LONG-TERM ECONOMIC GROWTH: MODELING THE RACE BETWEEN ENERGY AND TECHNOLOGY AND THE STRATOSPHERIC EFFECTS OF HYDROGEN AS A GENERAL PURPOSE ENERGY SOURCE

Anthony A. Noce

A Thesis

In the Special Individualized Program

of

The School of Graduate Studies

Presented in Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy (Pure Science)
(Economics and Chemistry)

Concordia University

Montreal, Quebec, Canada

September 2015

CONCORDIA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

This is to certify that the thesis prepared

By: Anthony A. Noce

Entitled: Long-Term Economic Growth: Modeling the Race between Energy and Technology and the Stratospheric Effects of Hydrogen as a General Purpose Energy Source

and submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy (Special Individualized Program)

complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the final examining committee:

____ Chair
Dr. I. Irvine

____ External Examiner
Dr. C. Gervich

____ External Examiner
Dr. R. Pascalau

____ Examiner
Dr. S. Robidoux

____ Examiner
Dr. W. Sims

____ Thesis Co-Supervisor
Dr. T. Koreshkova

____ Thesis Co-Supervisor
Dr. G. Peslherbe

Approved by: ____
Dr. C. Reiss, Graduate Program Director

September 11, 2015

____
Dr. P. Wood-Adams
Dean of Graduate Studies

Abstract

Long-Term Economic Growth: Modeling the Race between Energy and Technology and the Stratospheric Effects of Hydrogen as a General Purpose Energy Source

Anthony A. Noce, Ph.D.
Concordia University, 2015

This thesis presents an alternative approach to modeling economic growth by constructing a biosphere-energy-technology (BET) model that incorporates energy, technology and entropy as distinct factors that generate transitional competitive equilibriums. Technological progress under BET models assumptions is limited by recognized and available energy sources/carriers, named general purpose energy sources (GPESs), and that the recognition of such sources affect choices in technological development. This thesis represents a first attempt at incorporating the biosphere, which can experience catastrophic bifurcations, into a model of economic growth. The BET model, which puts strict conditions on the idea that no innovative society need accept Malthusian diminishing returns, predicts that energy and technology are both required for sustained growth given some temporal relationship between them.

The main findings from the BET model are that pervasive technology shocks lead to large increases in consumption, but that technology alone will not sustain economic growth; and, that energy shocks cause permanent labour resource movements from the consumption sector to the energy knowledge sector. Energy shocks in the BET model result in an increase in consumption and utility; however, the effect of a particular energy source that gives rise to the energy shock depends on various parameters that embody institutional factors and policy.

Using hydrogen as a GPES candidate that can give rise to an energy shock, the effects of deuterated molecular hydrogen and deuterated methane on the kinetic rate constants for selected stratospheric radical reactions, including the rate of ozone destruction, were examined computationally. In the case of a tethered hydrogen economy, an increase in deuterated molecular hydrogen in the stratosphere may result in a marked change in the rate at which chlorine radical acts as a sink for H_2 and can contribute to decreasing ozone concentrations.

However, the kinetic isotope effect results for methane oxidation reactions imply that decreases in polar stratospheric clouds formation and decreased solid HCl are possible with a tethered hydrogen economy resulting in less ozone destruction. In sum, monodeuterated molecular hydrogen and methane may not contribute to appreciable stratospheric ozone loss and may even have a net positive effect.

Acknowledgements and Dedication

This work would not have been possible without the full and continued support of my committee – Drs. Koreshkova, Peslherbe, Robidoux, and Sims. I am indebted to my economics supervisor, Dr. Tatyana Koreshkova for her patience and extremely helpful comments. Without her, my ideas would not have found economic clarity. Throughout the journey she became more than a supervisor – she became a colleague and a friend. I am grateful to Dr. William Sims, who was not only the one who suggested Dr. Koreshkova as a supervisor, but was, from the time of my initial application to Concordia University, a full supporter of my desire to complete a Special Individualized Ph.D. in Economics and Chemistry. Dr. Sims counseled me in times of difficulty with intriguing stories of his own defense.

Like Dr. Sims, Dr. Robidoux has been a wonderful mentor and friend from the time of application to the completion of the dissertation. The long discussions on polymer chemistry and his willingness to guide me through the choice of an appropriate supervisor in chemistry will leave me indebted to him for a long time. I must blame Dr. Robidoux for re-igniting my passion for chemistry and making chemistry a bigger than originally intended component of my Ph.D. Also, without Dr. Robidoux, I would never have been introduced to my chemistry supervisor, Dr. Peslherbe. I am grateful to Dr. Peslherbe for accepting me into his lab and helping model my idea into something more tractable. I also appreciate his trust in me and allowing me to carry out my research idea with much independence. Dr. Peslherbe was always approachable and I look forward to continued work with him.

I cannot forget to include members of Dr. Peslherbe's lab who helped me, without hesitation, through the initial struggles of coding in the various chemistry software programs - Drs. Soran Jahangiri and Denise Koch. I also want to thank Dr. Dhimitri Qirjo for our long and informative talks and useful suggestions.

I apologise to all those I have inadvertently left out.

Most importantly, I want to dedicate this work to all those who have encouraged me to always work hard and pursue learning for its own sake – my parents, Nicolina and Antonio, who never had the opportunity to a higher education but sacrificed much so that I was afforded the

possibility, my grandmother, Cesina, who taught me the value of education and faith from an early age, my uncle Ildebrando, whose stories about history, war, and politics I will never forget, and my aunt Ida, who always knew when I was studying.

The dedication also extends to those who have been patient with me as I completed this long journey - again my parents, my sister, Sandra, and perhaps most of all to my wife, Nesreen and my children. To the latter, Teodoro-Antonio and Costantino (and future generations), I thank you, love you, and wish you at least as much good fortune in the pursuit of knowledge. Let no one forget those in the past that have sacrificed so much to make the pursuit possible.

Ancora più importante, voglio dedicare questo lavoro a tutti coloro che mi hanno incoraggiato a lavorare sempre con perseveranza e continuare il percorso di apprendimento come fine a se stesso - in particolare i miei genitori, Nicolina e Antonio, che hanno tanto sacrificato anche se non hanno mai avuto l'opportunità di un'istruzione superior; mia nonna, Cesina, che mi ha insegnato il valore dell'istruzione e della fede fin dalla mia tenera età; mio zio Ildebrando, dal quale ho tanto imparato grazie alle sue narrazioni sulla storia, sulla guerra, e la politica che non potrò mai dimenticare, e mia zia Ida, che ha sempre saputo appoggiarmi quando studiavo.

La mia dedica si estende anche a tutti coloro che sono stati pazienti con me durante questo lungo percorso - ancora una volta i miei genitori, mia sorella, Sandra, e forse più di tutto la mia moglie, Nesreen, e i miei figli. Per quest'ultimi, Teodoro-Antonio e Costantino (e generazioni future), vi ringrazio e vi voglio bene. Allo stesso tempo vi auguro tanta fortuna e diligenza nella ricerca del sapere. Che nessuno di voi dimentichi quelli che ci hanno preceduto i quali hanno sacrificato così tanto per rendere possibile l'itinerario alla ricerca di una conoscenza specializzata.

Con il sentimento di profondo apprezzamento per tutti rinnovo i miei sentimenti di gratitudine,

Anthony A. Noce, Ph.D.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

A_t	Current stock of technology knowledge
a_t	Flow of produced knowledge
A_t^E	Current stock of composite energy knowledge
a_t^E	Flow of produced composite energy knowledge
B_t	Current level of new GPES adoption
b_t	Adoption flow of new GPES
BET	Biosphere-energy-technology
c_t	Current Consumption
CBSQ	Quadratic complete basis set
CFC	Chlorofluorocarbon
CVT	Canonical variational transition state theory method
d_t^E	Labour force allocated to the development of new ideas related to GPESs
d_t^G	Labour force allocated to the development of new ideas related to GPTs
EKC	Environmental Kuznet's curve
G_t	GPT productivity coefficient
G_t^E	GPES productivity coefficient
GDP	Gross domestic product
GHG	Greenhouse gas
GPES	General purpose energy source or carrier
GPT	General purpose technology
ICT	Information and communication technology
IRC	Intrinsic reaction coordinate
ISPE	Interpolated single-point energies
KIE	Kinetic isotope effect
MP-HF	Møller–Plesset perturbation theory-Hartree Fock
n	Non-technical labor force
POX	Partial oxidation
PSC	Polar stratospheric cloud
Q	Heat
S	entropy
SCT	small-curvature tunneling
SMR	Steam reformation of methane
TST	Transition state theory
U	Utility
VOC	Volatile organic compound
VTST	Variational transition state theory
X_t	Current biosphere level
ZPVE	Zero point vibrational energy

Introduction

Research into the determinants of long-run economic growth shows that there is no single causal rationale that leads to an empirically unchallenged theoretical growth model. For instance, endogenous growth theory underscores the importance of policies aimed at facilitating technology transfer. Some versions of such models predict that most countries should converge to the same growth rate. Yet, these widely held views are challenged. Empirical analyses show divergence in long-run trends of economic growth and, in the United States, long-term trends are not correlated with the various determinants of growth (such as education levels, government taxation, R&D intensities) advocated in endogenous growth theories (Jones, 1995). Capital accumulation does not seem to provide for the majority of cross-country differences in level and growth rate of per capita gross domestic product (GDP).

Theories suggesting that an increase in the size of population (referred to as “scale effects”) should raise long-run growth by providing both a larger pool of potential innovators and a larger market for the successful innovations are also refuted. Even if the relevant scale is a global one, postwar empirical evidence from the United States, which finds that the number of innovators (i.e. the number of scientists and engineers engaged in R&D) has risen by 400% since the 1950s, shows that there has not been a long-run increase in total factor productivity growth over the period corresponding to the predictions from (Schumpeterian) endogenous growth theory.

