Saving Stratospheric Ozone: Putting the Problem in Perspective and Evaluating Hydrohalocarbons and their Mixtures as Potential Solutions

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Dedicated to our Planet Earth and
to Pandora's Capture of HOPE.

Pandora, according to the Greeks, was the first mortal woman. She ignorantly released all mankind's ills into the atmosphere.

Another version of the legend has her losing all mankind's blessings except Hope.

The former (and older) version cannot be correct, as discussed in this paper. Strong evidence supports the latter version of the legend.

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ABSTRACT

Stratospheric ozone depletion by halocarbon gases is reviewed. Some insight is offered to explain the technical and political difficulties currently facing industrial producers and end use consumers. Industry estimates that 40% of the ozone destruction caused by halocarbons from the United States is a result of air conditioning and refrigeration.

A partial solution employing mixtures of gases relatively harmless to the ozone layer is investigated to replace refrigerant fluids currently in use. Computer subroutines developed at the National Institute of Standards and Technology for modeling mixtures using a semi-empirical equation of state are utilized to generate results. Superior properties are predicted for an application defined within the temperature range of human comfort. Benefits and shortcomings are discussed that are both specifically applicable to this approach and generally applicable to the development of replacements.

Introduction

Chlorofluorocarbons (CFCs) are the working fluids in modern refrigeration and find widespread applications as foaming agents for plastics. The scientific community agrees that CFC gases present a chemical risk to mankind by acting in a chain reaction that decomposes stratospheric ozone. It is this ozone that absorbs shorter wavelength ultraviolet light that otherwise might reach earth's surface. **Figure 1** compares the intensity of UV radiation at the surface of earth's atmosphere with the intensity at sea level. Ozone is the only molecule present in sufficient quantities in the atmosphere capable of absorbing in this electromagnetic region.

A spectrum of ill effects of UV light has been postulated. Direct effects include increased incidence of cancer and cataracts and the suppression of the human immune response system. Indirect effects range from significant reductions in some agricultural crop yields to the widespread destruction of plankton, the base of the ecological food chain and a major source of atmospheric oxygenation.

Chlorofluorocarbons also increase "the greenhouse effect." Basically, molecules in the troposphere that have absorbances in the infrared are transparent to higher energy sunlight, but block lower energy reflected heat from diffusing back into outer space. Global warming and its associated ramifications are covered in the literature (for example, **(4)**). Chlorofluorocarbons have been implicated as contributors to this possibility. Although their concentrations are much lower than CO_2, the suspected major contributor, their effective extinction coefficients are orders of magnitude greater and they contribute to this problem by trapping at least 15% **(5)** of the heat causing global warming.

A third concern that pertains to air conditioning and refrigeration is the improvement of energy efficiency. Any energy that is used to accomplish a task beyond the absolute minimum required by the laws of thermodynamics is generally not recoverable. Engineers and chemists have tended to overlook the fact that the Carnot Cycle is not always the most efficient cycle for refrigeration. Besides enhancing the problems discussed by requiring larger systems, lower efficiency is a source of increased waste and toxicity. Poor energy efficiency also directly compounds the problem of global warming by increasing CO_2 production through additional combustion of fossil fuels. Although some of us may have forgotten that world energy reserves have continued to decline even as oil prices have fallen, this issue alone deserves our close attention.

The Role of CFCs in Ozone Depletion

Recent measurements by NASA have reinforced the belief that fully halogenated chlorocarbons (CXCs) are most damaging to the protective stratospheric ozone layer. This layer has a maximum concentration of ozone of $5 \cdot 10^{12}$ molecules cm^{-3} at about 25 km above earth's surface. **Figure 2** shows a typical middle latitude profile of ozone concentration as a function of height. The total amount of ozone that forms this shield would be a few millimeters deep at sea level and standard conditions. **Figure 3** graphically depicts the approximate total worldwide ozone distribution.

From **Figure 4**, we notice that to reach the stratospheric ozone layer, molecules must diffuse through the troposphere. A complete description of tropospheric chemistry will probably elude chemists and engineers for many years **(9)**. The higher pressures, greater diversity of reactants, and complex mixing processes including stochastic factors that are found here make it quite a complex reactor. We do know that oxidation of the carbon-hydrogen bond occurs here by reactions with either OH or Cl radicals, and ultimately CO and CO_2 are formed. Non-hydrogenated halocarbons do not succumb to this significant removal process and thus have significantly longer lifetimes in the troposphere. **Table 1** shows tropospheric lifetimes of several CFCs. **Box 1** explains the theory of CFC initiated ozone depletion.

Reducing Atmospheric Concentrations of CFCs and Cl

The easiest approach to this problem is to reduce CFC usage dramatically. **Figure 5** shows the projected results of uniform cutbacks in emissions. But, how can modern society continue to function normally without these relatively essential compounds?

As previously mentioned, HCFCs have significantly shorter lifetimes in the troposphere due to oxidation (thus contributing to smog). Moreover, halocarbons containing fluorine do not seem to pose any threat to ozone since HF is easily formed under most conditions and readily precipitates from the atmosphere.

Considering these factors, there might seem to be a fairly straightforward answer to the current dilemma. One would need to find a new HCFC or HFC to replace the currently used CFCs. If it had similar properties, the new fluid could be employed to phase out the use of the old CFCs in existing machinery. Industry has invested a considerable amount of resources to this end and this approach has met mixed results **(17)**.

The traditional compounds are fully halogenated with one exception, and all contain chlorine atoms. A mixture of intrinsic properties and machine designs has evolved them to be relatively optimal fluids in their major areas of application. **Table 2** lists the traditional compounds used and some new candidates. As a first approximation, one can use the boiling points as a guide for prospective replacements. The code names of the compounds are listed along with their normal boiling points. Henceforth, we will refer to all hydrohalocarbons by their code name for convenience. **Box 2** explains CFC nomenclature.

The United Nations Environmental Program (UNEP), an international organization dedicated to the responsible solution to the ozone problem, has introduced a notion known as the "Ozone Depletion Potentials" (ODPs) for CFCs. The ODP compares the lifetime in the troposphere, upward diffusion rates and photolyzability into Cl versus the standard R11. A compound with an ODP of 0.5 would eventually destroy half the amount of stratospheric ozone as R11. **Table 3** shows the ODPs of several CFCs.

When the ramifications of replacements are explored, one quickly encounters a plethora of difficulties. These difficulties include its cost, toxicology, flammability, feasibility of manufacture and ability to closely mimic the properties of the traditional fluid. We should consider the sources of CFC and ponder the question, "Could the situation be significantly improved by legislation encouraging conservation of the CFCs?"

In the United States, which accounts for about 30% of the world's known CFC release, approximately 40% of the CFC emissions are from air conditioning and refrigeration units. (All market figures are based on EPA, Pennwalt Corporation and Du Pont Company estimates.) R12 mobile units alone, mainly automobile air conditioners, contribute one half of this value. The use of better hermetic sealing techniques would significantly reduce this type of emission.

About 30% of the American CFC usage is for foaming plastics and building insulation, both of which are principally applications of R11. Liquid R11 is soluble in polyurethane precursors and boils at about 30 °C to form a vapor with an extremely low thermal conductivity. When the reactive precursors are mixed, the resulting polymerization generates sufficient heat to maintain R11 vaporized throughout the setting of the foamed structure.

The remaining 30% consists of uses as "essential" aerosols, solvents and low residue cleaning agents (electronic parts, lenses, *etc.*).

Recycling of CFCs is not generally practiced since it is usually not economical (as in small refrigerators and air conditioners), impractical (in the case of foams) or impossible (as in aerosol propellants). Thus, almost all CFCs produced are eventually released. Significant increases in costs (currently between one and two U. S. dollars per kilogram), whether caused by taxation or by more expensive replacements themselves which are less damaging to ozone, would encourage conservation. Our opinion favors such regulation, but only to mitigate the current grave emergency. On the other hand, it is unlikely that such regulation could have the impact required on cutbacks.

One of the major sources of CFC emission is air conditioning and refrigeration units, especially mobile units. These units contribute nearly 30% of the overall ozone depletion, and mostly use R12. CFCs are also well-suited for use as foam blowing agents, mainly R11, in aerosol sprays, and as industrial cleaning agents and solvents. In light of this, it seems unlikely that regulation could have the impact required on cutbacks.

In the case of R12, the most stable and highest volume CFC, R134a has been the hopeful replacement. Currently, no commercial manufacturing process exists and its toxicological studies are incomplete. Its properties may be similar enough to those of R12 to allow it to be used as a direct replacement with minor modifications in some applications. However, this is a relative statement which depends on how much of a reduction in performance is acceptable to both equipment and user. Du Pont has estimated that a manufacturing process can be designed that produces R134a at 3-5 times the price of R12 **(16)**.

An Approach that Partially Meets the Challenge

In this work, we specifically address the problem of finding a replacement for R12 in a specific application. However, there is no special reason why the methods employed could not be used in other applications. We choose to concentrate on a replacement for R12 in a typical human comfort range since it is this single use that eventually causes the most damage to stratospheric ozone. The possibility of using multicomponent zeotropic fluids has been sporadically investigated as long ago as the 1870's **(21, 22)**. (The only practical revolution since then was Thomas Midgley's introduction of CFCs in 1930 **(23)** to replace the toxic and explosive, but more efficient refrigerant ammonia.) While the idea of using a fluid blend is not new, its evaluation in specific applications is necessary. Our approach will be to create new refrigeration fluids from the well characterized set of existing fluids by using binary zeotropic blends. The aim of the work is not only to demonstrate that R12 can be replaced in this application, but also to show that theoretical improvements in system performance and capacity are possible.

The Vapor Compression Cycle, Refrigerant Performance, and Capacity

Conventional air-conditioning subjects a condensable gas to a Carnot Cycle, the most efficient cycle for pumping heat between two constant temperature heat reservoirs. This strong statement of efficiency, a law of thermodynamics, has tended to overshadow the fact that for conventional refrigeration, there is a more efficient cycle. To better understand why, let us first briefly review how commercial refrigeration (and heat pumping) is accomplished.

The reader is referred to **Figure 6**. Beginning at point **A**, we proceed in a counterclockwise direction. At point **A**, the fluid (a general term applying to anything not solid) is cold and mostly liquid. It passes through a heat exchanger where it evaporates at constant temperature and absorbs heat. At point **B**, the fluid is low pressure and gaseous. It proceeds into an isentropic compressor and is converted into a high pressure hot gas at point **C**. Next, the fluid enters another heat exchanger where it condenses isothermally and rejects heat. At point **D**, the fluid is all liquid. Finally, it passes through an expansion valve where a small amount of the hot liquid is vaporized to isentropically lower its temperature to that of the evaporator. The cycle is now completed and the net effect is that heat has been transferred from the cooler to the warmer environment. We note that the materials to be heated and cooled need not be infinite reservoirs of heat (*i.e.*, remain isothermal).

