



Research article

MODELING THE KINETICS OF OZONE LAYER DEPLETION USING SYSTEMS OF ODEs

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ABSTRACT

In this project three ozone depletion chemical kinetics systems of ODEs were proposed and modelled. Following this, three computer programmes were written one for each group of the system of ordinary differential equation (ODEs), and, ran using boundary conditions and data from internet. The result conformed to a large extent to what is obtainable in the literature on ozone depletion characteristic profiles. The behaviour of the elements and compounds in the stratosphere and even the chlorofluorocarbon are real to what is expected in the ozone depletion phenomenon as seen from literatures. The knowledge of the concentration time history variations of these elements and compounds in the stratosphere during ozone depletion phenomena can be used by ozone monitoring stations to predict certain occurrences in the near future. **Copyright © IJRETR, all rights reserved.**

Key words; Ozone depletion, stratosphere, systems of ODEs, Chemical Kinetics.

NOMENCLATURE

Symbols	Element
y_0	O
y_1	O ₂
y_2	O ₃
y_3	NO



y_4	NO_2
y_5	Cl
y_6	ClO
y_7	ClO_2
y_8	CF_2Cl_2
y_9	CF_2Cl

1.0 INTRODUCTION

In the last decades there have been numerous reports of O_3 loss in the upper atmosphere (stratosphere). Often the atmosphere headline in the news media are too short to provide complete picture and are simplified to tell only one side of the story (*Van der Leun et al., 1995*). Some claim that ozone depletion is a monumental global problem, whereas others state that ozone loss is non-existent. Even current advertisement and science fiction movies are not immune to the dramatic story of ozone loss (*Manney, 1994*).

Although the facts have sometimes been misrepresented, massive ozone loss over the Antarctic continent has been observed annually since 1997, significant ozone loss above the Arctic has been observed recently and ozone has been eroding slowly above the United States and other populated regions (*Rind et al., 2005*). The question therefore is why we should care about ozone depletion.

Ozone naturally shields the planet from incoming ultraviolet radiations from the sun and these radiations destroy deoxyribonucleic acid (DNA) and proteins in all living organisms. Increased ultraviolet radiation causes increased incident of basal cell and squamous cell skin cancer, and, possible melanoma immune system deficiencies and cataracts in human. In addition, the productivity of ocean phytoplanktons and certain crop plants is diminished by the increased ultraviolet radiation. (*Heath et al, 2007, Farman et al, 2007*).

An interesting and profound aspect of ozone depletion is that it is a global problem caused by human activities. Many people find it difficult to realize that humans can affect the environment on a global scale.

In this work, we will offer brief description of the chemistry of ozone, how ozone destruction is attributed to human activities and finally mathematically model a system of ozone layer depletion mechanism (*Jackman et al, 2010*).

The problem of ozone depletion and attendant ultraviolet radiation penetration into the lower atmosphere cannot be over emphasized. It is a global problem indeed, and the guilty nations whose activities cause the depletion are USA, Russia, Japan, China, Korea, France, Germany, and, even Great Britain and so on. Jaramillo and Solomon (2003) said that the nuclear activities of these people coupled with the wild fires in open bushes in Africa sent and still sending lot of CO_2 into the air. This reacts with O_3 and depletes it causing ozone holes so that ultraviolet radiation can penetrate the lower atmosphere. On one hand, we are talking of the cure for ozone layer depletion and on the other hand we are talking of carbon sequestration. Lots have been said about how to capture carbon from the atmosphere and pump it into the earth or ocean floors without good explanations. Proper explanation of its leakage back into the atmosphere and then to the upper atmosphere has not been made. (*Mckenzie and Johnston 2007*).



The problem therefore is how to seal the ozone holes created in the atmosphere so that ultraviolet rays from the sun can be checked from reaching the planet earth. Ozone is a triatomic, very reactive form of oxygen and is a bluish gas with pungent odour that is formed naturally in the atmosphere by photochemical reactions. It is a major air pollutant in the lower atmosphere but a beneficial component of the upper atmosphere and that is used for oxidizing, bleaching, disinfecting and deodourizing. It is a pure and refreshing air (*Frederick C.M, 1998*).