The theory of “General Purpose Technologies” or GPTs purposes that growth is sustained by the occasional arrival of a major innovation - the GPT - that diffuses throughout the entire economy and thus has profound effects on the organization of the economy and supporting institutions, and further compliments other innovations associated with its increasing use. Although the theory of GPT-driven growth adds much to the literature, here, too, we find a missing link, which will be examined in this thesis, between technology and growth that does not allow these theories to fully explain pre- and post-Industrial Revolution growth.

In addition to the standard economic growth models, more heterodox approaches to growth have also been taken. Such approaches attempt to incorporate the thermodynamic notion of entropy and argue that continual economic growth will lead to environment collapse because of increasing anthropogenic disorder. This application of entropy to economic growth has generally been a failure due to the misuse of the concept of entropy or the difficulty of creating a quantitative entropy measure applicable to economic processes.

This thesis finds that there is a need to establish an energy-technology driven growth model that informs economic policy that is consistent with long-term stable environmental quality, where the time horizons extend beyond the traditional decades. This thesis will therefore present arguments that energy needs to be explicitly incorporated in a technologically driven economic growth model; and, once energy is an explicit model element, the growth model will require generating effects of growth on the biosphere (or natural environment). In Chapters 1-3, this thesis will define (1) the concept of a general purpose energy source (GPES) for which it will interact with technology to sustain growth; and, (2) the proper usage of the concept of entropy, which will circumscribe the conditions on the idea that no innovative society need accept Malthusian diminishing returns. In Chapter 4, the race between energy and technology will be modeled and numerical simulation of the model will follow. The thesis will use the characteristics of a GPES and apply them to hydrogen in Chapter 5; and, in Chapter 6, using hydrogen and its stratospheric effects, will show the limits of using entropy as the decisive element dictating policy on economic growth and energy use.

In sum, the objective of this thesis is to develop a general explanation of economic growth based on energy and technology, consistent with historical observations, applicable in a variety of contexts and time periods, and with implications for current policies using a potential future energy source. This is a work of history, economics, and chemistry.

Chapter 1: Technology and Economic Growth

1.1 Introduction to Economic Change

The last two centuries can be defined as an era of economic growth where output per capita not only increased markedly, but in a sustained manner that has no historical comparison. Specifically, this growth is 'intensive growth'; that is, a result of increases in gross domestic product (GDP) per capita. This era began with what most have termed the "Industrial Revolution", although the term itself is ambiguous in economic terms (Aghion and Durlauf, 2005). In order to explain this phenomenon, the literature has produced many economic models that try to (i) answer some of the questions listed below (Aghion and Durlauf, 2005), and (ii) remain consistent with the constraints of one or more of the 'stylised facts' listed below (Easterly and Levine, 2001):

(i) Questions:

1. What explains the *location* of the Industrial Revolution?
2. What explains the *timing* of the Industrial Revolution?
3. Is sustained economic growth and continuous change the "normal" state of the economy, or is the experience of the past 200 years a revolutionary regime change?
4. What was/is the role of technology in the origins of rapid growth?
5. What was/is the relation between demographic behavior in bringing about and sustaining modern economic growth? and
6. What was/is the role of institutions, and to what extent can we separate it from other factors such as technology and factor accumulation?

Questions 1 and 2 can be generalised, as in Jones (1998), and asked in other words, "What is the engine of economic growth?"

(ii) 'Stylized facts':

1. Cross-country differences in the level or growth rate of GDP per capita are not fully explained by factor accumulation;
2. Over the past two centuries, there has been divergence in cross-country growth rates;
3. While capital accumulation has been persistent in most countries in the last 200 years, growth rates have not been persistent over time;
4. Economic activity is highly concentrated such that factors of production flow to the same locations; and
5. National policies influence long-term growth.

1.1.1 Are Growth Models Limited to Generally Explaining Sustained Western Growth?

Most discussions on economic growth begin with references to the Industrial Revolution. Indeed, many formal growth models use U.S. data over the last two centuries and draw conclusions from those empirical observations. This is not to imply that European or American cultures have something unique about them which cannot exist with other societies. Simply, growth literature focuses on Western Europe and its offshoot because it was there that sustained economic growth first appeared in the late 18th century. While China and other regions (e.g. Islamic empire during the Mamluk rule) were successful in certain areas of technological development and could have spurred an economic revolution akin to the Industrial Revolution, it was Western Europe that achieved divergence in economic growth; and sustained it. The determinants of this sustained growth are the focus of many studies on economic history, economic history of technology and economic growth in general. In this thesis, we add to the literature by exploring a less studied co-determinant of economic growth - energy sources - and modeling its relationship with technology. We also explore how the relationship between energy and technology in Western Europe was different than in other regions such as China and how this lead to sustained growth in the West.

1.2 The Role of Technology in Economic Growth Models

There is consensus in the economic literature that such sustained growth over the last century and particularly in capitalist economies is a result of mainly technological progress. Most theoretical models of endogenous and exogenous technological growth have been constructed to explain this observed growth in income. These models, however, are based on data available for the last one to two hundred years and thus can explain growth patterns within this time period, but they cannot be used to describe or account for the highly unstable growth in income before the late 19th century. This is not a failing in the models per se as they are not constructed to model economic growth since antiquity. Any model designed to do so would be theoretical due to the lack of historical data and simulation of the model would necessarily rely on generated historical data. With neoclassical growth models, economic growth occurs by increasing labour or capital input, technological improvements and/or improved quality of capital and labour inputs. Long term growth is seen as an extension of an historical and stochastic path-dependent process in which various agents operate in an environment of uncertainty.

The first dynamic models of sustained economic growth were based on the assumption of exogenous technical change (e.g. Solow, 1956). However, modeling sustained growth using technology as an exogenous factor has its drawbacks. Long-run differences in economic growth exhibited by different countries, for example of up to 8% from -4% for Chad, to +4% for Japan over periods of up to 30 years (Jones and Manuelli, 1997) are not explained. If changes in productivity are a result of conscious decisions by economic agents, then exogenously determined productivity effects do not account for such decisions, nor can policy decisions affect changes in technologically-driven growth. For instance, Solow (1956) assumes that labor productivity grows continually and exogenously. Therefore, to overcome these inherent weaknesses of exogenously determined technical change, others (a few notable examples include Romer, 1986; Lucas, 1988; Sala-i-Martin, 1990; Grossman and Helpman, 1991; Helpman, 1992; Aghion and Howitt, 1992) endogenize technological change in economic models in order to account for long-run growth. Even then, however, these models help explain growth as observed over the last two centuries in the United States and other capitalist economies. They provide little insight into economic growth farther back in time and across all societies.

Endogenizing the technological parameter was achieved by endogenizing the underlying source of sustained growth in per-capita income, the accumulation of knowledge (Romer (1986) and Lucas (1988)). The accumulation of knowledge by individuals and society is realised through formal education, basic and applied scientific research, learning-by-doing, product innovation and processes and the like. For Aghion and Howitt (1992), knowledge accumulation also includes industrial innovations that improve the quality of products. Their model build's on Schumpeter's (1942) process of creative destruction such that competition among research firms is motivated by the possibility of monopoly rents from patents. These innovations are new intermediate goods, which are then used to produce final outputs in a more efficient manner. The monopoly rents, however, will destroy the next innovation such that the existing intermediate good becomes obsolete (Aghion and Howitt, 1992). Economic growth thus results exclusively from technological progress.

1.3 Economic Growth and General Purpose Technologies

Section 1.2 reviews some growth models that embodied endogenous technological progress. These models generally explain modern, Western long-term sustained growth. Given that these models explain growth for a subset of world countries and for a specified period of history, it is clear that the phrase 'long term' is ambiguous. In the view of evolutionary economists[1], 'long term' can be taken to mean thousands of years. Since the neoclassical approach to economic growth does not model change from the time of antiquity, one must turn to different constructs.

One class of models found in the literature assumes that long term growth subsists because the stochastic path-dependent process is sporadically disrupted by the arrival of General Purpose Technologies (GPTs), which transform economic and social interactions. A GPT is formally defined in Lipsey *et al.* (2006) as "a single generic technology, recognizable as such over its

[1] Evolutionary economic theory originated outside the orthodox neo-classical tradition and holds that neo-classical theory is a special case in a much more complex reality. Evolutionary economics is inspired by evolutionary biology and draws on evolutionary game theory. It is similar to mainstream economics in its stress of complex interdependencies, competition, growth, structural change, and resource constraints. The difference is in the approaches which are used to analyze these phenomena

whole lifetime that initially has much scope for improvement and eventually comes to be widely used, to have many uses, and to have many spillover effects."

The concept of the GPT, first introduced by Bresnahan and Trajtenberg (1995) and used in the modeling of technology in macroeconomic growth models, views a GPT as a technology or technological dynamism that performs some generic function that is vital to the operation of a large number of enabling products and/or production systems so that it embodies a "general purposeness". The internal combustion engine is a typical example of a GPT found in the literature. As noted previously, many other (non-GPT) growth models also embodied technology – the stock of knowledge[2] available to an economy – and endogenized changes in technology (e.g. Lucas, 1988 and Romer, 1990). However, beyond that general concept of a technology, a GPT should exhibit the property of "complementarity" so that it enables technical advances in other economic sectors as well as making it more profitable for its users to innovate and improve on other technologies. Thus, a GPT nurtures a broad spectrum of advances of applications. A GPT creates a positive loop that may result in faster, or at the very least, sustained growth for an economy as a whole. Note that Lipsey *et al.* (2006) argue that for GPTs the most profound effects came from the making of new products, process and organization form, and not from a fall in their price.

Since GPTs are technologically distinct from each other, knowledge of past GPTs provides little quantitative evidence about how novel, future ones will behave. For example, knowing how the steam ship engine affected the economy over the hundred plus years of its evolution reveals practically nothing to economic agents about the evolutionary path to be expected for information and communication technologies (ICTs) (e.g. the Internet) at the time of the invention of the computer chip. All models relating to GPTs describe GPTs as arriving randomly, with the average growth rate over long periods of time in which several GPTs succeed each other being determined by the accumulated amount of fundamental knowledge (Nicholas and Petra, 2004). This is determined partly endogenously by the allocation of resources to fundamental research and partly exogenously by random factors affecting the productivity of those resources.

