speculated upon and modeled (26, 27, 28, 29). The impact of electron-driven chemistry was the subject of a recent workshop (30). It was stated to be "well-known" that non-thermal, gas-phase plasmas that are electronically generated at ambient temperatures and atmospheric pressure, can destroy low concentrations of VOCs. Destruction of ten VOCs (10-100 ppmv) at ambient temperature and atmospheric pressure in a packed-bed pulse corona reactor also has been reported (31). Destruction and removal efficiencies (DREs) were roughly estimated by chemical ionization potential. Ionization and other corona processes were particularly applicable to treating air containing relatively low initial concentrations (<100 ppmv – 10 ppbv). Chemical compounds that are reported by a number of private and governmental researchers to be amenable to treatment, i.e. to be chemically altered or destroyed by air ionization or allied processes, represent a diversity of chemical compounds (Table I).

Table I.   Chemical Compounds Amenable to Treatment by Air Ionization (*).

No.	Chemical	MF	No.	Chemical	MF
1	Carbon monoxide	CO	16	Naphthalene	$C_{10}H_8$
2	Nitrogen Oxides	NO, NO_2	17	Ethylene	C_2H_4
3	Ammonia	NH_3	18	Pinene (α-)	C_8H_{19}
4	Methane	CH_4	19	Formaldehyde	CH_2O
5	Ethane	C_2H_6	20	Acetaldehyde	C_2H_4O
6	Butane	C_4H_{10}	21	Methyl Alcohol	CH_4O
7	Pentane	C_5H_{12}	22	Methyl Ethyl Ketone	C_3H_8O
8	Hexane	C_6H_{14}	23	Methylene Chloride	CH_2Cl_2
9	Cyclohexane	C_6H_{12}	24	Trichloroethane (1,1,1-)	$C_2H_3Cl_3$
10	Benzene	C_6H_6	25	Trichloroethane (1,1,2-)	$C_2H_3Cl_3$
11	Toluene	C_7H_8	26	Carbon Tetrachloride	CCl_4
12	Xylene (o-,m-,p-)	C_8H_{10}	27	Tetrachloroethylene	C_2Cl_4
13	Trimethylbenzene, 1,2,4-	C_9H_{12}	28	Hexafluoroethane	C_2F_6
14	Ethylbenzene	C_8H_{10}	29	FC-12B	$CClBrF_2$
15	Styrene	C_8H_8	30	CFC-113	$C_2Cl_3F_3$

(*) Reported treatment efficiencies vary with initial concentration, relative humidity, and oxygen content.

Air ionization is expected to follow similar mechanisms, involving both bipolar ions, and free radicals, to oxidize organic compounds to intermediate byproducts and eventually to terminal products of carbon dioxide and water. Four processes involving reactions with air ions include: (i) recombination with other air ions, (ii) reaction with gaseous molecules, (iii) attachment to larger particles, and (iv) contact with a surface. The former two processes may be involved in the removal of volatile organic compounds; the latter two processes may be involved in the removal of particulate matter.