In general, we measure performance by dividing output by input. For a heat pump (cooling or heating) this is the net heat supplied or removed divided by the energy input to the compressor. To simplify calculations, we will assume a frictionless compressor and no other losses. The cycle can be diagramed on pressure-enthalpy and temperature-entropy graphs (See **Figures 7 and 8**). The efficiency of refrigeration is conveniently calculated by dividing the NRE, net refrigeration effect, or change in enthalpy in the evaporator, by the work of compression. On the temperature-entropy diagram, this corresponds to the area under the evaporation segment divided by the area enclosed by the cycle trace. A quick calculation for the Carnot Cycle shows the efficiency, or coefficient of performance (COP) to be:

$$\mathrm{COP} = \frac{T_e}{T_c - T_e}$$

where T_e and T_c are the temperatures of the evaporator and condenser.

This equation implies that the closer T_e is to T_c, the higher the COP. In the limit of infinite efficiency, $T_e = T_c$, but the system is useless since it is isothermal and there is no heat flow.

Capacity is the quantity that quantifies a system's ability to remove heat. It depends on three factors (Fourier's law): (1) the difference in temperature of the cooling fluid and fluid to be cooled, (2) the properties of the fluids and heat exchanger themselves, and (3) the amount of time available for heat transfer.

In a typical application of an air conditioner, the heat sources and sinks do not maintain constant temperature. For example, 25°C room air may be cooled to 5°C. It is this fact that allows us to "cheat" the Carnot Cycle with the unconventional Lorenz cycle. By using a zeotropic fluid blend, instead of being isothermal, evaporation temperatures "glide" (See **Figure 9**). The effect of the temperature glide can be to bring the mean T_c and mean T_e closer together and thus raise the COP. However, direct comparison of Carnot and Lorenz work on graphs like these can be misleading. We must not only consider the refrigerant temperatures, but also the system's capacity. Thus, it is best to consider the problem by looking at the bottom line: How much energy is required for a given job? Similarly, if the system is not designed considering these temperature differences, these same assets can become liabilities. This can be restrictive during operation over a variety of conditions and necessitates careful designing. Also, the fluid to be cooled must be circulated in a countercurrent direction to the refrigerant, to accentuate the temperature differences in the heat exchangers.

Binary Refrigerant Mixtures and Equations of State

Even if zeotropic blends were not to be successful in significantly increasing COP, they certainly have the potential to bring freedom to the restrictive reality of single component refrigerants. Designers no longer would have to design systems around the refrigerant, but rather could choose any of a number of blends that would be relatively ozone safe for the specific performance to their system. In order to accomplish this and to be able to make constructive predictions, one needs a way to model refrigerant fluids. This is conveniently done computationally using an equation of state unique to the fluid. Modeling can be difficult even in the case of pure (single component) fluids. The simplest equation of all is the Ideal Gas Law, $Pv=RT$. In the reality of a refrigeration system, a saturated fluid can have two different specific volumes simultaneously, one for vapor and one for liquid. Therefore, if possible, for a total representation of liquid and gaseous equilibria of a fluid, we must find an equation of order greater than one in v. The minimum order of volume for a real fluid is actually three.

One of the simplest of all "cubic" equations is the Van der Waals Equation. It contains corrections to the Ideal Gas Law that have molecular interpretations of attraction and molecular volume. These corrections make it "cubic" in v with respect to P. The fundamental problem with van der Waals' equation is that the resulting interactions caused by the dense packing of molecules in the liquid phase are not considered.

An equation that does consider such packing is the Carnahan-Starling-De Santis (CSD) equation. A series of subroutines for computer modeling was created at the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards) using a modified form of this equation for binary mixtures by Dr. Mark McLinden. We will use a linked version of these subroutines in our modeling studies. The reader is referred to **Box 3** for a basic explanation of the theoretical and practical use of this equation.

Additionally, the basic input of the program was modified to appropriately compare the performance of different fluids in the same cycle. This was accomplished both by specifying the efficiencies of the heat exchangers by a mean temperature difference for use with Fourier's equation and by specifying the temperature of the entering and exiting fluids to be heated and cooled rather than those of the refrigerants **(32)**.

The Particular System Studied and Data Interpretation

Our representative R12 system was chosen because replacement of this fully halogenated CFC as a refrigerant would make a major impact on ozone conservation. The system studied would cool the source from 298 K (25°C) to 278 K (5°C) and warm the sink from 308 K (35 °C) to 320 K (47°C). The typical efficiency of a countercurrent heat exchanger in this application might be 7 K, expressed as a logarithmic mean temperature difference.

Pure components and binary mixtures (50/50 mole percent) were studied in the same system, and only refrigerants and blends that would completely vaporize in the evaporator were considered for mechanical reasons. From the "raw" data provided by the program, several quantities of interest were computed and compared. They were: (1) COP - the heat transferred in the evaporator divided by work of compression, (2) CAP - the volumetric capacity expressed as the amount of heat transferred per cubic meter of refrigerant, (3) P/P - the pressure ratio forced upon the compressor, and (4) the gliding temperatures in both the evaporator and condenser. For comparison, the high side pressure and low side pressure are also reported. Systems having less than 0.5 atm evaporator pressures, great P/P or high condenser pressures are mechanically impractical or undesirable.

The standard for all comparisons is R12. As stated in **Box 3**, the interaction coefficient, f_{12} is the factor that adjusts the semi-theoretical equation of state to the observed behavior of real fluid mixtures. Mixture data were available on the greater part of the blends studied. One of the NIST subroutines iteratively uses vapor-liquid equilibrium data to fit f_{12} , for which values were previously calculated. For those mixtures with unknown f_{12}, we used the empirical observation that most f_{12}'s fall between -0.01 and 0.03, although some are significantly higher. Data were generated for both possible values in order to get an approximate idea of the utility of that particular blend. Recently, f_{12} values were correlated to moleculear dipole moments **(33)**. To simplify calculations considerably, all fluids were taken to have identical heat transfer coefficients. While this could cause problems in some cases, it is generally applicable to our work.

Real systems are riddled with losses (inefficiencies). We considered the efficiency of the compressor to be unity. This is not a bad assumption since we are comparing fluids and not seeking absolute figures. However, it would be expected to have some dependence on pressure and pressure ratio.

Another idealization we made was to ignore pressure drops which occur across all real heat exchangers. We justify its omission by the same reasoning as that of the assumption of identical heat transfer coefficients.

The Significance of the Data

The results of the modeling are shown in **Table 4**. Based solely on the results as presented, it seems that there should be no magical reason for using R12. In fact, the single component hydrofluorocarbon R152a is predicted to perform similarly to R12. The results would indicate that if the system could withstand the slightly higher pressure ratio, R152a could act as a direct replacement (not unreasonable). R12 and R152a even form an azeotrope which is commonly used in modern refrigeration. Other reasons that will be briefly mentioned later have prevented R152a from widespread use.

R22 is the only commonly used hydrohalocarbon in refrigeration today. To use it in an R12 system would require a significant modification to make the system capable of withstanding higher pressures and changes concerning the compatibility of materials. However, the fact is that it probably could be used. For example, General Motors estimated in 1980 that a fixed investment of at least 500 million U. S. dollars plus an unknown higher variable cost would be associated with an R22 based auto air conditioner. These liabilities would be compounded by extra weight added to the car to contain the higher pressures of R22.

The low capacity coupled with the high pressure ratio of R142b in this application would make it a poor choice. Additionally, it has problems similar to 152a. The blends of R12 each have advantages and disadvantages. R12/142b is a good candidate to lower overall system pressure and increase the COP while R12/R22, by sacrificing overall system pressure would dramatically increase capacity. The overall combination of calculated parameters makes the R22/R114 blend about as desirable as R12. Unfortunately R114 is fully halogenated.

Next, we move on to the blends with zero or negligible ozone depletion potentials. The R22/142b (50/50) blend is superior to R12 in every property calculated. Other compositions were investigated to demonstrate the latitude a designer using this blend would have for his system. The R11/152a system was shown to give better properties with a sacrifice in pressure. The R142b/143a blend appears clearly better than R12, and the remaining blends were shown to have mixed benefits and losses.

The equation of state on which we based this report is accurate enough for the present purposes. However, it should be noted that a greater accuracy is desireable when one is actually selecting components for a particular system. It is for this reason that a modified cubic 32 constant Benedict-Webb-Rubin equation is currently being used to describe R134a. The results of modeling R134a with the CSD equation seem to indicate that it is a direct replacement candidate for R12. It is unlikely, however, that 134a would perform better than an appropriately selected blend if major consideration is given to chemical properties and not to system complexity.

Further Discussion

Other problems exist with finding any replacement. Midgley began his landmark paper by discussing these problems and he continued by showing the apparent advantages R12 had compared to all the then commercial refrigerants **(34)**. We must remember that a convergent evolution has taken place among refrigerants, their machinery, and processes designed for their use. The enormous heats of vaporization (heat absorbing abilities), the stability, the convenience and the known safety of CFCs have fueled this evolution. Finding replacements involves surmounting the hurdles of such properties as toxicity, flammability, miscibility and solubility with oils (refrigerant gases are not good lubricants for compressors), dynamic and static thermochemical stability **(35, 36)** and compatibility with system materials. Some compromises may be made. It was already mentioned that ammonia is toxic and explosive; all of the alternates mentioned have various degrees of flammability with the exception of R134a. As a general rule, the more hydrogens and the less chlorines the compound contains, the greater its flammability (R152a is worst). R22 is not flammable, and many of its blends might be expected to be non-flammable as well. Several CFCs previously developed were shown to cause cancer and sterility. The toxicological testings of the new fluorocarbons (including R134a) have not been completed, and generally, the procedures take several years. After extensive testing in laboratory animals, questions remain about the carcinogenicity of R22, although it is considered safe for general commercial use. The compounds we studied, with the exception of R143a, similarly have been shown to be safe. Such compounds, and their blends, could be used today. They could have been used in 1974 when stratospheric chlorine concentrations from CFCs were nearly half of their current value.

Research on mixtures will center on modifying equipment to best take advantage of blends, on determining more accurate interaction coefficients by careful pressure and liquid-vapor distribution measurements, and perhaps on improving the basic form of the equation of state.

In recent years, the declining trends in the worldwide production of R11 and R12 had reversed. Since 1974, when a peak production of 0.74 thousand million kilograms was reached, production fell to a minimum of 0.54 thousand million kilograms. By 1984, production was again 0.63 thousand million kilograms **(10)**, and has not decreased to the present date. The worldwide CFC industry itself is estimated to be 2.2 thousand million U. S. dollars. However, industries directly using CFCs as raw materials account for many times this value, and more importantly, modern society is rooted in the special properties of these compounds. We have explored one promising approach to attacking this current dilemma. A solution is needed immediately, or else we will continue to risk greater peril. The lifetimes of the CFCs are relatively long and the current reservoir that will eventually be released into the atmosphere is sufficiently large so that the proposed increased ozone destruction could take decades to go into decline.