The importance of the study of the ozone layer depletion and its scenario is such that it will help in the understanding of any solution to be offered. The solution will actually be first how to sequester carbon (take away) from the atmosphere so that the carbon dioxide and ozone reaction will reduce and so that ozone holes will begin to close, thereby checking the ultraviolet radiation reaching the lower atmosphere. Also frequent bush burning and wild Fire outbreaks have to be controlled for the ozone holes to heal as this releases ozone depleting substances.

The objective of this study is to mathematically model different phenomenal mechanism of ozone depleting substances taking part in ozone depletion chemistry, so as to have a full insight to what occurs in this depletion activity. Such development will lead to the generation of chemical kinetics system of ODEs and their solutions. The understanding of this model will go a long way to furnish us with ideas and orderly steps on how to solve the problem of ozone layer depletion and save ourselves from the attendant global warming.

The scope of this work will cover different phenomenal chemical kinetics mechanism that constitutes ozone layer depletion and their modeling into groups of system of ordinary differential equations (ODEs). The solutions of such group of ODEs and plots will give an insight to the crust of the matter in the ozone layer phenomena and perhaps the solution.

2.0 ROLE OF OZONE

The unique role of ozone in absorbing certain wavelengths of incoming solar ultraviolet light was recognized in the latter part of the nineteenth century by (*Cornu et al., 1990*). Interest in ozone stems from the fact that such absorption of solar radiation is important in determining not only the thermal structure of the stratosphere (*Andrews et al., 1998*) but also the ecological framework for life on Earth's surface. Ozone is a consequence of oxygen-only chemistry. Decreased ozone results in increased ultraviolet transmission, which can affect the health of humans, animals, and plants (*VanderLeun et al, 1995*). Observations of the total integrated column ozone based on ultraviolet absorption began in the twentieth century (*Fabry et al., 1993*). Systematic measurements of this type have revealed that the total ozone abundances over many regions of the globe have decreased markedly since about 1980. Without it, life would have remained under water (*Dobson, 2000*). Indeed, the depletion of the global ozone layer has emerged as one of the major global scientific and environmental issues of the twentieth century.

Quantity or concentration of Ozone varies from year to year at all locations but the behaviour seen in recent decades in Antarctic spring lies very far outside of the historical variability. Throughout much of the atmosphere the abundance of ozone molecules is the result of a balance between production by UV radiation from the sun and chemical loss. However, in those regions of the stratosphere where most of the ozone resides, such a balance does not obtain. Instead, the distribution of ozone is shaped largely by atmospheric transport (*DuEtsch, 1994*).



Trace gases play an important role in the atmosphere through their interactions with solar and terrestrial radiation and consequently, effects on global climate. There has been much concern that increased anthropogenic release of trace gases such as CO₂, CH₄, NO₂ and chlorofluorocarbons (CECs) from industrial, agricultural and domestic activities will, in addition to enhancing the greenhouse effect, significantly modify the chemical composition of the atmosphere, so as to cause global warming and stratospheric ozone depletion (*Johnston, 2009*). These changes result in the warming of the troposphere (the bottom 8-16km of the atmosphere) and the cooling of the stratosphere (the layer above that extends to an altitude of about 50km and contains the ozone layer). Recent findings linking the rise in chlorine (a by-product of extensive CFC build-up in the atmosphere over the past 3 decades) and oxides of nitrogen (due to emissions from aircraft) to the destruction of stratospheric ozone (*Prather et al, 1990*) have stimulated renewed interest in the development of interactive chemistry-climate models. Such models may be used to diagnose the combined effect of physical and chemical processes, thus including both direct and indirect radiative effects, and to assess potential changes associated with future trace gas emissions to the atmosphere. The net effect of these linkages is an intensification of both climate change and ozone depletion and possibly a delay in the recovery of the ozone layer as it responds to diminishing levels of CFCs and other ozone depleting substances (*Stedman, 2002*).