[2] Knowledge can be embodied in humans as skills, in machinery or in (organizational/societal) processes.

Carlaw and Lipsey (2006) find that earlier GPT growth models omitted empirical observations about GPTs. That is, the first generation of GPT theories predicted that each new GPT would be accompanied by a temporary slowdown in the rate of productivity growth. Observation, however, shows that some GPTs produce slowdowns while others do not (Lipsey *et al.,* 2006). Carlaw and Lipsey (2006) introduce the following alternative assumptions in order to modify GPT/technology-based models so that they are empirically more likely to describe historical growth patterns:

(i) Agents cannot foresee the course of the entire GPT when it is initially introduced.

(ii) Agents face uncertainty and cannot attach probabilities to the range of possible outcomes of their current innovation activities.

(iii) Growth is driven by a succession of endogenously generated GPTs; each one different in duration and effect on productivity.

The above assumptions result in GPTs that will either accelerate or decelerate growth, but always sustain it as long as successive GPTs continuously appear.

In their conceptually interesting contribution, Lipsey *et al.* (2006) argue that a GPT is either a technology or a technique (or both) that is complementary with a lot of other technologies or techniques. However, the features of this "complementarity" are somewhat enigmatic. It is a little puzzling to include, on the one hand, a ship or the printing press as GPTs, which are final goods, used for dissemination of information and cargo and, on the other hand, classifying microprocessors as GPTs, which are intermediate goods used as inputs into the production of other goods without having a unifying property or precondition associating a GPT and its complementary links with other technologies.

1.4 Technology and GPTs: Necessary but Not Sufficient for Growth

Gains from trade and allocative efficiencies as a result of institutional changes, referred to as Northian and Smithian effects, were primarily responsible for economic growth prior to the Industrial Revolution (Mokyr, 2005). Technology post-1750, however, is seen to be responsible for an increasing portion of accelerating economic growth. The pre-Industrial Revolution average growth rate of 0.15% to 0.20% per year with large year-to-year variations and at times negative growth rates was replaced by a less variable yearly growth rate of 1.5% or more (Mokyr, 2005). Yet, technological innovations and adoptions from other societies in pre-1750 European abounded; to list a few notable ones: the mechanical clock, printing (a GPT), the waterwheel (a GPT), iron-casting, spectacles, Hindu-Arabic numerals, and paper. Furthermore, improvements in technologies itself helped the interaction with Smithian growth. A prime example is marine technology of the pre-Industrial Revolution era. The three-masted sailing ship, a GPT, of the fifteenth century made the expansion of trade possible.

The impact of the technological innovations on aggregate growth was relatively less profound likely due to the fact that the majority of the labour force was employed in agriculture. More importantly, however, according to Mokyr (2005), technological progress made only small impacts on aggregate growth because most of those inventing the technology or techniques (e.g. mechanics, chemists, biologists, and farmers) “knew relatively little of what could be known about the fields of knowledge they sought to apply”. Although these inventors/scientists made break-through discoveries, not enough was known about the fields for which these break-through discoveries could be applied (that is, iron-making was carried out without in-depth knowledge of metallurgy, water-power without hydraulics, dye-making without organic chemistry, etc.). However, in any era, no one knows all which is to be known or could be known. Thus, lack of appropriate *known* applications is an inadequate reason to describe why technology in an economy is necessary, but is not the engine of sustained growth in a given era.

A theory of long-term economic growth needs to apply to pre- and post-Industrial Revolution eras. Economic historians put forward economic factors, such as relative prices, better property rights, endowments, changes in fiscal and monetary institutions, investment, savings, exports, and changes in labor supply, as possible explanations for sustained growth[3]. Still, this does not explain the relative importance of technology and the rapid diffusion of technology *after* 1750. Lipsey *et al.* (2006) claim that the increase in the diffusion of technology and in the quantity of GPTs is due to the growing number of GPTs. That is, a positive feedback loop occurs with GPTs. As more are invented, more applications occur which leads to further GPT discoveries. However, one is still left with an unanswered question of what spurs the creation of general purpose technologies or limited-use technologies in the first place.

Certainly, basic complementarity between invention and diffusion of new technology and institutional factors are critical for technological knowledge to be applied. Furthermore, institutional factors (e.g. patent laws) help the applications become profitable. Although not all those who contributed to useful knowledge did so for monetary gains. Some inventors, thinkers and scientists wished to be rewarded by honour and fame or were looking for peer recognition. For example, Claude Berthollet, Joseph Priestley and Humphry Davy made numerous discoveries that were invaluable to industry, but often wanted credit, not profit (Mokyr, 2005). Nevertheless, other institutional factors, such as the establishment of intellectual property rights, the supply of venture capital, the operation of well-functioning commodity and labor markets, and so forth are fundamental for growth and are discussed in detail in the literature (see Mokyr,1998; Lipsey *et al.*, 2006).

So, there is a missing link between technology and growth that is not fully explained by institutional factors, such as intellectual property rights, that is needed to explain pre- and post-Industrial Revolution growth and why Western Europe in the 16th century already contained the requisite beginnings of the future divergence in 1750, while China did not. The evolutionary sequence of this economic divergence that took place in the 18th and 19th centuries involved a great deal of contingency and could have been reversed by wars and bad governance. In the West, it was not reversed, and the inventions of those two centuries and later did not lose momentum or fail quickly as was common pre-1750. Rather, the marginal product of scientific knowledge proper on technology was augmented by coupling many inventions to increasing numbers of newly recognized energy sources. Steam, coal, coke and various petroleum distillates

[3]For a full survey, see Mokyr (1998).

were being used in far greater sectors and applications post-1750. Previously one-application or one-sector use of particular energy sources limited the scope of applicability economy-wide of fuels. This limited fuel use hindered new technological inventions. Fundamental energy constraints that were removed in the Western Europe economy in the 18^{th} century allowed it to forge ahead of China with sustained growth rates. This created a race between energy and technology which allows for mutually reinforcing returns to research and development in each respective area and the generation of spillovers. This thesis explores this 'race' in detail in Chapter 2.

Chapter 2: The Race between Energy and Technology

Chapter 1 illustrates that growth cannot result solely from technology or accumulation of knowledge and suggests that the missing link may be energy. The interaction and race between developing a GPT and recognising a general purpose energy source (GPES) can be used to explain the engine of economic growth, albeit within the framework of appropriate institutional dynamics. The explicit inclusion of energy in a GPES-GPT growth model will necessitate a discussion of a further model element: the environment.

2.1 General Purpose Energy Sources (GPESs): The Unifying Property Linking a GPT and Its Complementarity with Other Technologies

Economic growth needs to occur in an environment in which knowledge can be applied and supported by society via institutional factors. Geographically, natural resources from which technologies are made also need to exist or be accessible. Energy resources, because of their supreme value in any production, are treated differently from other natural resources, such as iron or gold[4]. However, one should not put too much importance on the role of geography because geography does not adequately answer the question of "when" economic growth became sustained and highly influenced by technological inventions; or, "when" certain technological breakthroughs occurred. For example, geographical explanations that explain Europe's success (relative to China's) by its milder climate or conveniently located coal reserves (Mokyr, 2005) should not be used as an overarching reason to explain the timing of the Industrial Revolution. To be certain, the Chinese already had a coal industry by the year 1000, whereas, after the Romans left Great Britain in the fifth century, there is no mention of widespread coal mining or use in historical records until the sixteenth century.

[4] Although it can be argued that without air and water life would not exist, discussing necessary elements of life distracts from and is tangential to discussions of natural resources required for economic growth.

A different view of sustained economic growth is required. Once a new technology has a recognised use, a society needs to be convinced to adopt it widely. Technological progress (and, by implications, GPTs) is limited by recognized and available energy sources and/or carriers and that the recognition of such energy affect choices in technological development, which, in turn, determines the economic development of a society. A society's recognition of energy, from readily available forms (e.g. plants and animals) to complex, but high-yield forms (e.g. nuclear) influences the development of technologies necessary to use those various forms of energy. Those technologies can, but do not necessarily, become GPTs, and can, but do not necessarily influence the development of new technologies, which, in turn, can result in the recognition of new higher-yield forms of energy. Some authors note that energy availability drives economic growth rather than economic growth compelling the use of more energy (Ockwell, 2008). Sachs (2005) asserts that the invention of the steam engine in Britain, for example, depended on coal deposits. It has also been argued by others that technology itself is not a sufficient condition for a resultant period of high economic (and population[5]) growth, but that the coupling of technology and a high quality, high grade energy resource is necessary (Reynolds, 1994).

2.1.1 GPT and GPESs Interactions

Coupling a technology to a new general purpose energy source (GPES) can improve its chances of acceptability. This thesis formally defines and characterises a GPES as a single generic energy source or energy carrier, recognizable as such prior to its use and then over its whole lifetime of use that initially has limited use, but eventually comes to be widely used in the production process, and influences the development of technologies *from* its use and/or influences the development of technologies *for* its use, thus having many spillover effects. One does not and cannot know, *a priori*, whether a particular technology or technique will become a GPT. Similar to technology, the concept of a GPES does not, however, remove the requirements of other necessary elements (some historical; others, institutional) for the development of GPTs; namely,

[5] According to Mokyr (2006), the view of modern economists [e.g. Galor and Weil (2000)] that "'the key event that separates Malthusian and post-Malthusian regimes is the acceleration of the pace of technological progress' is a bit misleading, since it draws a link between technological progress and demographic change that thus far has not been closely examined."

national economies with readily available information, a critical mass of well-educated populous, representative institutions, religious attributes[6], cooperative innovations, and political and industrial policies.