Concerning this issue, it is clear that our society must make some compromises to maximize our safety. International cooperation concerning both production and consumption is required due to the global scope of CFC emissions. Most nations have expressed willingness to work together. Current agreement is based on the Montreal Protocol and the Helsinki Declaration. The Protocol freezes production of the major commercial CFCs (those listed in **Table 1**) at 1986 levels in 1989, reduces production to 80%

of 1986 levels in 1993 and to 50% in 1998. **Figure 5** predicts that an immediate cut of at least 85% is necessary to stabilize chlorine concentrations at current (elevated) levels It is clear that compliance with the goals of the Montreal Protocol will not avert the dilemma.

In 1985, UNEP initiated major international cooperation for the protection of the ozone. By 1987, the Parties to the Vienna Convention had drafted the Montreal Protocol. To date, nations responsible for over 80% of CFC production have signed the Protocol. The Helsinki Declaration of May, 1989, reaffirmed the critical nature of the situation and recommended that all nations completely phase out CFCs controlled by the Protocol by the year 2000, tightening the Protocol's timetable. The Declaration further recognized the special situation of developing countries which use only a small fraction of world CFCs whose industrialization and development will be hampered in their absence **(37)**. At its headquarters in Nairobi in September, UNEP hosted another meeting in which the Helsinki Declaration was basically supported. Furthermore, there was a general agreement that HCFCs are part of the solution rather than being part of the problem. Previously, some advocated their phase out as well since they do contribute to chlorine release. The next meeting will convene in London in April, 1990, to assess the impact of the past legislation and to draft future plans. The alternates discussed should have been implemented in use sooner. We believe that the blend approach is internationally acceptable and has the potential for other benefits. Of course, direct replacement of R12 with R134a may solve a major portion of the problem. In any case, a cutback in total CFC production equivalent to at least an 85% reduction of the current ODP is predicted to be necessary. Although mixture technology is more complex, some of the blends presented are expected to have ODPs equivalent to a cutback greater than 95%. This is something to consider as we work in our air conditioned offices while our children are outside playing and while more than half of the world seeks to emulate us. If we wish to continue with the commercial application of the vapor compression cycle, we must and protect and prepare ourselves by responsibly studying our options in a timely manner.

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35. Dawn, D. D. and Crooker, R. M. 1987. *Accelerated static thermochemical stability of blends of ISOTRONs 22, 12 and 142b with refrigerant oil and steel.* Document TSR 8704. Pennwalt Corporation, King of Prussia, PA.

36. Srinivasan, P., Devotta, S. and Watson, F.A. 1985. Thermal stability of R11, R12B1, R113 and R114 and their compatibility with some lubricating oils. *Chem. Eng. Res. Des. 63,* 230-233.

37. Barnaby, F. 1989. The Barnaby Report: Saving the ozone layer. *AMBIO 18,* 252.

38. Acknowledgements: Many thanks to Drs. Arthur Lane, Moustafa Chahine, Stan Sander, to Ron Alley, all from JPL, to Drs. Mark McLinden and Graham Morrison of the NIST, to Jim Houser of the Pennwalt Corp., to Dr. Arlin Krueger of NASA, to Dr. Yuk Yung of Caltech, and to Wendy Moerder of the Du Pont Co.

Table 1: Tropospheric lifetimes of several chlorofluorocarbons **(10)**. This number represents the half life, the time at which 37% of an arbitrary initial amount of molecules will persist unreacted. Most ozone destruction occurs upon the transport of these molecules to the lower stratosphere. Since lifetimes are estimated based on laboratory data and atmospheric theory rather than direct measurement, an error of about 20% is reasonable.

Formula	**Lifetime(years)**
$CClF_3$	65
CCl_2F_2	120
CCl_2FCClF_2	90
$CClF_2CClF_2$	180
$CClF_2CCF_3$	380

Table 2: Major commercial fully halogenated CFCs and hydrogenated HCFC alternatives.

Formula	Code	Normal Boiling Point(°C)
$CClF_3$	R11	-81.
CCl_2F_2	R12	-29.8
CCl_2FCClF_2	R113	-36.4
$CClF_2CClF_2$	R114	3.6
$CClF_2CF_3$	R115	-38.
	Alternatives	
$CHClF_2$	R22	-40.8
$CHCl_2F_3$	R123	28.
$CHClFCF_3$	R124	-12.
CHF_2CF_3	R125	-48.5
CH_2FCF_3	R134a	-26.5
CH_3CCl_2F	R141b	30.5
CH_3CClF_2	R142b	-9.1
CH_3CF_3	R143a	-47.3
CH_3CHF_2	R152a	-24.7

Table 3: Ozone depletion potentials (ODPs) of several compounds **(18-20)**. The ODP estimates the relative destruction of stratospheric ozone for each compound using R11 (CCl_3F) as a standard. For example, twenty kilograms of R22 would destroy an equal amount of ozone as one kilogram of R11.

Fully Halogenated CFCs

Compound	**ODP**
R11	1.0
R12	1.0
R113	0.8
R114	0.6
R115	0.3

HCFCs

R22	0.05
R123	0.02
R124	0.02
R125	0.00
R134a	0.00
R141b	0.1
R142b	0.06
R143a	0.00
R152a	0.00

Table 4: The Modeling Results

Fluid (Mixtures are 50/50 mole percent unless otherwise indicated)	f_{12}	COP	Volumetric Capacity (kJ/m^3)	Pressure Ratio (P/P)	Condensor ΔT (K)	Evaporator ΔT (K)	Evaporator Pressure (kPa)	Condensor Pressure (kPa)
R12	0	4.772	2105	3.43	0	0	346.7	1188.7
R22	0	4.846	3471	3.34	0	0	557.8	1865.7
R134a	0	4.657	2150	3.89	0	0	332.9	1295.6
R142b	0	5.057	1240	4.06	0	0	168.1	682.5
R152a	0	4.971	2109	3.76	0	0	304.0	1143.6
R12/142b	.036	5.128	1824	3.51	2.8	3.2	274.2	963.5
R12/R22	.041	4.884	2986	3.23	2.0	1.6	502.3	1618.9
R12/143a	.03*	4.688	2898	3.16	2.9	2.5	529.3	1675.0
R12/143a	-.01*	4.751	2710	3.25	2.6	2.0	475.7	1544.3
R22/114	0.03	5.607	1987	3.43	18.6	16.0	282.0	968.5
R22/142b	-0.01	5.564	2240	3.42	8.0	6.9	312.9	1071.5
R22/142b (35/65)	-0.01	5.508	1908	3.56	7.0	5.6	261.4	931.4
R22/142b (65/35)	-0.01	5.527	2597	3.33	7.6	7.1	372.7	1239.6
R22/143a	-.01*	4.583	3387	3.26	0.1	0.2	606.2	1978.9
R22/143a	.03*	4.481	3588	3.19	0.1	0.2	672.7	2146.6
R22/152a	-0.014	5.093	2700	3.50	1.9	1.7	400.1	1401.2
R22/152a (35/65)	-0.014	5.072	2499	3.58	1.5	1.3	365.9	1309.6
R22/152a (65/35)	-0.014	5.085	2920	3.43	2.0	1.9	439.9	1509.5
R142b/143a	.03*	5.468	2512	3.23	11.0	10.5	383.7	1240.4
R142b/143a	-.01*	5.455	2308	3.33	10.0	8.8	343.0	1143.8
R142b/152a	.03*	5.180	1792	3.70	2.5	2.2	253.8	939.2
R142b/152a	-.01*	5.189	1630	3.83	2.1	1.7	223.9	856.3
R143a/152a	-.01*	4.925	2787	3.36	3.0	2.9	454.3	1524.9
R143a/152a	-.03*	4.871	2996	3.27	3.2	3.5	507.2	1657.5

*An asterisk indicates f_{12} was unkown. Unasterisked values were calculated using the fitting routine mentioned in the text.

Figures

Figures

Main text

Figure 1:	(a) The intensity of UV radiation at the surface of earth's atmosphere, from U. S. Air Force LOWTRAN7 calculations which neglect scattering **(1, see also 2, 3)**, superimposed with the intensity reaching earth's surface with and (hypothetically) without ozone. Harmful radiation is about 0.25-0.30 μm. Ozone is the only significant constituent of the atmosphere absorbing in this region.
Figure 2:	A typical middle latitude profile of ozone concentration as a function of height from LOWTRAN7 data **(1)**. Ozone, a bluish gas present in many large metropolitan areas in much lower concentrations than in the stratosphere is a reactive pollutant **(6)**. It is thinnest at the earth's equator and poles **(7)**. Anomolies of the polar regions are discussed in **Box 1**.
Figure 3:	(a) Total worldwide distribution of ozone measured in Dobsons. 100 Dobsons is equivalent to collecting all of the ozone in a given column of atmosphere at sea level and standard conditions, where it would occupy a one millimeter high shell. The data from NASA were recorded on 16 August 1979 by the Nimbus 7 satellite/Total Ozone Mapping Spectrometer. (b) Data recorded two days earlier show natural variability in ozone concentrations. The Ozone Trends Panel, an international team investigating these same data, reported its conclusions after careful analysis: Over an eleven year solar cycle ending in 1986, ozone concentrations in middle latitudes had decreased about 2.5% **(8)**. The U. S. Environmental Protection Agency estimates that for each 1% loss of ozone, 1.5 to 2% more damaging UV radiation reaches earth's surface. The EPA also estimates that at current depletion rates, millions born before 2075 will die as a direct result and many more will suffer from cancers and cataracts.
Figure 4:	Profile of earth's atmosphere. When CFCs diffuse above major ozone concentrations, they readily dissociate in the intense UV radiation.
Figure 5:	The projected results of uniform cutbacks in CFC emissions **(16)**. Curve A represents the limits set by the Montreal Protocol (See discussion).
Figure 6:	The simple vapor compression cycle referred to in the text. Although most commercial systems have been

optimized by various modifications, all share these basic components **(24, 25)**.

Figure 7:	The Carnot Cycle represented as pressure versus enthalpy, the usual plot used in machine design. The theoretical net refrigeration effect (NRE) and the energy required to drive the compressor (work) are apparent.
Figure 8:	The Carnot Cycle represented on a temperature-entropy plot. The work of compression is shaded.
Figure 9:	The Lorenz Cycle represented on a temperature-entropy plot. The effect of the temperature glide is to bring the mean temperatures of the evaporator (T_e) and condenser (T_c) closer together. The work of compression is shaded.

Box 1

Figure:	Summary of the reactions believed to be involved in stratospheric ozone depletion. Additional reactions thought responsible for the Antarctic "hole" are noted.