3.0 DEVELOPMENT OF SYSTEMS OF ODE MODELS

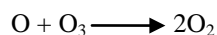
In this section three different groups of Cox et al (2010) Ozone chemical reaction system of equations were adopted for modeling. Modeling helps us to understand the working of the atmosphere and allows us to forecast the effects of changes in external factors such as solar variability, seismic and other earth catastrophes, or the addition of greenhouse gases.

Group of phenomenal chemical mechanisms for ozone layer depletion are represented and their kinetic mechanisms are formulated in each case as a system of ordinary differential equations (ODEs). The groups of models were solved and plotted in a graphical form for each case.

In developing these, the chemical engineering reaction rate law was utilized to arrive at the system of the ordinary differential equations (ODEs).

3.1 Ozone Depletion Chemical kinetics

An updated version of this framework is shown by the three reactions presented below:



Based on the above kinetic reactions, the various rate of reaction for each of the reaction is obtained and used in obtaining the system of first order ordinary differential equations (ODEs). They are given below:

1.) Chapman Chemistry

$$\frac{d[O_2]}{dt} = -K_1 [O_2] - K_2 [O][O_2][M] + K_3 [O_3] + K_4 [O]^2 [M] + K_5 [O][O_3]$$

$$\frac{d[O]}{dt} = 2K_1 [O_2] - K_2 [O][O_2][M] + K_3 [O_3] + K_4 [O]^2 [M] - K_5 [O][O_3]$$

$$\frac{d[O_3]}{dt} = K_2 [O][O_2][M] - K_3 [O_3] - K_5 [O][O_3]$$



Substituting, the symbols from the nomenclature yields:

$$\frac{dy_1}{dt} = -K_1y_1 - K_2y_0y_1M + K_3y_2 + K_4y_2y_0^2M + K_5y_0y_2$$

$$\frac{dy_0}{dt} = 2K_1y_1 - K_2y_0y_1M + K_3y_2 - K_4y_0^2M - K_5y_0y_2$$

$$\frac{dy_2}{dt} = K_2y_0y_1M - K_3y_2 - K_3y_0y_2$$

2.) Illustrative Odd Nitrogen Catalytic Cycles

$$\frac{d[NO]}{dt} = K_{11}[NO][O_3] - K_{12}[O][NO_2]$$

$$\frac{d[O_3]}{dt} = -K_{11}[NO][O_3]$$

$$\frac{d[NO_2]}{dt} = K_{11}[NO][O_3] + K_{12}[O][NO_2]$$

$$\frac{d[O]}{dt} = -K_{12}[O][NO_2]$$

Substituting, the symbol from the nomenclature yields:

$$\frac{d[y_6]}{dt} = -K_{11}y_3 \cdot y_2 + K_{12} \cdot y_0 \cdot y_4$$

$$\frac{d[y_2]}{dt} = -K_{11}y_3 \cdot y_2$$

$$\frac{d[y_7]}{dt} = -K_{11}y_3 \cdot y_2 - K_{12} \cdot y_0 \cdot y_4$$

$$\frac{d[y_1]}{dt} = -K_{11}y_3 \cdot y_2 - K_{12} \cdot y_0 \cdot y_4$$

$$\frac{d[y_0]}{dt} = -K_{12} \cdot y_0 \cdot y_4$$

3.) Reactions of chlorofluorocarbon

$$\frac{d[CF_2Cl_2]}{dt} = -K_{17}[CF_2Cl_2]$$

$$\frac{d[Cl]}{dt} = -K_{17}[CF_2Cl_2] - K_{18}[Cl][O_3] + K_{20}[ClO_2]$$

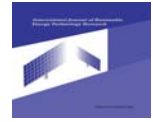
$$\frac{d[O_3]}{dt} = -K_{18}[Cl][O_3]$$

$$\frac{d[ClO]}{dt} = -K_{18}[Cl][O_3] - K_{19}[ClO][O]$$

$$\frac{d[O_2]}{dt} = -K_{18}[Cl][O_3]$$

$$\frac{d[O]}{dt} = -K_{19}[ClO][O]$$

$$\frac{d[ClO_2]}{dt} = -K_{19}[ClO][O] - K_{20}[ClO_2]$$



Substituting, the symbols from the nomenclature yields:

$$\frac{dy_{13}}{dt} = - K_{17}y_8$$

$$\frac{dy_{14}}{dt} = K_{17}y_8$$

$$\frac{dy_8}{dt} = - K_{17} \cdot y_3 \cdot y_{13} - K_{18} \cdot y_5 \cdot y_2 + K_{20} \cdot y_7$$

$$\frac{dy_2}{dt} = - K_{18} \cdot y_5 \cdot y_2$$

$$\frac{dy_9}{dt} = - K_{18} \cdot y_5 \cdot y_2 + K_{19} \cdot y_6 \cdot y_1$$

$$\frac{dy_1}{dt} = - K_{19} \cdot y_6 \cdot y_1$$

$$\frac{dy_{12}}{dt} = - K_{19} \cdot y_6 \cdot y_1 - K_{20} \cdot y_7$$

The three first order ODE systems of models that were developed are: Chapman Cycle, Illustrative Odd Nitrogen Catalytic Cycle and the Reactions of Chlorofluorocarbon

3.2 DATA COLLECTION

The data for verification and validation for this group of models were obtained from the experiment of the ozone monitoring station in advanced countries through the internet. This is because such data cannot be obtained within or through any third world countries like ours as we have no such earth moving equipment for weather and climatic analysis

3.3 CURVE FITTING

Three computer programs were written for the three different groups of systems of ODEs and were solved using Matlab package 7.9. The programs were ran for the three different systems of ODEs and their graphs (individual and group) were plotted to reveal the variation nature of the elements and compounds that constitute the ozone layer depletion of a system. The programs are:

4.0 RESULT PRESENTATION AND DISCUSSION

4.1 RESULT PRESENTATION

The results of the plots of the system of ODEs in the previous section through programs in appendix A, B and C are as shown below:

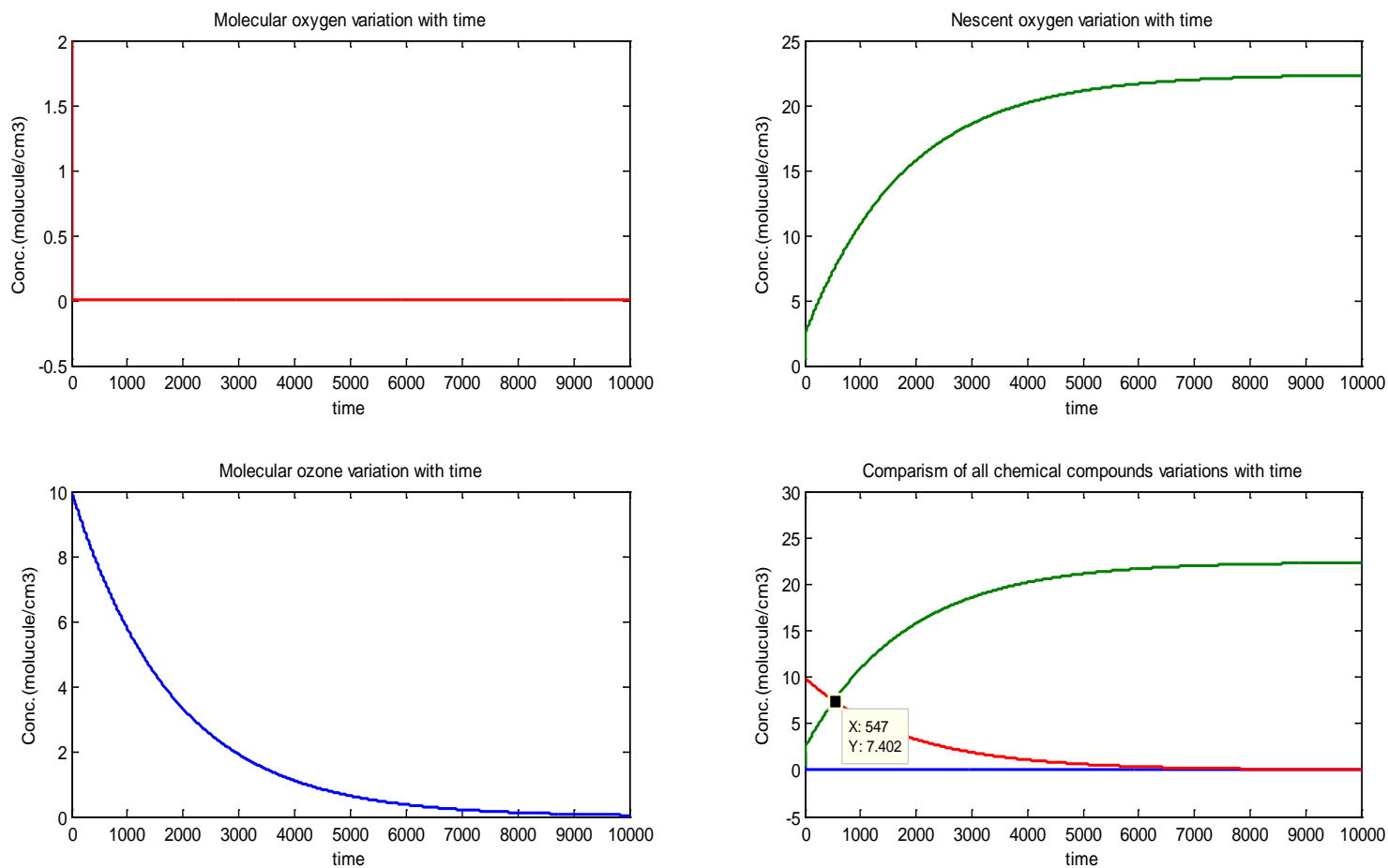


Fig.1: Chapman chemistry (Concentration-time variation)