Lipsey *et al.* (2006) divide GPTs into three classifications: product, process and organizational. Interestingly, almost all product-classified GPTs listed by Lipsey *et al.* (2006) can be argued to be dependent on the recognition of or seek to conserve a GPES. Table 2.1 on the next page lists the twenty-four GPTs, their respective era of development and their classification, all of which can be found in Lipsey *et al.* (2005). Next to each GPT a requisite GPES is appended.

[6] Lipsey et al. (2006) have a full discussion on the influence of religion (Catholicism vs Protestantism vs Islam) on economic growth and the establishment of higher learning institutions.

Table 2.1: Transforming GPTs and Requisite General Purpose Energy Sources or Carriers

GPT	Date[7]	Classification[8]	GPES
Domestication of plants	9000-8000 BC	Pr	Grain, nuts, wood, game (non-domesticated animals)
Domestication of animals	8500-7500 BC	Pr	Animals with specific criteria which lend themselves to domestication
Smelting of ore	5000-4000 BC	Pr	Wood, charcoal
Wheel	4000-3000 BC	P	Domesticated animal
Writing	3400-3200 BC	Pr	
Bronze	2800 BC	P	Carbon (may not be a true GPES, because it was limited to certain industries)
Iron	1200 BC	P	Carbon (in a bloomer[9]; may not be a true GPES, because it was limited to certain industries)
Waterwheel	Early medieval period	P	Flowing water
Three-masted sailing ship	15th century	P	Wind
Printing	16th century	Pr	
Steam engine	Late 18th to early 19th century	P	Steam
Factory system	Late 18th to early 19th century	O	Coal, coke
Railway	Mid-19th century	P	Coal
Iron steamship	Mid-19th century	P	Steam
Internal combustion engine	Late 19th century	P	Gasoline
Electricity	Late 19th century	P	Electricity is a convenient form of energy conversion
Motor vehicle	20th century	P	Petroleum (various hydrocarbon fractionates)
Airplane	20th century	P	Petroleum (various hydrocarbon fractionates, e.g. jet fuel)
Mass production, continuous production, factory[10]	20th century	O	Energy intensive activities requiring various energy sources, both new and preceding (e.g. coal, nuclear) via a convenient carrier (electricity)
Computer	20th century	P	
Lean production	20th century	O	
Internet	20th century	P	
Biotechnology	20th century	Pr	
Nanotechnology[11]	21st century	Pr	

[7] Date is approximate based on estimates of the timing when the GPT was in widespread use in the West.
[8] P = product; Pr = Process; O = Organizational
[9] A bloomer or bloomery was one of the first type of furnace capable of smelting iron from its oxides.
[10] The date is based on the emergence of mass production based on Henry Ford's innovations.
[11] Not yet a GPT. However, Lipsey *et al.* (2005) find that its potential is so obvious that it will be one of the most pervasive GPTs of the 21st century.

2.1.2 Surveying Individual GPTs and Their Associated GPES: The Wheel, the Waterwheel, and the Three Masted Ship

The adoption of the wheel as a GPT provided tremendous advantages to societies that adopted it. The wheel, which began exerting its transformative effects around 5,000 B.C., can be argued to have been adopted for the purpose of reducing transportation energy requirements given the recognition of the need of a more efficient caloric expenditure. However, ancient native Mexicans invented the wheel separately from Western society, but did not adopt it as a GPT. Specifically, according to Diamond (1999), they invented wheeled vehicles with axles for use as toys, but not for transport. Other authors, such as Diehl and Mandeville (1987) believe that the wheel was used so as to mount human and animal figurines. These wheeled figurines, in turn, were likely used as household ritual objects in Mesoamerica, not as toys for children (Diehl and Mandeville, 1987). In any case, the wheel in Mesoamerica was not used as a means of transporting goods. Why? The recognition of a new GPES (the domesticated animal) was a missing condition. Although the lack of domesticated animals may have also prevented the native Mexicans from recognizing the still advantageous use of the wheel in transporting goods via carts over human porters, it is also possible that no appreciable benefit over long distance would have been gained by human porters using wheeled vehicles laden with cargo if the terrain in which the ancient Mexicans lived was broken, slopped or severely rugged.

The waterwheel, a GPT from the Early Medieval period, was preceded by requisite recognition of (flowing) water as a low-cost GPES. The kinetic energy contained in the moving water captured by the waterwheel replaced animal energy sources was used in a variety of production processes (cereal grinder, sawing logs, cutting metal, papermaking, fulling cloth, etc.), and became a recognized general purpose energy source. Likewise, the masted sailing ship, a GPT which exerted its transformative effects during the 15th century A.D., required that wind be recognized as a low-cost GPES. It is unlikely that the sailing ship was first invented and then followed by a search for an appropriate source of energy.

2.1.3 Why is the recognition of a new GPES or at least the increased efficiency of energy use a necessary condition for a product GPT to be recognised as such?

Once a new technology has a recognised use, a society needs to be satisfied with it to adopt it widely. Coupling a technology to a new GPES can improve its chances of acceptability. Even when product-classified GPTs come first and then an appropriate fuel is found, recognition of a low-cost general purpose energy sources transforms a mere invention into a GPT. Gasoline, the fuel that allowed the motor vehicle to claim itself as a product-classified GPT, had to be recognized as a general purpose energy source. In fact, uses for petroleum were known by the Ancient Greeks. Petroleum derivatives were widely used for building roads, mastic for waterproofing ships and bitumen was used for warfare, but the application of such derivatives were eventually limited to areas where the resource was easily available through surface seepage (Maugeri, 2006). Its resurgent uses in the 1850s in Europe and the United States from petroleum distillation by 19th century amateur and professional chemists (Maugeri, 2006) found the middle distillate fraction useful as fuel for oil lamps (Diamond, 1999), but like coal, petroleum had only occasional use before becoming a major energy source. That is, gasoline was the most volatile fraction of the petroleum distillate and was discarded as waste – even regarded as a nuisance by-product until it was *recognized* as an ideal fuel for internal-combustion engines (Cottrell, 1955). Likewise, coal gas came into use when William Murdock, a Scottish engineer, *recognized* its potential as an alternative to oil and tallow as lamp fuels. Improved technologies for removing foul odours and for determining optimal heating temperatures for extracting the maximum amount of coal gas followed the recognition of coal gas as a fuel.

Given that GPESs and GPTs numbered far less as one goes backwards in time, it seems easier to look at how economies were developing with respect to the synchrony/race between energy and technology by examining the years between 1000 AD and 1800 AD. A comparison of Chinese economic performance with that of Western Europe in the eighteenth and early nineteenth centuries by Pomeranz (2000) concludes that both economies were subject to Malthusian/ecological constraints, and that Chinese performance was in many respects better than that of Europe before 1800. Pomeranz (2000) suggests that Western Europe's economy diverged from the world norm only when "unexpected and significant discontinuities in the late eighteenth and nineteenth centuries enabled it to break through the fundamental constraints of energy and resource availability that had previously limited everyone's horizons".

Examining historical GDP per capita estimates (Table 2.2; Maddsion; OECD 2006), one sees that China's GDP per capita (both level and growth rates) between 1000 AD and 1300 AD was about equal to that of Western Europe. Prior to that period, for 1 AD to 1000 AD, China may have had a slight advantage in growth rates. Then, between 1300 AD and 1820 AD there was zero growth in per capita GDP for China, but the West experienced the Industrial Revolution. So what can we say about GPESs and GPTs for these periods?

Table 2.2: The China/West European Dichotomy, 1–2001 AD[12]

Year	China Per Capita GDP (1990 int. $)	West Europe Per Capita GDP (1990 int. $)
1	450	450
1000	450	400
1300	600	593
1400	600	676
1500	600	771
1820	600	1 204
1913	552	3 458
1950	439	4 579
2001	3 583	19 256
Period	China, GDP Growth Rate (annual average compound growth rates)	West Europe Growth Rate (annual average compound growth rates)
1-1000	0.00	-0.01
1000-1500	0.17	0.29
1500-1820	0.41	0.40
1820-1870	-0.37	1.68
1870-1913	0.56	2.11
1913-1950	-0.02	1.19
1950-1973	5.02	4.79
1973-2001	6.72	2.21

[12] Adapted from Maddsion (2006).

One can examine two GPESs of that period: coal and coke. By the 11th century, the Chinese had used wood as a primary fuel source and, like Europe, it resulted in large amounts of deforestation. In order to avoid excessive deforestation, the Song Chinese began using coke made from coal as fuel for their metallurgic furnaces instead of charcoal derived from burning wood. By the first decades of the eleventh century, Chinese ironworkers began to fuel their furnaces with coke. Note that coke is superior to coal in that it does not smoke when burned, thus allowing for indoor uses and it produces a higher temperature when burned. But, as is the case for many Chinese inventions, many that were dependent on the use of coal or coke were not improved upon in centuries that followed – and coke never became a true GPES in China.

Coal use was limited and was not of significance in England before 1000 AD. However, England was the first European country to transitioned from a plant-fuels economy to coal economy. As coal grew in importance, England also learned how to "cook" coal (i.e. transform coal into coke). Starting in 1589, various patents were granted for making iron and steel and smelting of ores using coke. This GPES allowed, in a part, for the industrial revolution (and a variety of GPTs) to occur and occur first in England. Here we see how some GPTs lagged behind the GPESs. By 1900, several European economies were almost completely fueled by coal, yet the fuel use in rural China was practically unchanged from about five centuries earlier. Even though the Chinese discovered coke first and used coal for various reasons, it was not adopted as a GPES. According to Smil (1994), even in the early 1950s, more than one-half of China's total primary energy supply was derived from woody biomass and crop residues. The share of these fuels had been reduced to 15% of China's total energy use by the year 2000, but it remains above 70%, or even 80%, for most of the countries of sub- Saharan Africa (Smil, 1994).