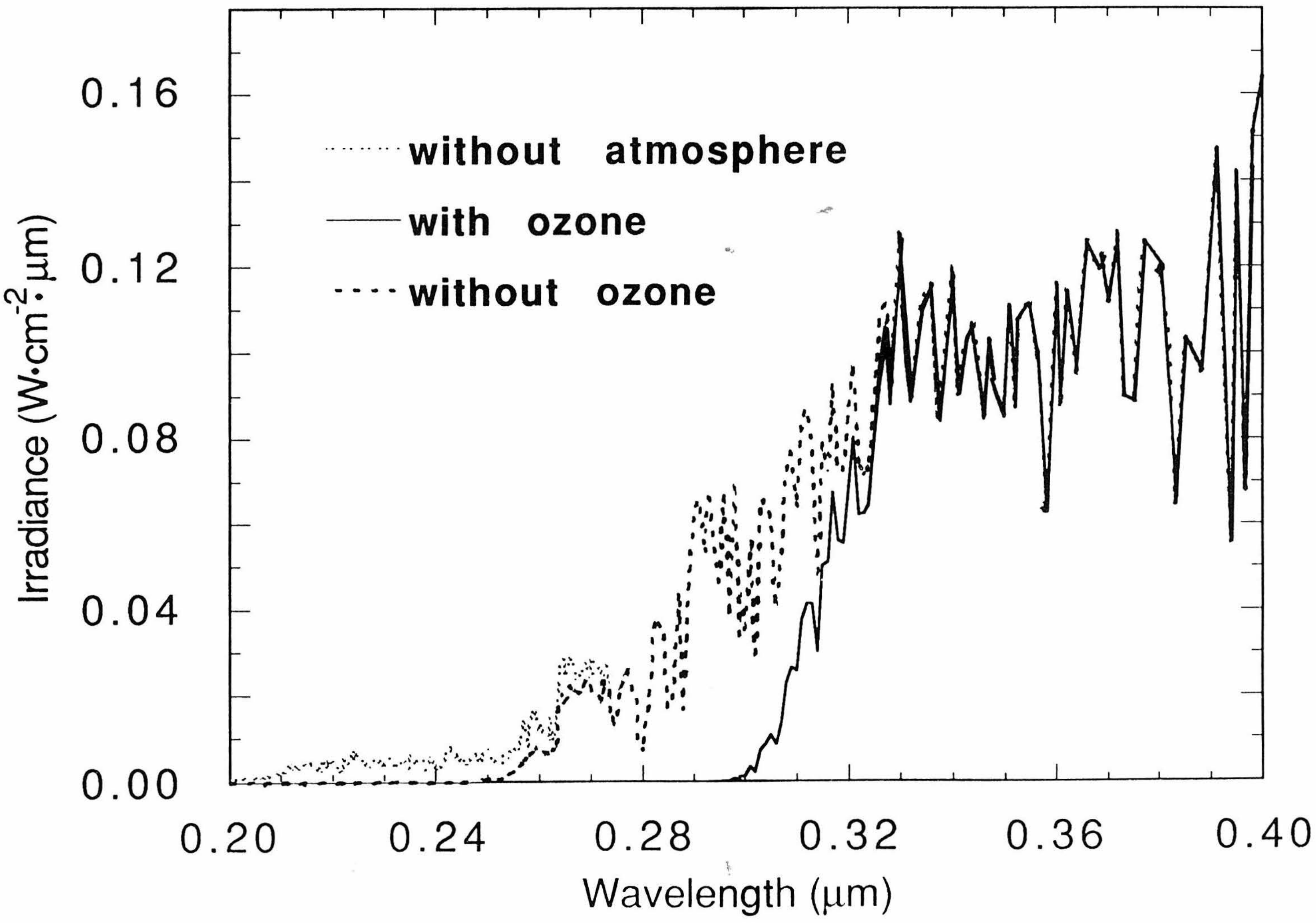

without atmosphere
with ozone
without ozone
Irradiance (W•cm^{-2}•µm)
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
Wavelength (µm)

Figure 1: DD Dawn & SI Chan

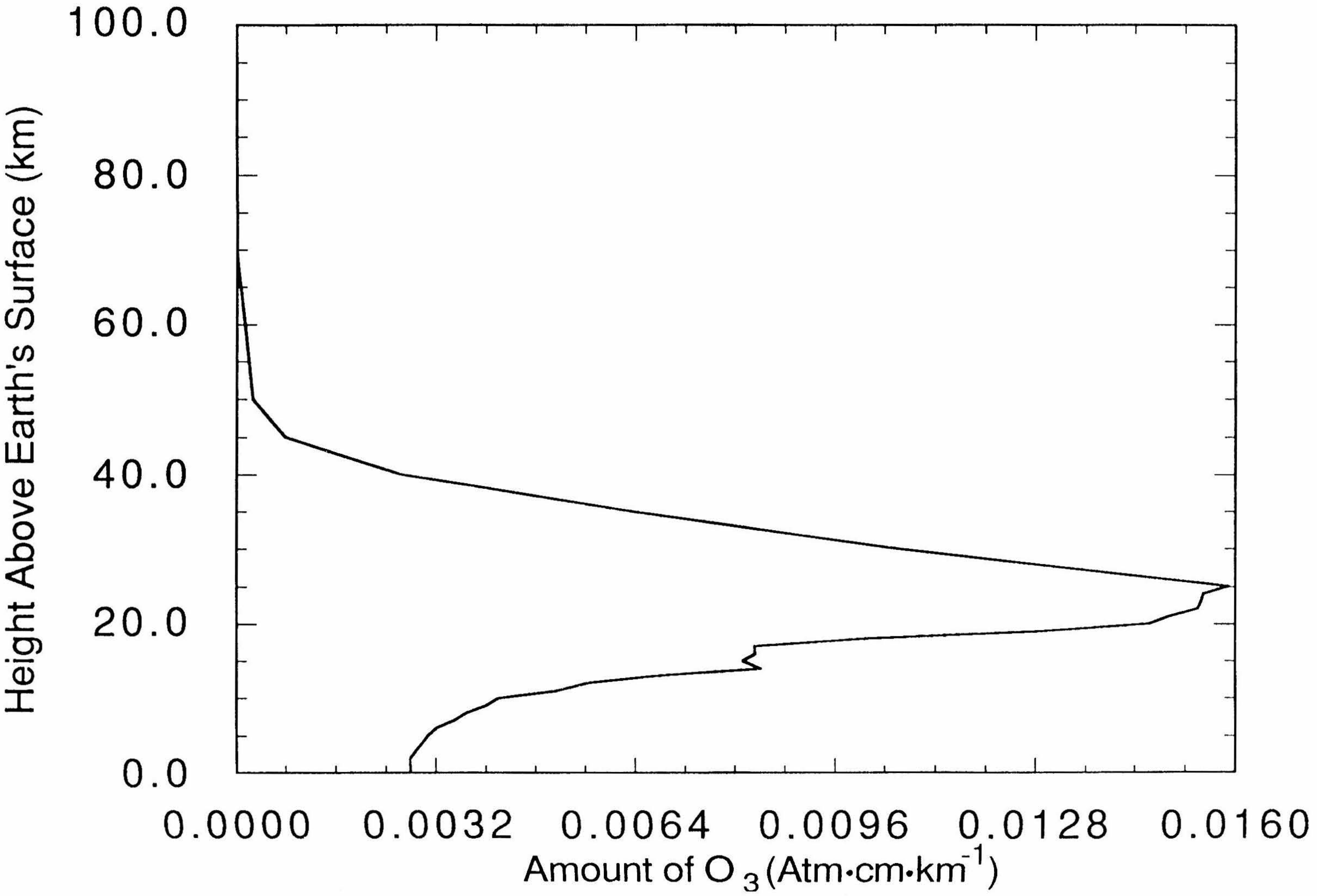
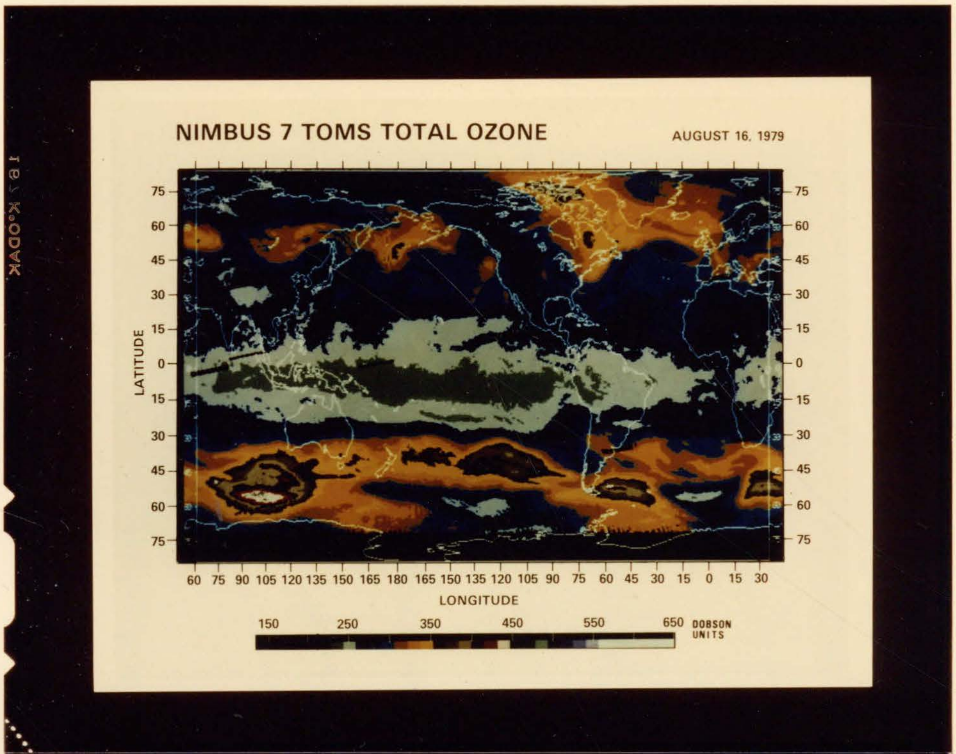
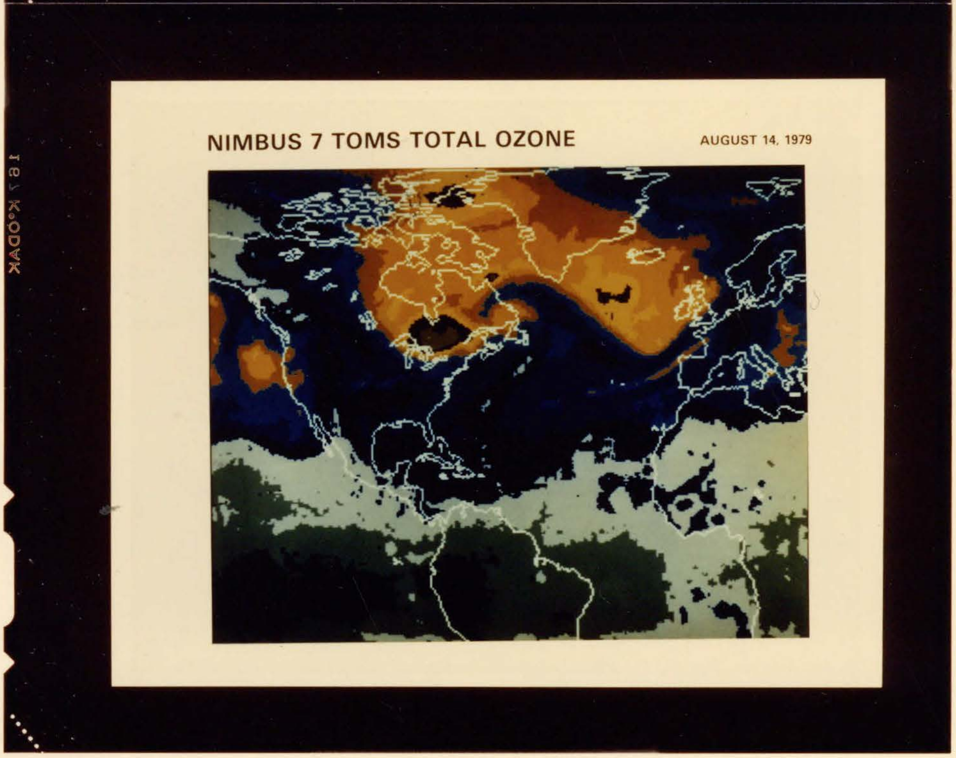
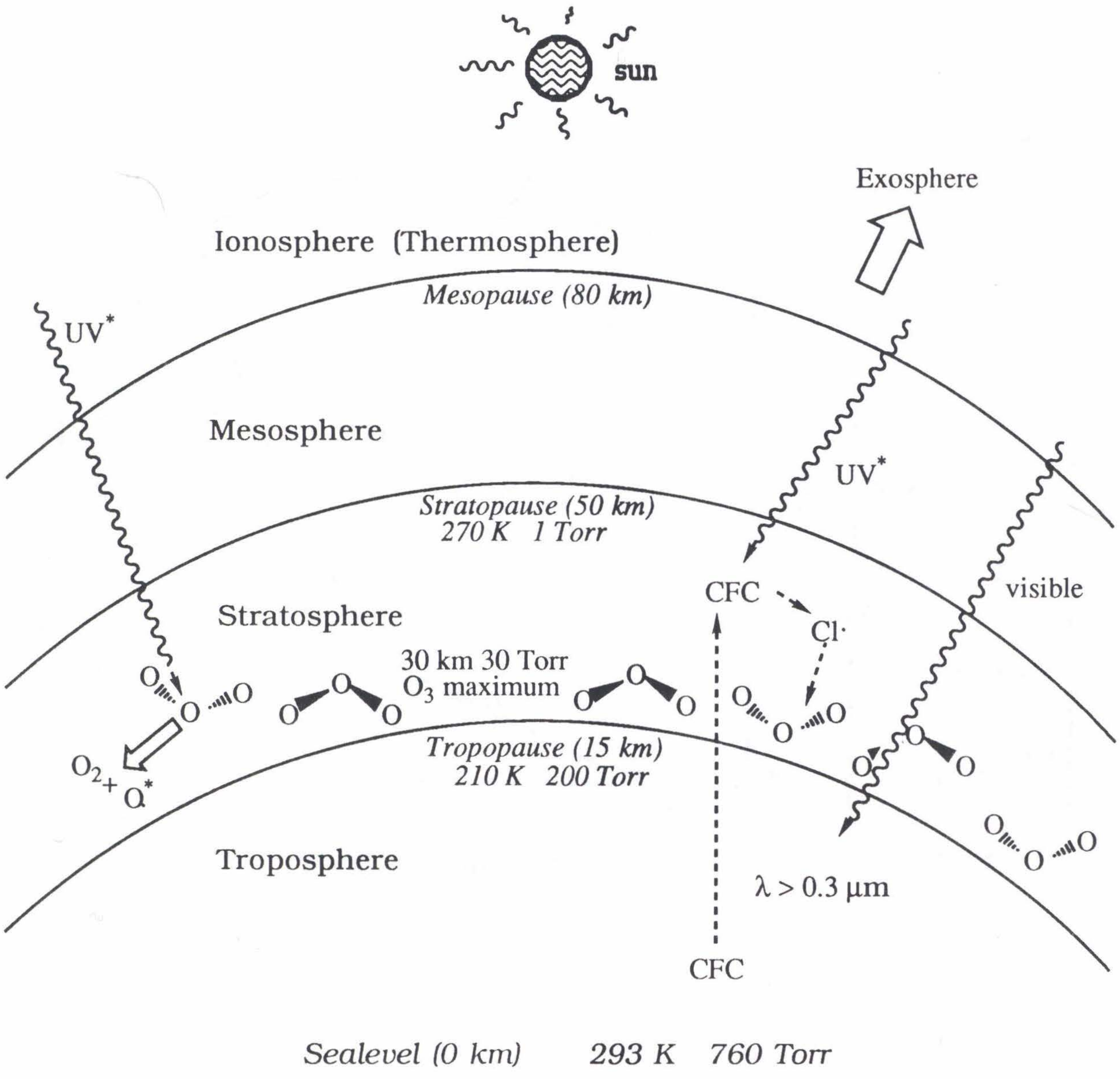

