The Montreal Protocol

Cha-am Jamal

http://chaamjamal.com

The Montreal Protocol subsumes that without human intervention the amount of ozone in the stratosphere is invariant and that a decline in ozone over time is a trend and not part of long run cyclical phenomenon. The observed depletion is thus assumed to be man-made and the causative agent is identified as CFC. As a result of these conclusions a global ban on Freon refrigerants was hastily issued. The ban and its rationale are controversial.

The Protocol has caused hundreds of billions of dollars in economic losses worldwide and at the same time it has created a black market for Freon of which the news media have taken note. News reports portray the Montreal Protocol as good and the black market as bad. A close examination of the data raises serious questions as to the validity of this judgement.

The ultraviolet spectrum in incident solar radiation comes in three frequency bands. The high energy band (200-240 nanometers in wavelength) and the medium energy band (240-300 nanometers in wavelength) are harmful to living matter and are absorbed in the ozone layer while the low energy band (300-480 nanometers in wavelength) reaches the earth's surface and causes tanning. Ozone plays a role in the absorption of harmful UV radiation. It is both created and destroyed in the absorption process.

The high-energy band UV is absorbed by oxygen molecules. The energy absorbed causes the oxygen molecule to break apart into extremely reactive oxygen atoms. A subsequent chance collision of these particles with other oxygen molecules causes the formation of ozone. The ozone thus formed then absorbs the medium-energy UV band and disintegrates back into oxygen. The UV absorption process is a cyclical one that begins and ends with oxygen. Ozone is a transient intermediate product of this process. Incidentally, these absorption reactions convert UV energy to heat and are responsible for relatively high temperature of the stratosphere.

The reason that there is any ozone accumulation at all in the stratosphere is that, of the three reactions, the second is the slowest. Sunset finds the stratosphere with an excess of single oxygen atoms still looking for a date with an oxygen molecule. Overnight, with no radiation to destroy their product, these particles build up an inventory of ozone whose destruction will begin anew at sunrise. There is therefore, a diurnal cycle in the ozone content of the stratosphere whose amplitude, incidentally, is of the same order of magnitude as reported ozone depletion that caused Montreal Protocol to be invoked.

A longer but irregular cyclical pattern in stratospheric ozone coincides with the sunspot cycle. The period is approximately eleven years. It has been as long as 17 and as short as 8 years. High-energy band UV increases by 6 to 10% during periods of high sunspot activity but the medium-energy UV emission is largely unaffected. Therefore, high sunspot activity favors ozone accumulation and low sunspot activity is coincident with ozone depletion. These changes have to do with solar rather than human activity.

A somewhat similar pattern exists in the case of polar ozone holes. The UV induced reactions described above occur only over the tropics where sunlight is direct. Ozone is formed over the equator and not over the poles. Equatorial ozone is distributed to the poles by the polar vortexes. These are very large hurricane-like roughly circular wind formations around each of the poles. They exist only in the upper atmosphere where there is no weather but where there is ozone. The shape and position of the vortex varies seasonally and also shifts over a longer time cycle. Under certain conditions and in certain seasons each vortex blows ozone from the equator to the pole. Under other flow patterns the vortex does not distribute ozone to the pole. The latter state of nature becomes manifest as an ozone hole. These holes come and go by cyclical changes in the polar vortexes. CFCs or other artificial devices are neither necessary nor sufficient to explain the ozone hole phenomenon.

The case against CFCs is that when they get to the stratosphere by diffusion, they absorb high-energy band UV and form unstable and reactive chlorine atoms. The chlorine atom particles then participate as catalytic agents to convert ozone back to oxygen. In other words they mediate the reaction between atomic oxygen particles and ozone. It is alleged that the destruction of ozone by this mechanism exposes the surface of the earth to dangerous levels of medium-band UV because there is not enough ozone in the stratosphere to absorb them. Although these reactions can be carried out in the chemistry lab, there are certain rate constraints that make them irrelevant in the stratosphere.

The air up there in the stratosphere is rather thin, containing less than one percent of the molecular density of air at sea level. It is not easy for a molecular particle in random thermal motion to find another particle to react with. Photochemical reactions occur instantaneously while those that require a collision of two particles take longer. This difference in the reaction rate is the reason that ozone accumulates overnight and why there is an inventory of ozone in the ozone layer.

The atomic oxygen particles that react with oxygen molecules to form ozone could in theory react with an ozone molecule instead and cause its destruction or it could react with another atomic oxygen particle and form oxygen instead of ever forming any ozone. Some of the oxygen atoms do behave in this manner but these reactions proceed too slowly to be important to the chemistry of the stratosphere.

The reason is that the stratospheric chemicals in question exist in minute quantities. One in a million particles is an ozone molecule or an atomic oxygen particle and one in a billion is CFC or chlorine generated from CFC. The accidental collision between chlorine atoms and ozone molecules or between chlorine atoms and oxygen atoms are rarer than those between two oxygen atoms or that between an oxygen atom and an ozone molecule. Therefore the latter collisions are more important to ozone depletion than those mediated by chlorine.

Considering that more than 200,000 out of a million molecular particles in the stratosphere are oxygen molecules it is far more likely that charged oxygen atoms will collide with oxygen molecules rather than with each other or with ozone. Therefore ozone rather than oxygen is formed. Ozone formation is a rate phenomenon. Since chlorine atoms are a thousand times rarer in the stratosphere than atomic oxygen particles, it is not likely that chlorine’s mediation in short circuiting ozone generation will occur sufficiently fast to be important. Nature already contains an ozone destruction mechanism that is more efficient than the CFC mechanism but ozone forms anyway.

All of the ozone depletion and ozone hole data may be explained in terms of natural processes. The explanation offered by the CFC theorists and the Montreal Protocol is a redundant innovation and in any case it suffers from deficiencies having to do with rate phenomena. In other words, these reactions are too slow to be important.

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