The history of coke and coal described above illustrates how the availability or use of a GPES is one condition for societal adoption. If a GPT and the GPES are related then a low-cost GPES can represents a precondition for the arrival of one or more GPTs. The railway and the factory system can be used to illustrate this point. The railway, another GPT, was necessarily preceded by the recognition of coke as a low-cost GPES. Automated machinery[13] and the factory system,

[13] Originally used in the textile industry.

two GPTs whose spillovers during the Industrial Revolution in Great Britain were vast, can be argued to have required the precondition of recognizing coal as a low-cost GPES. That is, the low-cost GPES provided incentive in Great Britain to develop technologies that substituted low-cost coal (and capital) for high-cost labour.

The low cost of energy is also a necessary, but not a sufficient condition for an energy source to become a GPES. The effects of great consequence outside of energy source availability of petroleum most likely resulted from its widespread novel applications (such as the availability of chemical precursors) and not its low cost.

Sometimes a fuel can be designed for a technology. Diesel fuel, for example, is specific to diesel engines. However, this does not negate the notion that petroleum can be regarded as a GPES. Internal combustion engines were invented long before the availability of petroleum derivatives such as diesel. Recognition of petroleum (and its derivatives) as a GPES advanced the internal combustion engine as a 'true' GPT and thus transformed the transportation sector. Prior to the availability of petroleum as a GPES in the mid-1800s, the internal combustion engine's applicability was generally hindered and it should not be considered a GPT until the mid- to late 1800s.

2.1.4 Concluding with a Mental Experiment

With no new GPES, only technology (GPTs) can sustain growth, but not in the long term. GPTs alone are not a sufficient condition for sustained growth. At times GPTs precede GPESs (especially if they are unrelated) and sometimes the GPT follows from the GPES (e.g. information and communication technologies (ICTs) from electricity). As a mental experiment, assume that we fix coal as the GPES and that petroleum, uranium, hydrogen, etc., will never be used as sources of energy. We allow for GPTs to be invented. Two things will occur:

(1) because sustained growth requires increased energy consumption, limited reserves of coal will eventually be exhausted; and

(2) only GPTs that

(i) use coal as a GPES or
(ii) are unrelated to coal, but not using any other energy source for their functions

can be invented.

This limits the amount of future GPTs and other technologies. With coal as the last GPES in the hypothetical history of GPESs, the motor vehicle and the airplane (both GPTs) would not be possible, plastics and most of our modern pharmaceuticals (both dependent on petroleum) would not exist. Electricity (a GPT) would still be possible as would the computer (if made from non-petroleum derivatives), but the energy to power them would be dependent on coal only. Myopic agents, who are unable to anticipate changes in the evolution of their economy, will experience:

(1) diminishing stocks of the current GPES; and eventually,
(2) an asymptotically decreasing growth rate as the number of new possible GPTs dwindles.

2.2 Energy and the Environment

Even as early as the 18th century did economic treatment of growth pay attention to the interaction between the economy and the natural environment; albeit usually focusing the conversation around agricultural production. This led to discussions on limits to growth by both David Ricardo and Thomas Malthus. Post-classical economics places less emphasis on the natural environment, but it still analyses it from the view of optimal depletion of natural resource stocks and of externalities caused by pollution (e.g. Pigouvian taxes). To be certain, degradation of the biosphere in environmental economic analysis is described as an allocation problem. The analysis stresses the relative scarcity of resources, allocation of scarce resources, optimal welfare and externalities and inter-temporal resource allocation and capital investment. However, a focus on optimal externalities in environmental economics is not necessarily in agreement with sustainable development because comparing different equilibria, in a comparative static framework, provides poor information about transition paths (Mulder and Van Den Bergh, 2001).

This thesis has been arguing that energy, specifically GPESs, needs to be explicitly incorporated in a technology driven economic growth model. Once energy is an explicit model element, interactions with the natural environment or biosphere cannot be avoided. Therefore, any GPES-GPT growth model requires generating effects of growth on the biosphere. Introducing 'the biosphere' in a GPES-GPT driven growth model informs economic policy that is consistent with long-term stable environmental quality. The time horizon used in this thesis extends beyond the traditional decades. As Mulder and Van Den Bergh (2001) argue, to study sustainable development, "environmental economics needs to be complemented by an evolutionary approach, which focuses the attention on irreversible, path-dependent change, and long-run mutual selection of environmental and economic processes and systems". In the approach used in this thesis, the effects to the biosphere take into account the qualitative anthropogenic entropy production ratio to that of the biosphere. Chapter 3 discusses entropy and its use in economic growth models in detail. Chapter 4 builds a theoretical biosphere-energy-technology (BET) model.

Chapter 3: Entropy and Earth's Biosphere

This section establishes the theoretical foundation for the meaningful use of entropy in economic growth models with environmental components. It gives an overview of the concept of entropy, how entropy and energy are related, a discussion of Earth's entropy balance and how the concept of entropy has been misused in economics. This section concludes with a discussion of the drawbacks of using entropy, quantitatively, in economic modeling and proposes that a qualitative approach provides for better modeling and policy formulation.

3.1 The Second Law of Thermodynamics

Entropy is a concept clearly defined in physics (thermodynamics) and used analytically within the discipline, but it can be used within a conceptual framework in economics to describe how technology and energy sources affect growth. Defining entropy necessarily requires a discussion on energy and defining the boundaries of the system which is affected.

3.1.1 Quantifying Energy and Entropy

One of the most significant 19th century discoveries, the *first law of thermodynamics,* which is the law of energy conservation, states that the sum of mechanical, thermodynamic, and electromagnetic[14] is conserved. In other words, the total energy of an isolated system is constant. The origin of the word energy derives from Greek, where it originally meant effective force. As a technical term, it was put into use by Thomas Young (1773–1829), in 1807, who used it for the sum of kinetic energy and gravitational potential energy of a mass and the elastic energy of a spring to which the mass may be attached. Although Young used energy as a technical term, calorie was the usual word used in the nascent days of the emerging field of thermodynamics (Mϋller, 2007). Our modern understanding of energy now recognises it as having a mass component, in accordance to $E = mc^2$, where m is mass (usually in kg) and c is the speed of light.

[14] Nuclear energies are also conserved, but were unknown at the time.

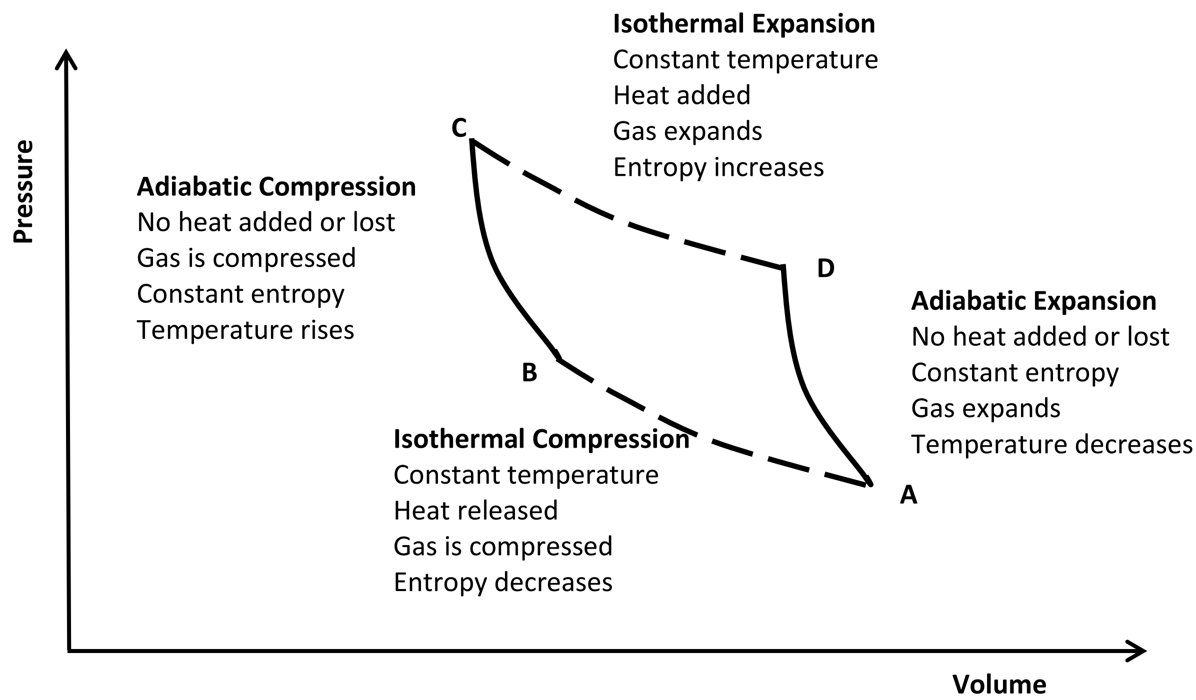
The more subtle concept of entropy, however, first emerged in the circumstance of an engineering application: one of improving the efficiency of heat engines. Simply stated, a heat engine is a system that employs heat (i.e. thermal energy) to perform work. The most common example of a heat engine is the gasoline engine. Denis Papin (1647–1712) was the first to use condensed water to lift a weight; thus employing steam power to perform work. However, it was James Watt (1736–1819) with his rotative engine that made the steam engine into more than a pump (Müller, 2007). The increased efficacy of Watt's steam engine allowed it to spin wheels, looms, drills, etc. and is thus credited with playing a central role in the industrial revolution. This invention that spread quickly across countries also gave rise to new ideas and theories in the still bourgeoning field of thermodynamics. Over the years, many people and their unique contribution/inventions to the steam engine allowed for incremental improvements to its efficiency. Yet, it was Sadi Carnot, who was determined to find the efficiency limits who in 1824, published a book entitled, *''Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance",* in which he addressed the issue:

"The process in which heating and cooling occurred at constant pressures might be improved by letting the heat exchange occur at constant volumes or constant temperatures, and perhaps working agents like sulphur or mercury might have an advantage over water." (Müller, 2007).