100.0
80.0
60.0
40.0
20.0
0.0
Height Above Earth's Surface (km)
0.0000
0.0032
0.0064
0.0096
0.0128
0.0160
Amount of O_3 (Atm•cm•km^{-1})

Figure 2: DD Dawn & SI Chan


NIMBUS 7 TOMS TOTAL OZONE
AUGUST 16, 1979
LATITUDE
75
60
45
30
15
0
15
30
45
60
75
LONGITUDE
60 75 90 105 120 135 150 165 180 165 150 135 120 105 90 75 60 45 30 15 0 15 30
150
250
350
450
550
650
DOBSON UNITS

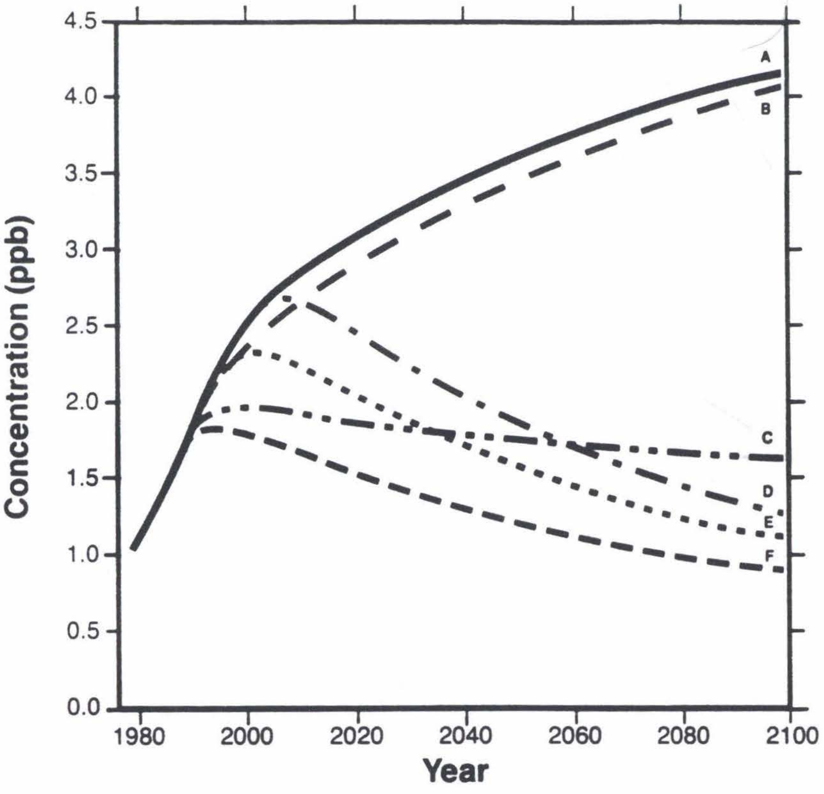

NIMBUS 7 TOMS TOTAL OZONE
AUGUST 14, 1979



sun
Exosphere
Ionosphere (Thermosphere)
Mesopause (80 km)
UV*
Mesosphere
UV*
Stratopause (50 km)
270 K 1 Torr
visible
CFC
Cl·
Stratosphere
30 km 30 Torr
O3 maximum
O
O
O
O2+ O*
Tropopause (15 km)
210 K 200 Torr
Troposphere
λ > 0.3 µm
CFC
Sealevel (0 km) 293 K 760 Torr

Figure 4: DD Dawn & SI Chan

Effect of CFC Reduction Rates
Chlorine From CFCs



CFC Consumption

	1989	1993	1998	2003	2100	
———	Freeze	– 20%	– 50%			A
— —	– 20%	– 50%				B
—··—··—	– ~85%					C
·—·—	Freeze	– 20%	– 50%	– 95%		D
·······	– 20%	– 50%	– 95%			E
– – –	– 95%					F