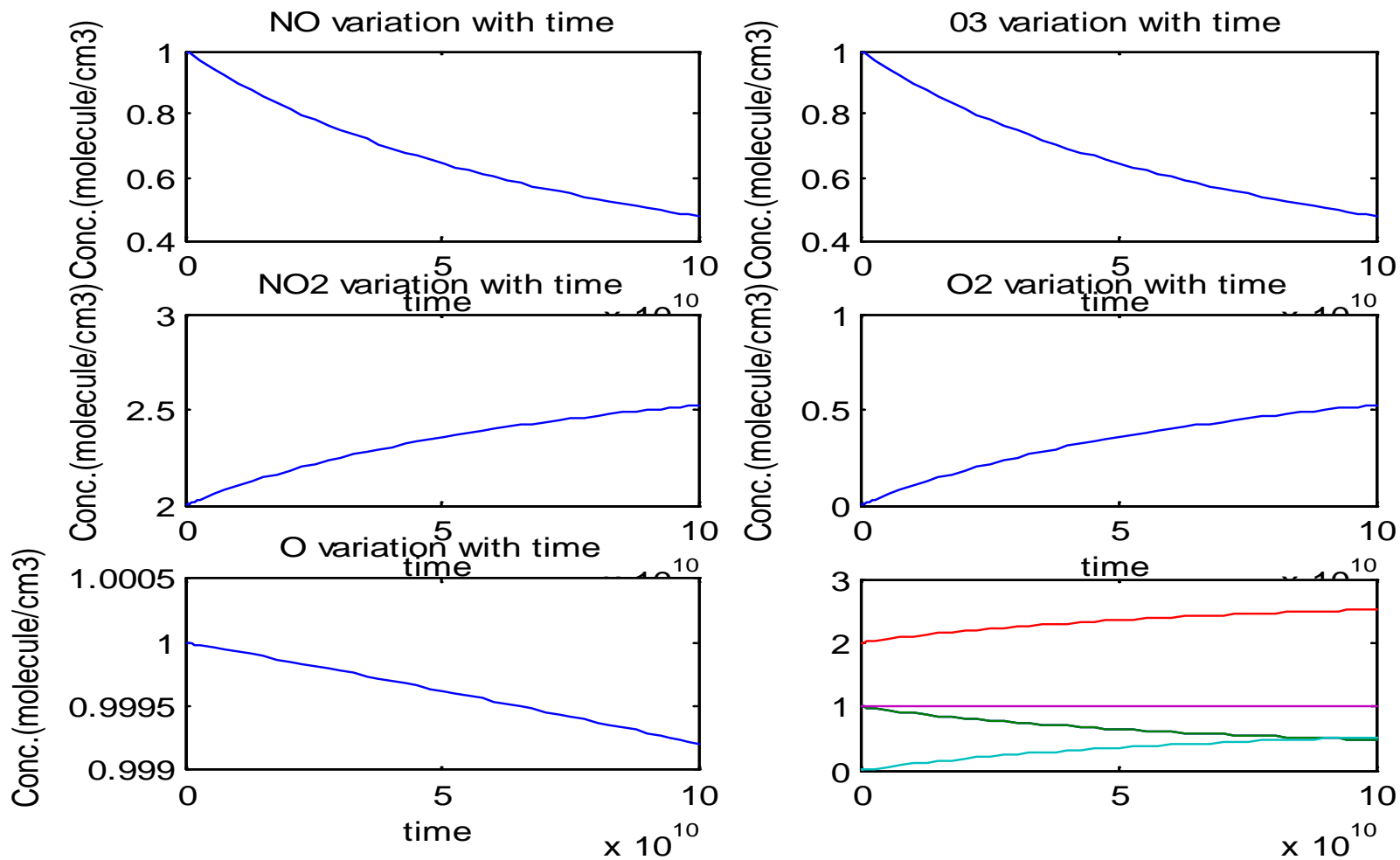


Fig. 2: Illustrative odd nitrogen catalytic cycle(Concentration-time variation)