Carnot came to correct conclusions concerning both propositions. Although Carnot was not able to formulated his findings quantitatively, he was able to distinguish between reversible and irreversible cycles. Carnot postulated that a theoretical heat engine that functions in an ideal reversible process or cycle (also called a Carnot engine) between two reservoirs of different temperatures[15] is the most efficient engine achievable because there are no dissipative effects that convert mechanical energy to internal energy. Hence, a reversible process is then defined as one in which every point along some path is an equilibrium state and one for which the system can be returned to its initial state along the same path. Conversely, irreversible systems, which characterise all natural, real processes, are not in an equilibrium state at every point along some path. Figure 3.1 outlines an idealized Carnot cycle on a pressure-volume (PV) diagram.

[15] All Carnot engines operating between the same two temperatures will have the same efficiency.

Figure 3.1: A Carnot (Ideal) Heat Cycle



The Carnot cycle can involve any electrical, magnetic of chemical cycle. Here, it is assumed the working substance is an ideal gas confined to a cylinder with a frictionless piston. In an adiabatic process, there is no heat exchange with the environment. In contrast, an isothermal process is a process in which a system's temperature remains constant due to an exchange of heat with an external thermal reservoir.

It was Benoît Pierre Émile Clapeyron (1799–1864), after Carnot's death, (Gößling, 2001), who mathematically reproduced Carnot's ideas of a reversible heat. He described the efficiency of a (Carnot) heat engine, ε, as follows:

$$\varepsilon = 1 - \frac{|T_C|}{|T_H|} \tag{3.1}$$

where T_C and T_H represent the absolute temperatures, cold and hot, respectively, of the two heat reservoirs. If one were to consider a finite series of Carnot cycles, where Q is the quantity of heat, we have

$$\sum \frac{\Delta Q}{T} = 0. \tag{3.2}$$

In the case of infinitely many Carnot cycles, where the cycles must be reversible we have

$$\oint \frac{dQ}{T} = 0. \tag{3.3}$$

The quantity dQ represents an infinitesimal transfer of heat into or out of the system at a temperature T, which varies along one of many possible paths the system can follow. Expression 3.4 is a property that defines the entropy function, S. Thus, an infinitesimal change in entropy is defined as

$$dS = \frac{dQ}{T}. \quad (3.4)$$

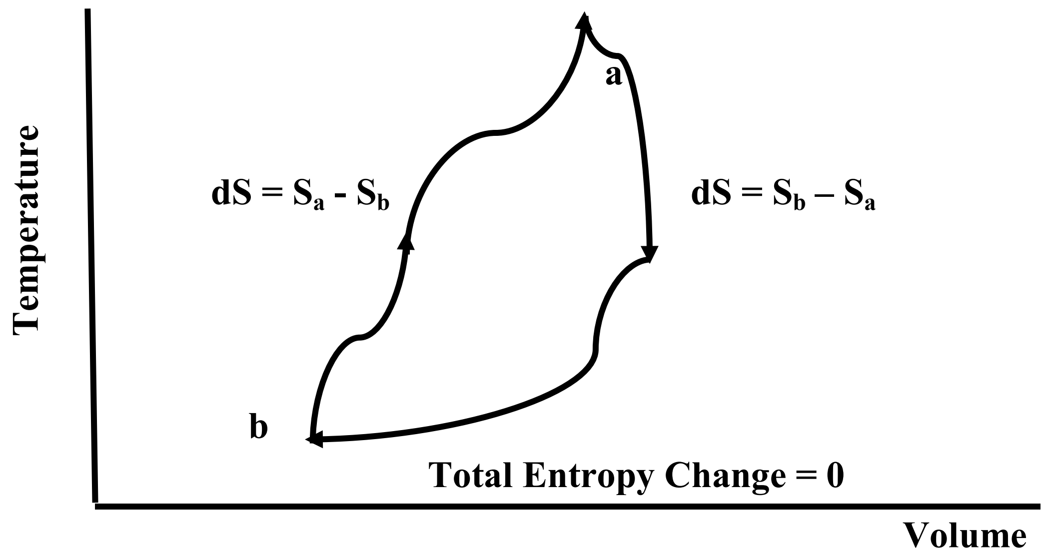
For a finite change, the change in entropy is

$$\Delta S = S_b - S_a = \int_a^b \frac{dQ}{T}. \quad (3.5)$$

It should be noted that Equation 3.5 gives only the change in entropy, not the absolute value of entropy. The absolute value of entropy can be defined only indirectly by calculating it, for example, after measuring the thermal capacity for the isochoric process[16]. However, in order to find the absolute value of entropy, one must function under the law that as temperature approaches zero, entropy tends to zero. For the *change* in entropy, however, one needs only knowledge of the initial "a" and final "b" equilibrium states, but not knowledge of the thermodynamic path (Figure 3.2). As such, entropy is a defined as a state function or variable because its value depends only on the thermodynamic state of the system (e.g. temperature, pressure, phase, chemical composition) and not on the thermodynamic path. To be sure, Rudolf Julius Emmanuel Clausius' (1822–1888) work led to an almost equivalent conclusion to that of Clapeyron with the exception of Clausius' conclusion that the total heat exchange of an infinitesimal Carnot cycle is not zero, but is equal to the work (Möller, 2007). This conclusion implied that heat, Q, is not a state function anymore; rather it is, as Clausius denotes it, U, now known as internal energy (i.e. the sum of all kinetic and potential energies).

[16] An isochoric process is a thermodynamic process during which the volume of the closed system undergoing such a process remains constant.

Figure 3.2: A Thermodynamic Path



The change in entropy is the same for any path between the initial “a” and final “b” states.

3.1.2 A More Tangible Definition of Entropy: Probability and Disorder

The thermodynamic definition of entropy positions the change of entropy as a result of a process, be it physical or chemical, for example, but it does not easily lend itself to an easily connotative understanding in the physical sciences and even less so as an applicative concept in economics. In 1877, L. Boltzmann (1844–1906) was able to do what Clausius failed to do: add a molecular interpretation to the notion of entropy. Because the laws of mechanics are said to be time-reversal invariant (i.e. remain the same when time is reversed), one needed to reconcile the fact that the principle of increasing entropy which distinguishes reversible and irreversible processes is in contradiction to the laws of mechanics. J. Clerk Maxwell first suggested that the second law of thermodynamics is not an absolute truth, but a highly probable, statistical truth. Building on this statistical interpretation of entropy, Boltzmann suggested that systems tend to transition from states of low probability to states of higher probability. Boltzmann in 1877 connected the microscopic realm of molecules to the macroscopic realm of entropy by defining entropy as

$$S = kln\Omega \tag{3.6}$$

where k is some constant (now referred to as Boltzmann's constant) and Ω is the number of possible microstates associated with the macroscopic state of the system. This formulation gave rise to the notion of disorder. For instance, the molecules in a system at high temperature are highly disordered in terms of location and of the occupation of their available translational, rotational and vibrational energies (i.e. modes of thermal oscillation). Boltzmann used the notion that heat was kinetic energy, which he could not observe directly, but that, in the aggregate, he could observe as a thermodynamic property. As kinetic energy is transferred from a hot body to a cold body via molecular collisions, on average, molecules with more kinetic energy lose kinetic energy while molecules with less kinetic energy gained kinetic energy until, on average, the kinetic energy is optimally dispersed among all the molecules. Temperature is the average kinetic energy per mode of oscillation and therefore the more modes of oscillation within a system, the more total kinetic energy is confined within the system. Thus, on the molecular level, a greater number of kinetic energy modes of oscillation within a system, the greater its entropy. For Boltzmann, a system is in "perfect order" when all the molecules are confined in perfect array (e.g. crystalline order) without freedom of movement.

Martyushev (2013) uses a simple example to illustrate entropy as a notion of disorder as measured by the number of microstates within a macrostate. Martyushev (2013) portrays a vessel divided into two sections with two particles, *N* (e.g. two molecules). He creates the first macrostate, Ω_1, by placing the two particles in one section (say, the left side) of the vessel. Ω_1 can only be described or create in one way and thus $\Omega_1 = 1$. Now Martyushev (2013) assumes that the particles can move without restriction in the vessel between the two sections. As such the system will reach the second macroscopic state, Ω_2. This second macrostate can be implemented in three equiprobable ways: (1) having both particles on the left side of the vessel, or (2) having both particles on the right side of the vessel, or (3) having one particular in each section of the vessel, and therefore $\Omega_2 = 3$. If one were to use Equation 3.6, the second state will result in higher entropy. This example is in agreement with the second law of thermodynamics: an isolated system changes from an initially nonequilibrium state to an equilibrium state thereby increasing entropy. Furthermore, Ω_2 is more disordered than Ω_1 because the particles can be located in any one part of the vessel at any point in time.

One can also define a system consisting of a large number of particles. To define a microscopic state, one needs to specify the state of *a* particle. In statistical mechanics, a particle, which is fixed in position, has only two possible and distinguishable quantum spin states ↑ or ↓ ($+\frac{1}{2}$ and $-\frac{1}{2}$ moments). If one assumes that particles have the same energy for $N = 10$, then one has $\Omega_2 = 2^N$. If one were to assemble all the microstates with the same number of $+\frac{1}{2}$ and $-\frac{1}{2}$ moments, the relative number of spin states is constrained by

$$N\uparrow + N\downarrow = N. \qquad (3.7)$$

The collective microstate can then be characterised by one number, *m*:

$$m = N\uparrow - N\downarrow. \qquad (3.8)$$

Thus *m* represents the distribution of N particles among possible states:

$$N\uparrow = \frac{N+m}{2} \text{ and } N\downarrow = \frac{N-m}{2}. \qquad (3.9)$$

3.1.3 Warning: Entropy is not Disorder

By creating a distribution of particles with different possible states, one establishes the physical significance of entropy as the relative probability distribution frequency of movement (of molecules) assuming that each of the microstates is equally likely. So, for example, if one were to set up an initial state where the molecular spins, in zero magnetic field, are all in an up state, then this would be referred to as a highly ordered state[17]. This initial state of the molecular system will then spontaneously move towards the more disordered (and more probable) equilibrium state.