Figure 5: DD Dawn & SI Chan

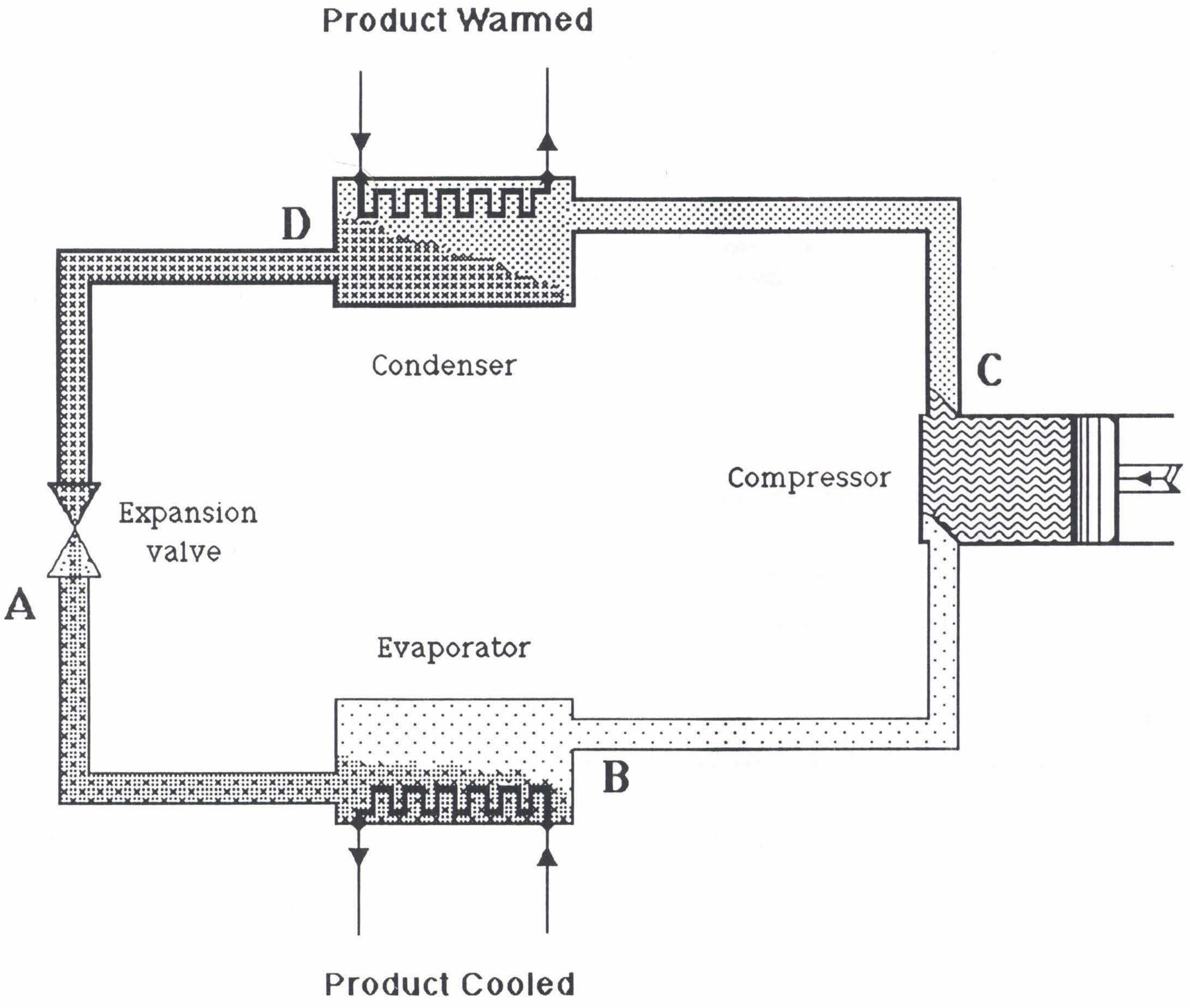

Product Warmed
D
Condenser
C
Compressor
Expansion
valve
A
Evaporator
B
Product Cooled

Figure 6: DD Dawn & SI Chan

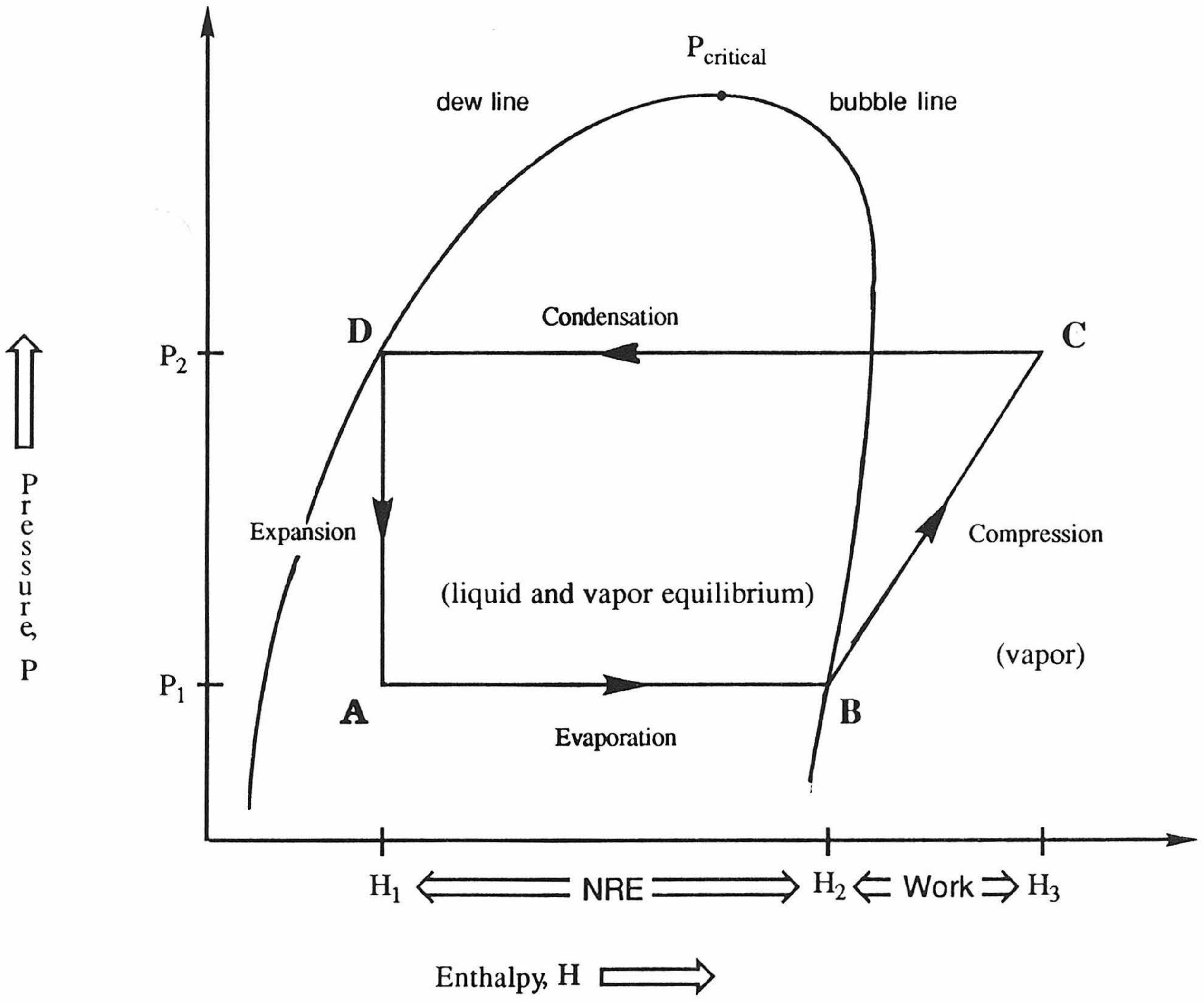

P_critical
dew line
bubble line
D
Condensation
C
P2
P1
Expansion
Compression
(liquid and vapor equilibrium)
(vapor)
A
Evaporation
B
H1
NRE
H2
Work
H3
Enthalpy, H
Pressure, P

Figure 7: DD Dawn & SI Chan

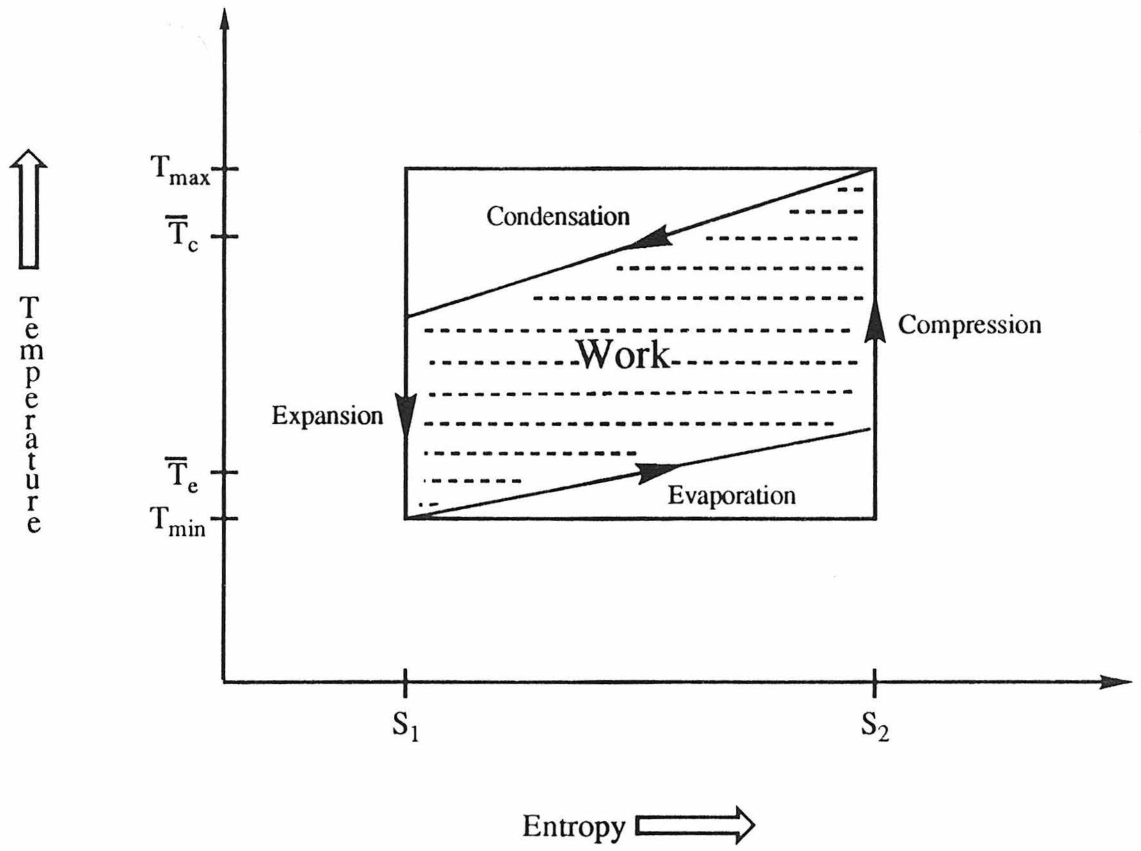

T
e
m
p
e
r
a
t
u
r
e
T_{max}
$\overline{T}_c$
$\overline{T}_e$
T_{min}
Condensation
Compression
Work
Expansion
Evaporation
S_1
S_2
Entropy