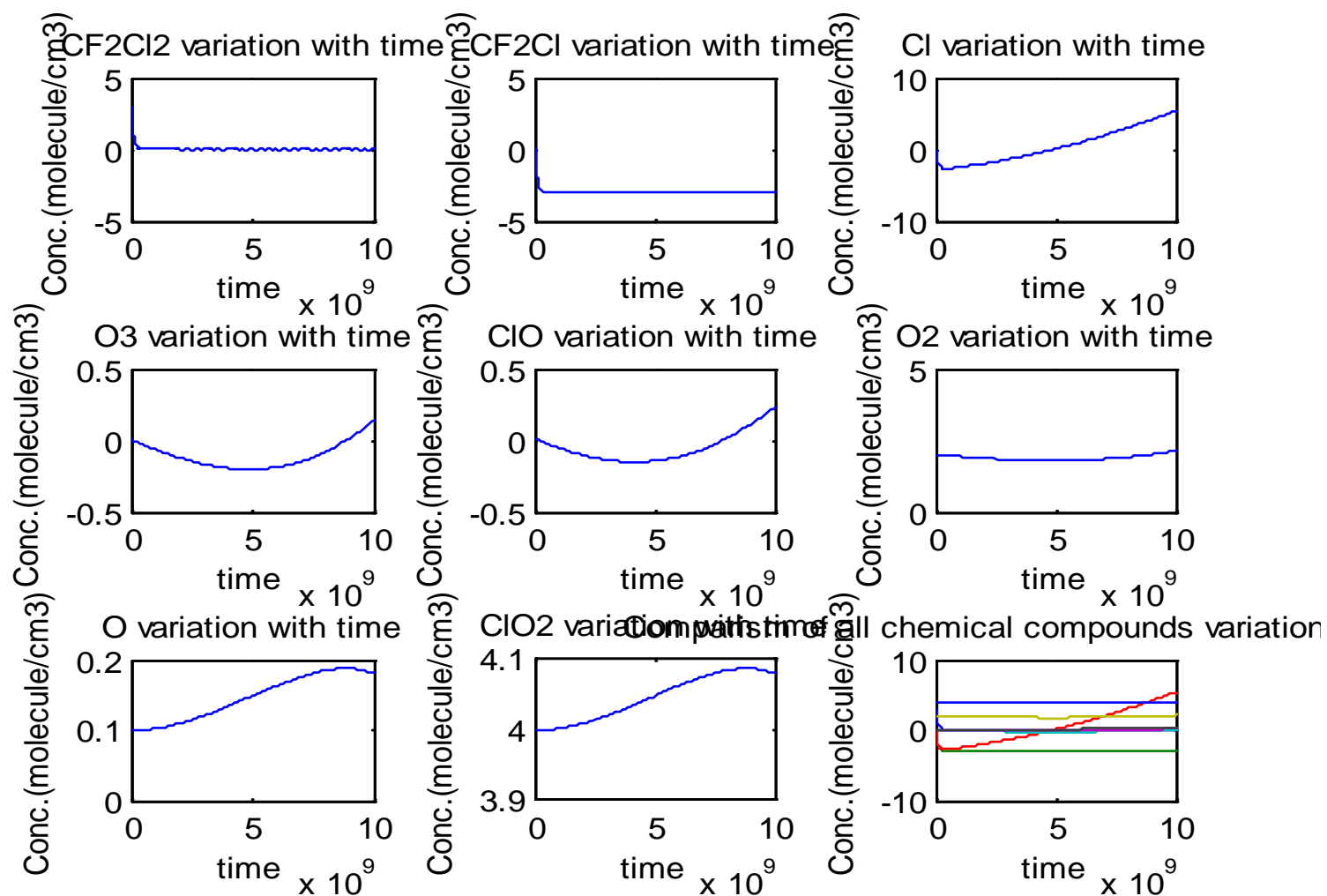


Fig. 3: Reactions of chlorofluorocarbons (Concentration-time variation)



4.2 RESULT DISCUSSION

In Fig. 1 (Chapman Chemistry) it is seen that the concentration of molecular oxygen does not vary in the stratosphere with time. However, the nascent oxygen varies like a natural growth phenomenon rising and then tapering off to an ultimate. Also, the concentration of ozone continues to fall exponentially as it is attacked by nascent oxygen with time. At about 547 seconds, the nascent oxygen and the ozone concentration becomes equal to $7.402 \text{ molecule/cm}^3$ after which they diverge with nascent oxygen increasing to an ultimate value and molecular ozone decreasing to a minimum.

In Fig. 2 (Illustrative Odd Nitrogen Catalytic Cycle), nitrogen monoxide (NO) just like ozone concentration continues to fall exponentially with time while nitrogen dioxide (NO_2) just like molecular oxygen continues to rise to an ultimate, like a natural growth profile, but nascent oxygen continues to fall in a parabolic exponential form.

In Fig. 3 (Reactions of Chlorofluorocarbon), variation of dichlorofluorocarbon (CF_2Cl_2) with time is unique. It quickly comes to zero in few milliseconds and remains at that while the monochlorofluorocarbon (CF_2Cl) has the same variation profile with dichlorofluorocarbon but started from zero and continues to decrease with time to -3 molecule/cm^0 where it remained constant. The chlorine fell from zero to $-2.5 \text{ molecules/cm}^3$ and then rose exponentially to 5 molecules/cm^3 .

There is a similarity in the variational shape of O_3 , ClO and O_2 with time. They first decrease from their initial concentrations to their respective minimum and then rise (trough) but the nascent oxygen and ClO_2 displayed a kind of sinusoidal variation with time.

From Figs 1, 2 and 3, it therefore means that the variation of these compounds and elements are dependent on their stoichiometry and path they play in the stratospheric interaction of ozone layer depletion.

5.0 CONCLUSION/RECOMMENATION

In this work three ozone depletion chemical kinetics were proposed and modelled. Following this, three computer programmes were written for each group of ordinary differential equation (ODEs) and ran using boundary conditions and data from internet. The result conformed to a large extent to what is obtainable in the literature on ozone depletion. The behaviour of the elements and compounds in the stratosphere and even the chlorofluorocarbon are real to what is expected in the ozone depletion phenomenon as seen from literatures. The knowledge of the concentration time history variations of these elements and compounds in the stratosphere during ozone depletion phenomena can be used by ozone monitoring stations to predict certain occurrences in the near future.

More kinetic system of ODE models should be worked on so as to have more systems of ODEs that will clarify the intricacies in the mechanisms and bring the understanding closer to mankind.

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