[17] This is not a state of internal thermodynamic equilibrium. An equilibrium state is random with equal numbers of up and down spins.

Clearly, the words 'order' and 'disorder', in the physical sciences, have a clear and distinct meaning. Extending the notional of entropy from the molecular state (as in statistical thermodynamics) or from the definition of the change in heat capacity per unit temperature to "higher entropies" such as growing complex organisms or economic activity presents problems. In particular, entropy does not depend on one's perception of order in a system. For instance, most theories of the development of life state that all living organisms become more complex and organized with time thus become more ordered with time (Martyushev, 2013). This observation, however, is in contradiction to the second law of thermodynamics, which states that the entropy (disorder) grows in the nonequilibrium isolated system. Or, is it?

Care needs to be taken as to the importance of entropy when it is ascribed to higher levels. Entropy as a measure of disorder outside the realm of statistical thermodynamics may lead one to conclude that the evolution of unicellular organisms to humans represents a more ordered state (in the latter's case). However, quantitative calculations of the thermodynamic entropy change during the self-organization are complicated due to spatial and temporal inhomogeneity and the nonequilibrium state of such systems (Martyushev, 2013). A study by Blumenfeld (1981) evaluates the thermodynamic entropy change during the construction of an organism from cells, the cells from biopolymers, and the biopolymers from monomers. Blumenfeld (1981) concludes that "*All talks about "antientropic tendencies" of the biological evolution, about the exclusive order of the animate matter are based on an evident misunderstanding. According to the thermodynamic criteria, any biological system is ordered no more than a lump of rock of the same weight*." Furthermore, according to Martyushev (2013), calculating the absolute thermodynamic entropy, under normal conditions, of one kilogram of wood is 2.8 kJ/K, while that of "inanimate bodies" that surround the tree having the same mass can be both lower (e.g. 0.7 kJ/K, the entropy of quartz SiO_2) and higher (e.g. 3.9 kJ/K or 6.8 kJ/K, the entropy of water and air, respectively). These values support Blumenfeld's conclusion and add evidence to the notion that entropy is not a characteristic that can be used for distinguishing between the animate and inanimate matter and therefore, for the calculation of the degree of order or disorder. Moreover, the use of absolute entropy for the comparison of different objects is generally uninformative because, as stated earlier, it is the variation or change in entropy that is normally relevant.

3.2 Uses and Misuses of Entropy in Economics

The second law of thermodynamics started from an axiom, *heat cannot pass by itself from a colder to warmer body*, which can be attributed to Clausius (Mϋller, 2007). Although suggestive, the axiom is imprecise. The previous sections outline that for reversible processes, the change in entropy is zero, but for irreversible ones it must be greater than zero. This brings one to a modern formulation of the second law of thermodynamics which states that entropy increases in any irreversible process that occurs in an isolated system. That is, the entropy of a system plus that of its environment always increases. Local decreases in entropy can occur as long as it is complemented by a greater increase elsewhere in the universe.

3.2.1 Defining Boundaries: Open, Closed, and Isolated Systems and the Second Law of Thermodynamics

What does one mean by closed or isolated? How do these terms relate to economic processes? The economic system is defined as an open system because it allows for the exchange of matter and energy with its surroundings. The earth's ecosystem or biosphere can be considered to be a good approximation of a closed system[18], where energy, but not matter, can be exchanged with its surroundings (i.e. outer space). The universe is regarded as an isolated system because both energy and matter are bound within it and they cannot be exchanged with any other system. When extended to open systems as defined above, entropy is the sum of two components: the transfer of entropy across the boundaries of the open system and the entropy produced within the system. The generation of entropy inside the system is always nonnegative. Thus, entropy can increase, decrease, or remain unchanged in a closed system, but any decrease in entropy within an open or closed system needs to be compensated for by an increase in entropy in the surrounding system because total entropy always increases in time.

[18] An open system allows for the exchange of energy and matter (mass) with its surroundings. An isolated system allows for no exchange of either energy or matter with its surroundings. A closed system includes energy, but no mass flow across its boundaries. Note that mass contains entropy as well as energy, both entropy and energy contents of a system are proportional to the mass. When a mass in the amount of m enters or leaves a system, entropy in the amount of (S)(m) accompanies it.

In order to appreciate whether anthropogenic entropy production is a useful a measure or input in economic modeling of negative environmental impacts, a consideration of the availability of energy and natural production of entropy of the Earth needs discussion. This topic is treated in the next section.

3.2.2 The Availability of Energy and Earth's Entropy Balance

The Sun, via incoming radiant energy, is responsible for almost all of the energy that reaches the Earth. The energy radiated by the Sun that reaches the Earth covers the entire electromagnetic spectrum and is responsible for Earth's terrestrial temperatures. It should be noted that the Earth's average temperature, however, remains tolerably constant because the Earth's surface and the Earth's atmosphere re-radiate back into space an amount equal to the incoming solar energy (referred to as Earth's energy balance). The wavelengths, however, at which the incoming solar energy and outgoing terrestrial energy are emitted, are quite different. The disparity is due to the temperature differences between the Sun and the Earth. The amount of energy the Earth or the Sun (or any other body) can radiate depends heavily on its temperature,[19] and the monochromatic emissive power[20] of these bodies moves to short wavelengths as temperature increases. As such, hot bodies radiate more energy than cold ones. The Sun, which has a surface temperature of approximately 6000 K, radiates about 200,000 times more energy per square meter with a maximum solar wavelength of 480 nm than the earth does at 300 K with a maximum terrestrial wavelength of 10,000 nm (Seinfeld and Pandis, 2006). Furthermore, atmospheric aerosol particles, clouds, water vapour, and greenhouse gases, are all net absorbers of energy because they are at temperatures lower than those found at the Earth's surface. About half (168 Wm^{-2}) of the 342 Wm^{-2} (shortwave) incoming solar radiation is absorbed by the Earth's surface. This amount is then re-absorbed by the atmosphere from the Earth's surface as sensible heat, latent heat via water vapour and thermal infrared radiation[21]. In sum for the

[19] For any given temperature, there is a maximum amount of radiation, called blackbody radiation, that can be emitted per unit of area of a body per unit of time.

[20] Power is measured in Watts per square meter (Wm^{-2}).

[21] Sensible heat is heat exchanged by a body that has temperature change as its only effect. Latent is the amount of heat exchanged without a change of temperature. Latent heat is associated with changes of state, measured at constant temperature, such as the phase changes of atmospheric water vapor (vaporization and condensation).

Earth's energy balance, 107 Wm^{-2} of 342 Wm^{-2} (shortwave) incoming solar radiation is reflected by the terrestrial surface and atmosphere, while the remainder, 235 Wm^{-2}, is emitted into space as outgoing (longwave) radiation (Seinfeld and Pandis, 2006).

The Earth's temperature regulates so that the energy that reaches the Earth is equal that that which leaves the Earth. Given that energy and temperature are determinants of entropy, is there an entropy balance for Earth's thermodynamic system? Yes; however, unlike Earth's energy balance where the incoming solar energy is equal to that which leaves the terrestrial-atmosphere body, Earth's entropy balance does not net to zero. Indeed, a systems-theoretical approach by Aoki (1988), which determines entropy flows and productions based on energy flows of the Earth, calculates Earth's net entropy flow to outer space to be 4300 $Jcm^{-2}yr^{-1}K^{-1}$ and the net entropy flows into the atmosphere and the Earth's surface to be -2140 $Jcm^{-2}yr^{-1}K^{-1}$ and -1767 $Jcm^{-2}yr^{-1}K^{-1}$, respectively. The largest radiative process sources of atmospheric entropy are the absorption of solar radiation and the release of latent heat from water phase transitions (Peixoto *et al.,* 1991).

Although the net export of entropy to space by the Earth's atmosphere must be equal to the earth's internal production of entropy by the irreversible processes that occur on and within the Earth, computation of entropy fluxes for the atmosphere indicate that, the entropy exported by outgoing terrestrial longwave radiation is about 22 times larger than the entropy associated with the incoming solar radiation (Peixoto *et al.,* 1991).

As a closed system, the rate of entropy increase of the earth as a whole infrequently remains constant, but fluctuates regularly – sometimes increasing rapidly while at other times increasing more slowly – and depends on the activities with the system (e.g. economic, photosynthetic, population dynamics, etc.).

To understand why the amount of entropy associated with the incoming solar radiation is much lower than the amount of entropy associated with the emitted terrestrial radiation, one recalls that for an isolated system, entropy, according to the second law of thermodynamics, increases monotonically until it reaches its maximum value when the system is in thermodynamic equilibrium. That is,

$$\frac{\Delta S}{\Delta t} \geq 0 \; or \; \frac{dS}{dt} \geq 0. \qquad (3.10)$$

Extending the above notion to open or closed systems, Earth being an example of the latter, the entropy of the universe must then be the sum of two components: the entropy produced within a system (e.g. the Earth, the economy), ΔS_{inside}, and the transfer, of entropy across the boundaries of the system (e.g. space, environment/biosphere), $\Delta S_{outside}$. The generation of entropy inside the system is always nonnegative, $\Delta S_{outside} \geq 0$ such that the total change in entropy is

$$\Delta S = \Delta S_{outside} + \Delta S_{inside} \geq 0 \; or \; \frac{dS}{dt} = \frac{dS_{outside}}{dt} + \frac{dS_{inside}}{dt} \geq 0. \quad (3.11)$$

If Earth were an isolated system, entropy would grow continuously within the isolated system, which would result in a "heat death" destruction of the living environment.