Figure 8: DD Dawn & SI Chan

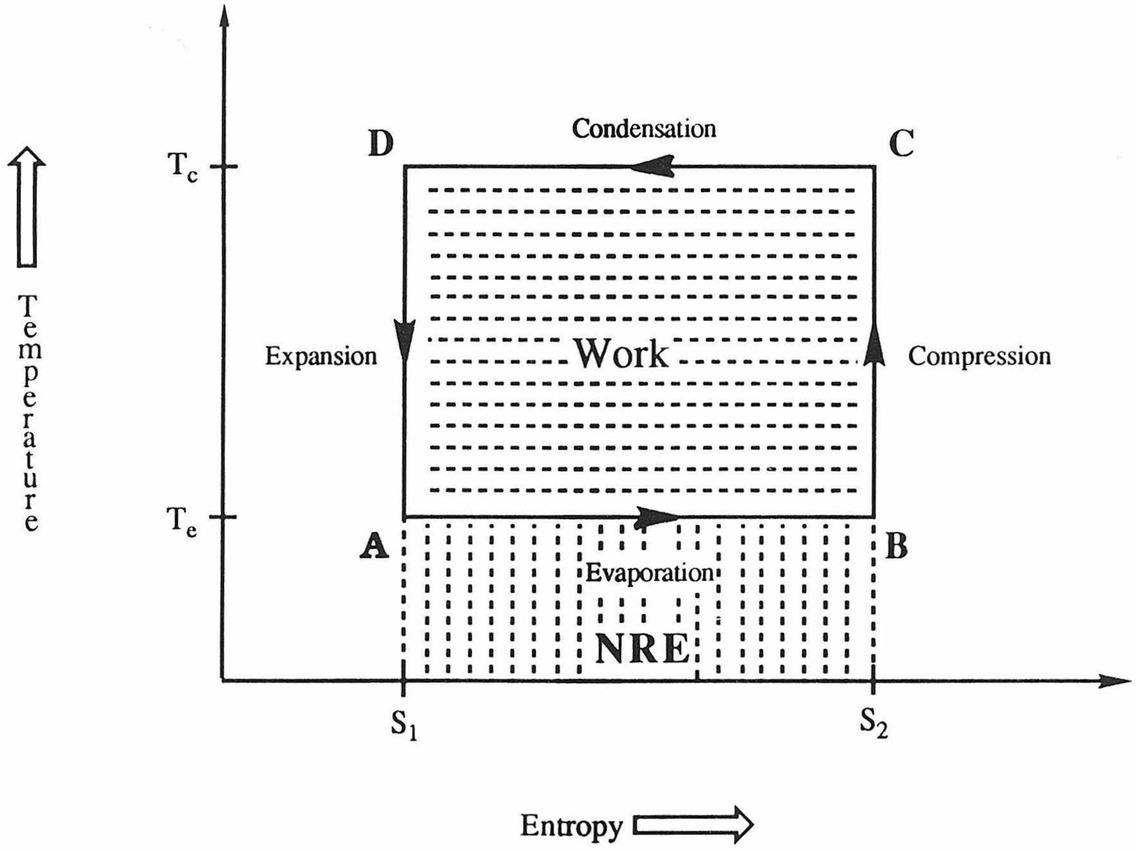

Temperature
Entropy
T_c
T_e
S_1
S_2
A
B
C
D
Condensation
Expansion
Compression
Evaporation
Work
NRE

Figure 9: DD Dawn & SI Chan

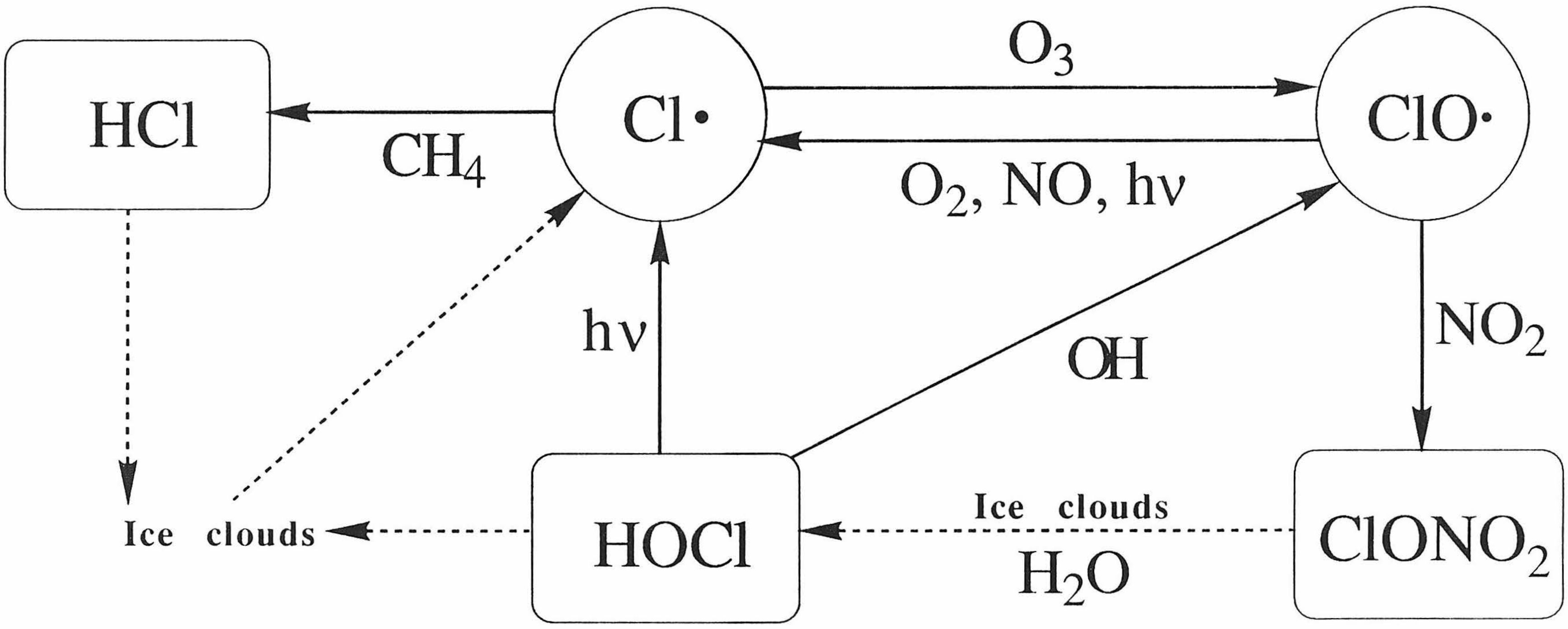

HCl
CH4
Cl·
O3
O2, NO, hν
ClO·
hν
OH
NO2
Ice clouds
HOCl
Ice clouds
H2O
ClONO2

Figure (Box 1): DD Dawn & SI Chan

Photographs

Photographs

(Photos 1, 2: Possible journal cover and article openers)

Photo 1: (palm tree with halo shot by Walter Dawn)
Cirrostratus sun halo ice cloud over Miami. Reactions on ice surfaces in the Antarctic are suspected to cause the 50 to 95% decreases in ozone concentrations during that region's springtime.

Photo 2: (thundercloud shot by Walter Dawn)
Funnel cloud surmounting cumulonimbus "thunderhead" which extends well into the ozone layer. Complex weather phenomena have compounded the difficulties encountered when quantifying the CFC induced ozone depletion.

(photos for presentation within the text)

Photo 3: (zooplankton larvae shot by Walter Dawn)
Zooplankton (live larvae) are sensitive to UV exposure. The base of the ecological food chain is being threatened by ozone depletion.

(Photos 4, 5, 6 are best presented together)

Photo 4: (Aerosol spray can shot by Walter Dawn)
"Non-essential" aerosols were banned in the United States after the theory of CFC induced ozone depletion was accepted. Although a high visibility use, most CFCs were and continue to be released from other sources.

Photo 5 (Auto junk yard shot by Walter Dawn)
Nearly 1% of the world's CFC emission is from junked mobile air conditioning units in the U. S. However, only 10% of the emissions from such air conditioners result on disposal (EPA estimate). Most occur from leakage and during recharging.

Photo 6: (Men on roof shot by Walter Dawn)
The most efficient building insulation is CFC-polyurethane based. This photo showing the replacing of roofing insulation around air conditioning and refrigeration machinery at a local supermarket demonstrates how deeply rooted CFCs are in modern society.

Photographs; *D. D. Dawn*

LEGEND for proof sheet

1. Palm tree with halo	2. Thundercloud	(wind-blown spume loaded with phytoplankton)	(wind-blown spume loaded with phytoplankton)
(Lightning - creation of small quantities of ozone in the troposhpere)	(Tabellaria phyto-plankton) May be used in place of zooplankton for Photo 3	(Thalassiosira phyto-plankton) May be used in place zooplankton for Photo 3	(Licomorpha phyto-plankton - stalks) May be used in place of zooplankton for Photo 3
5. Auto junk yard	4. Aerosol spray can	6. Men on roof	3. Zooplankton larvae

TOP

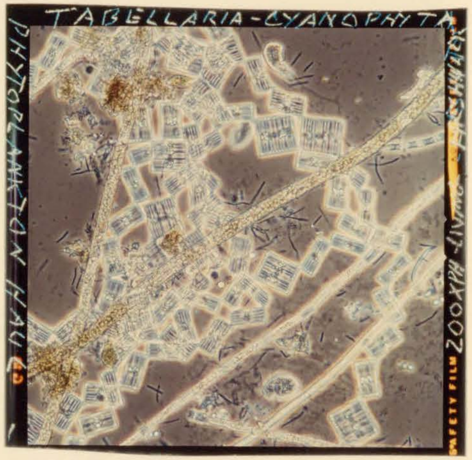

BEGINNING OF OZONE LAYER
CIRROSTRATUS SUN HALO
38MM POLA-MIAMI-FLA·3X76


CUMULONIMBUS MIAMI-FLA.
ELECTRICAL DISCHARGE CREATION
FUNNEL CLOUD ON TOP THUNDERHEAD
250MM-POLA 2876


FROTH LOADED W/PHYTOPLANKTON
WIND-BLOWN SPUME
MARINE SCENE

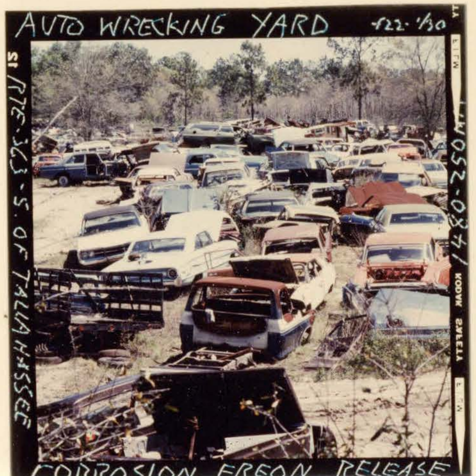

WIND-BLOWN SPUME SEASHORE
FROTH LOADED W/PHYTOPLANKTON
CB0 20 -CAPE HATTERAS-N.C-CROP SKY


OZONE CREATION
LIGHTNING BOLTS

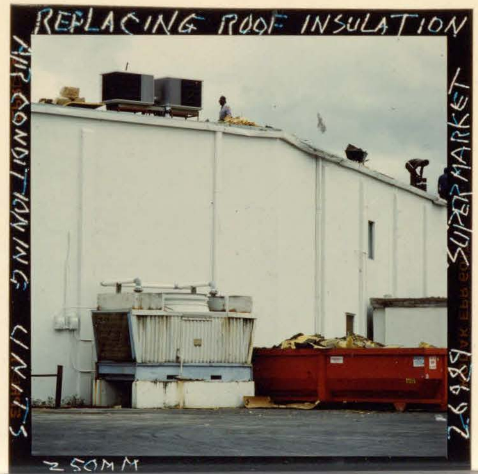

TABELLARIA-CYANOPHYTA
PHYTOPLANKTON HAUL
200XPH-LIVING


PHYTOPLANKTON HAUL-7165
MARINE-LIVING-120XPH
THALASSIOSIRA
LONG ISLAND WATERS-NEW YORK


LICMOPHORA 200XPH
LIVING MARINE STALKED DIATOMS
PHYTOPLANKTON HAUL MARINE
LICMOPHORA ATTACHED TO POLYSIPHONIA


AUTO WRECKING YARD F22·1/30
RTE·363·S. OF TALLAHASSEE
1480-250MM
CORROSION FREON RELEASE


AEROSOL CHLOROFLUOROCARBON
OZONE DEPLETION
38MM
26989


REPLACING ROOF INSULATION
AIR CONDITIONING UNITS
SUPERMARKET
26989
250MM


LIVING-MOVING 60X
ZOOPLANKTON LARVAE-15563

Box 1

The basic hypothesis of CFC ozone depletion was proposed in 1974 by Sherry Rowland and Mario Molina at the University of California at Irvine **(11)**. Recent work has focused attention on the ozone above the Antarctic where major depletion has been observed. The theory that accounts for the chemistry follows.

The CFC diffuses into the stratosphere, above the major ozone-concentrations where it is readily dissociated:

$$(1) \qquad C_aClX_z + h\nu \rightarrow C_aX_z + Cl$$

where X are halogens or hydrogens and a and z are atoms per molecule.

Bromine atoms can be produced and behave like Cl under similar conditions. Several catalytic cycles including Cl (or Br) have been proposed:

$$\begin{array}{llcll}
(2) & Cl + O_3 & \rightarrow & ClO & + O_2 \\
 & O + ClO & \rightarrow & Cl & + O_2 \\
\hline
\text{NET} & O + O_3 & \rightarrow & 2O_2 &
\end{array}$$

$$\begin{array}{llcll}
(3) & HO + O_3 & \rightarrow & HO_2 & + O_2 \\
 & Cl + O_3 & \rightarrow & ClO & + O_2 \\
 & HO_2 + ClO & \rightarrow & HOCl & + O_2 \\
 & HOCl + h\nu & \rightarrow & HO & + Cl \\
\hline
\text{NET} & 2O_3 & \rightarrow & 3O_3 &
\end{array}$$

$$\begin{array}{llcll}
(4) & Cl + O_3 & \rightarrow & ClO & + O_2 \\
 & Cl + O_3 & \rightarrow & ClO & + O_2
\end{array}$$

$$\begin{array}{llcl}
 & \mathrm{ClO + ClO + M} & \rightarrow & \mathrm{(ClO)_2 + M} \\
 & \mathrm{(ClO)_2} + h\nu & \rightarrow & \mathrm{Cl + ClOO} \\
 & \mathrm{ClOO + M} & \rightarrow & \mathrm{Cl + O_2 + M} \\
\hline
\text{NET} & \mathrm{2O_3} & \rightarrow & \mathrm{3O_2}
\end{array}$$

Here M represents a catalytic O_2 or N_2 .

$$\begin{array}{llcl}
(5) & \mathrm{Cl + O_3} & \rightarrow & \mathrm{ClO + O_2} \\
 & \mathrm{Br + O_3} & \rightarrow & \mathrm{BrO + O_2} \\
 & \mathrm{ClO + BrO} & \rightarrow & \mathrm{Cl + Br + O_2} \\
\hline
\text{NET} & \mathrm{2O_3} & \rightarrow & \mathrm{3O_2}
\end{array}$$

At middle latitudes, these reactions are supposed to be less important than the "reservoir" reactions which effectively check the concentrations of Cl (and lead to an effective removal of Cl from the atmosphere in the form of acid rain):

$$\begin{array}{llcl}
(6) & \mathrm{Cl + CH_4} & \rightarrow & \mathrm{HCl + CH_3} \\
(7) & \mathrm{ClO + NO_2} & \rightarrow & \mathrm{ClONO_2}
\end{array}$$

In the polar stratosphere, particularly in the isolated Antarctic vortex, it has been proposed that reactions (6) and (7) do not to buffer the atmospheric Cl concentrations sufficiently to overcome heterogeneous reactions occurring on polar stratospheric clouds. In such an environment, it is thought that HCl becomes adsorbed on ice surfaces which then facilitate active molecule formation **(12, 13)**. Specifically, Cl may be released from its reservoir molecules as follows:

$$\begin{array}{llcl}
(8) & \mathrm{H_2O + ClONO_2}\ \text{(reservoir)} & \rightarrow & \mathrm{HNO_3 + HOCl}\ \text{(active)} \\
(9) & \mathrm{HCl}\ \text{(reservoir)} + \mathrm{ClONO_2}\ \text{(reservoir)} & \rightarrow & \mathrm{HNO_3 + Cl_2}\ \text{(active)}
\end{array}$$

Both "active" species are insoluble in ice. Reaction of a hydroxyl radical, OH, with HOCl leads to the formation of ClO (see Reaction (3)) and both HOCl and chlorine gas readily dissociate to form Cl radicals:

(10) $HOCl + OH \rightarrow H_2O + ClO$
(11) $Cl_2 + h\nu \rightarrow 2Cl$

The **Figure** is a flow chart showing all of these balances. The infamous ozone "hole" over the Antarctic is believed to be a result of this chemistry. Mean springtime ozone levels there have dropped 50% since 1957 **(14)** and up to 95% in specific instances. Observations supporting theory were recently made as part of the Airborne Antarctic Ozone mission: ClO and O3 were shown to have a strongly negative correlation over the Antarctic **(15)**.

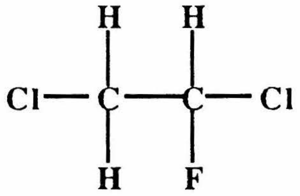
Box 2

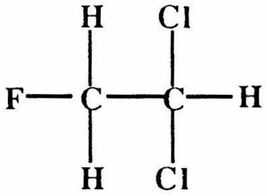
After the invention and successful application of CFC refrigerants in the 1930's, Kinetic Chemicals, now the Freon Products Laboratory of the DuPont Corporation, invented a convenient, but purposely confusing system of nomenclature to maintain the confidentiality of the proprietary compounds. The naming scheme, which became the industry's standard, is as follows:

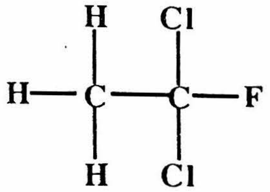
Each code number is formed using a possible four digits sometimes followed by a lower case letter:

- The ones digit represents the number of fluorine atoms per molecule.
- The tens digit represents the number of hydrogen atoms per molecule + 1. (All codes become at least two digits.)
- A hundreds digit represents the number of carbon atoms per molecule - 1. A zero is not written. (Thus, methanes are two digits while ethanes are three.)
- A one in the thousands digit represents unsaturation.
- For compounds containing more than one carbon, the most symmetric isomer is not appended with a letter. The second most symmetric form receives the designation a, the third, b, and so on. Symmetry is determined with priority to atomic identity followed by atomic weight.

In this manner, the following CFCs are assigned their unique names:


R141


R141a


R141b

The nomenclature was originally intended only for methanes, ethanes and ethenes containing fluorine and chlorine. The amount of chlorine atoms per molecule is then determinable by difference since the numbers of other atoms per molecule and the degree of saturation are explicitly calculable from the code. Various extensions have been made such as that for CF_3Br. For example, this compound can be considered a derivative of R13 (CF_3Cl) with bromine replacing chlorine. As such, it has been named both R13B1 and R1301. Alphabetical characters preceding the number such as R (refrigerant), FBA (foam blowing agent), P (propellant) and F (Freon™, hellenized abbreviation for Fluorine refrigerant) supply no additional information about chemical structure.

Box 3

The CSD Equation

The CSD equation contains two terms, the first describing hard sphere repulsion in dense state, and the second describing van der Waals type attraction **(26, 27)**:

$$\frac{Pv}{RT} = \frac{1 + y + y^2 - y^3}{RT(V + b)} + \frac{a}{(1-y)^3}$$

where $y = b/4v$

The values of a and b are specific to the individual fluids and can be fit with **(28)**:

$$a = a_o \exp(a_1T + a_2T^2)$$
$$b = b_o + b_1T + b_2T^2$$

We will use this equation to model both pure fluids and mixtures. The assumption for mixtures is that some appropriate a and b can be found and that the equation will apply as with a single component fluid. For a binary mixture, a and b are estimated as follows **(29)**:

$$a = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j a_{ij} \qquad \text{and} \qquad b = \sum_{i=1}^{2} \sum_{j=1}^{2} x_i x_j b_{ij}$$

where x is concentration and i and j refer to the two components.

a_{12}, which relates to the interaction between the two unlike species may be taken as:

$$a_{21} = a_{12} = (1 - f_{12})(a_{11}a_{22})^{1/2}$$

where f_{12} is an empirical correction factor and a_{11} and a_{22} are the values of the pure components.

b_{12}, which relates to the volume occupied by the molecules for hard spheres is:

$$b_{12} = \frac{(b_1^{1/3} + b_2^{1/3})^3}{8}$$

where b_1 and b_2 are the values of the pure components.

For similarly sized molecules, this can be estimated as **(28)**:

$$b_{12} = \frac{b_1 + b_2}{2}$$

Extracting Information from the CSD Equation

To make use of the equation for our work we must derive properties of interest in refrigeration from the equation of state. This is accomplished in the program by first calculating the Helmholtz free energy,

$$A = U - TS,$$

where U is internal energy, T is absolute temperature and S is entropy.

From thermodynamics, once A is known, all other thermodynamic functions may be evaluated by standard mathematical manipulations. A slight modification is made so that

$$A(v,T) - A^\circ(v,T) = \Delta A,$$

the difference between A and A°, the A of an ideal gas. This modification is made so that the integrals converge over volume space.

Use of such *departure functions* is a standard mathematical trick in thermodynamics **(30)**:

$$\Delta A = A(v,T) - A^{\circ}(v,T) = \int_{v}^{\infty} (P - \frac{RT}{v})\, dv$$

Note that when $v = \infty$ the CSD equation reduces to the ideal gas equation and the value of the argument of the integral is zero. In addition to an equation of state, the ideal gas heat capacity as a function of temperature **(31)** is required for each substance. Using this information, the computer subroutines can be linked together to determine any thermodynamic function. In this work, they were linked to provide information on the vapor compression cycle described earlier. The results of the calculations included temperature, T (K), pressure P (kPa), enthalpy H ($kJ \cdot kg^{-1}$), entropy S ($kJ \cdot kg^{-1} \cdot K^{-1}$), distribution of each component between liquid and vapor phases, heat transferred in the evaporator and work necessary to drive the ideal compressor.