3.2.3 Contribution of Anthropogenic Entropy

It is clear from the preceding sections that entropy production may be decomposed into two parts: entropy production of radiation and entropy production of matter (also called material entropy). It is the latter's production rate that is relevant to the life processes on Earth. If one were to assume that the total energy consumption of civilisation is approximately 10^{13} Watt (W) and further assume that if all of this energy were converted to heat at the temperature of the lithosphere, the corresponding entropy production rate would be 3.48×10^{10} WK^{-1} or 6.83×10^{-5} $Wm^{-2}K^{-1}$ (Weiss, 1996). Weiss (1996), using equations of balance of energy of matter and radiation, finds that contrasting these values to the total material entropy production on Earth and the lithosphere, civilisation is responsible for less than 0.08 % of the earth's material entropy production rate and 1.4% of the lithosphere's entropy production. By comparison, Gößling

(2001) estimates[22] that human activity contributes at least 0.01% to the total entropy production of the Earth.

Rosen and Scott (2003) detail entropy production rates for the Earth, the biosphere, people and civilization's energy system and find the following:

1. Earth's entropy production rate, considering all incident solar radiation, is 580-680 x10^{12} WK^{-1};
2. Earth's biosphere entropy production, defined as consisting of all living organisms, ranging from plants, people and animals to single-cell bacteria, is 0.32 x10^{12} W; and
3. Civilization's entropy production rate, accounting for all energy sources used, is 0.048 x10^{12} W. Comparatively, anthropogenic production of entropy is about 15% that of the whole biosphere.

This implies that human activity contributes about 0.008%[23] of the total entropy production of the Earth. Therefore, anthropogenic contribution to overall entropy production rates on Earth is trivial.

3.2.3 The Limits to Entropy in Economic Theory

By the early 20th century, interactions of producers and consumers were already captured by objective functions for households and firms, and conditions under which the decisions of all economic agents in the economy came to a general equilibrium were also postulated. Labor and capital were the first factors of production to be considered as scarce resources. Conditions for

[22] Gößling (2001) approximates the actual contribution to the overall entropy production rate from humans by considering the energetic throughput of the human subsystem. Using the physiological activity of every human, Gößling (2001) estimates an entropy production rate of about 0.5 W/K per person times 6 billion persons or 63 GW/K. Gößling (2001) also finds that additional entropy production (economic entropy production) varies with the level of industrialization; for example, USA = 30 W/K, Germany = 20 W/K, India = 2 W/K, world average = average 10 W/K.
Compared to a total entropy production of the Earth of 600,000 GW/K, this means that human activity currently contributes at least 0.01% to the total entropy production Gößling (2001).

[23] This value would be 0.012% if one compares it to Earth's entropy production considering only net input from solar radiation.

optimality were derived and when those conditions were not met, interventions such as taxes, regulation/de-regulation, and incentives were pursued to achieve economic equilibrium. Later, other factors were included, such as natural resources as well as the environment's waste assimilation and absorption capacities. Ruth (2007) notes that the notion of equilibrium and stability was contrasted by one in which the economy grows within the constraints of finite resource endowments and that energy into and out of the earth system.

Modern mainstream economics is based on the ideas of Newton's mechanics and the first law of thermodynamics (i.e. energy is conserved in any process/reaction), but it does not take into account the concept of entropy generation, energy devaluation or the finiteness of natural resources (Cleveland and Ruth, 1997). On the last point, ecological economists argue that standard economic analysis (i.e. environmental and resource economics) does not put a value on the outflow of emission and wastes because markets do not exist to value them and, where markets do exist, the values are distorted due to ubiquitous externalities and public goods (Proops and Arons, 2006). Non-market valuations, with their many assumptions, have to be employed in such cases.

Once economic interactions explicitly include resource and waste streams, one needs to consider ecological processes. No longer detached from the environment, the economy is then considered a subsystem of the ecosystem or biosphere, whose relationship with the biosphere is never static. In this vein, publications such as *The Population Bomb* (Ehrlich, 1968) and *Limits to Growth* (Meadows *et al.,* 1972) challenge neoclassical assumptions. Neoclassical economists, however, highlight that these growth models, which predict catastrophic consequences, ultimately failed because they do not appreciate the power of technology to overcome resource scarcity and environmental degradation (Porter and van der Linde, 1995). In response, some ecological economists ascertain that even the process of inventing new technologies itself increases entropy. This thesis also argues that technology does play a critical role and should not be easily dismissed in economic growths, neoclassical or otherwise, and further argues that the concept of entropy can provide insight into economic growth without dominating the model in such a way to ultimately predict economic and/or environmental catastrophe.

Georgescu-Roegen, who pioneered the use of entropy in (ecological) economics, wanted to ground economic analysis in the biophysical realities of the economic process. Georgescu-Roegen's contribution to ecological economics was achieved independently of efforts of other economists such as Boulding and Odum, who were investigating the environmental implications of mass-balance and energy flow analysis, respectively (Cleveland and Ruth, 1997). Georgescu-Roegen is most famous for his postulation of a 'fourth law of thermodynamics' in which he asserts that entropy forbids the complete recycling of matter, given the assumption that material entropy can only increase (Georgescu-Roegen, 1971, 1976, 1977, 1986). A summary of Cleveland and Ruth (1997) outlines the Georgescu-Roegen's main arguments:

1. There is a biophysical interdependence between manufactured capital and natural capital.

2. Conventional economic analysis confuses funds and flows. This results in a distortion of the relation between manufactured and natural capital. For instance, using the Cobb-Douglas production function, $Q = K^{\alpha_1} L^{\alpha_2} R^{\alpha_3}$, where Q is output per time period; K is the stock of capital; R is the flow of natural resources; L is labor supply per time period; and α1, α2, α3 are fixed parameters. Georgescu-Roegen observes that with a constant labor force L_0, one could obtain any given Q_0 if the flow of natural resources satisfies the condition $R^{\alpha_3} = \frac{Q_o}{K^{\alpha_1} L_o^{\alpha_2}}$. Thus, one can maintain a constant output indefinitely with an ever-diminishing amount of R if the quantity of K can be increased sufficiently. Since manufactured capital cannot create the resources it transforms, these production functions imply the physically impossible assumption that a given output can be maintained as energy or material inputs vanish if manufactured capital can be increased sufficiently.

3. According to Georgescu-Roegen, material dissipation and the declining quality of resource utilization, materials may ultimately become more crucial than energy. Cleveland and Ruth (1997) quote Georgescu-Roegen, '*"the Entropy Law in its present form states that matter, too, is subject to an irrevocable dissipation"*'.

The above arguments set forth by Georgescu-Roegen's and their implications have been disputed by others and, in some instances[24], are in contradiction to the first law of thermodynamics (Cleveland and Ruth, 1997; Faber *et al.,* 1996). Nevertheless, the continuing use of Georgescu-Roegen's arguments in the literature or in popular writings undermines not only Georgescu-Roegen's contribution of incorporating biophysical principles and the importance of ecosystem-economy interactions into the patois of economics, but also the intelligent use of entropy as a useful concept in technology and energy-based economic models with useful policy implications. For example, Georgescu-Roegen's views carry weight among neo-Malthusians and Hubbert Peak theory supporters (Scwartzmann, 2007). Garrett Hardin (1993), a neo-Malthusian who assumes that Earth is an isolated system, argues that the second law of thermodynamics is the physical basis for the limits to a sustainable human population level. However, the second law of thermodynamics when applied to finite reserves of fossil fuels only states that energy required to do work is not renewable and that waste heat cannot be re-used continually. It does not imply limits to sustainable levels of population. By focusing on the second law as a limit on population, authors like Hardin ignore the role of technology and yet unrecognized/unused sources of energy. Others, according to ecologist Forrest M. Mims III, report that some ecologists advocate the use of airborne Ebola virus to cull the world's population by up to 90%. Others still, advocate for pre-industrial population levels and go as far as rejecting the use of computers because they generate entropy (Scwartzmann, 2007).

In the mainstream academic literature, some economists have also argued that one can use entropy as a measure of economic value. That is, a good with low entropy (defined as 'orderly') will have a higher economic value. This notion is analogous to Marx's Labour Theory of Value. It is a flawed concept not just because of their erroneous use of entropy, but because the concept of value is inherently based on the human (i.e. economic agent's) perception of worth and thus, 'value' cannot be related to entropy. Even a simple example using their erroneous definition of entropy as a measure of disorder illustrates how this notion is flawed. A 'disorderly' mixture of ready-to-use concrete made up of cement, sand and pebbles has a higher economic value than the unmixed, 'orderly' ingredients, yet its entropy is also higher.

[24] The fallacy of his fourth law is due to its conflation of isolated and closed systems.

More serious authors have postulated that because entropy production is a common feature of all processes, it can be used as measure of resource use. Here, too, the use of entropy production as a measure in resource efficiency does not lend itself easily to economic growth or efficiency. Does lower entropy production as a result of more efficient use of a particular resource (such as production of copper, coal, or bauxite) automatically imply that it is *economically* more efficient? Moreover, it is not clear from an ecosystem or ecological impact perspective whether a more efficient use of resource (as defined by entropy production) is a valuable quantitative measure. As Gößling (2001) also notes, entropy production is not coupled to economic parameters.

Other authors, including those in the physical sciences, use entropy as an index of environmental pollution. For instance, Fugii (1982) proposes entropy as an index of environmental pollution and discusses economic growth with entropy as a constrained optimization problem not unlike mainstream economic models. Fugii (1982) assumes that entropy is produced in proportion to the consumption rate of resources whose coefficient may vary with technological innovation. Fugii (1982) also assumes that the production function, whose inputs include capital and resources, has a constant elasticity for substitution. As with many other similar models (see reference in the next sentence to Kümmel (1989)), Fugii (1982) shows that the level of individual welfare can only increase when the economy expands through increased technological innovation, or by reducing the population. A similar suggestion by Kümmel (1989) uses entropy production as an overall pollution indicator by weighing different pollutants by the additional heat one generates if one were to prevent the emission of pollutants; therefore, a variety of pollutants are made equivalent by their heat equivalents. In this case, one has the reverse problem (and an additional issue) from the previous case of using entropy as measure of efficiency with regard to resource use. First, using entropy as a measure of pollution does not capture the consequences of irreversibly over-using renewable resource. Second, it implicitly assumes that the consequences or effects of the various pollutants on the biosphere are equivalent (i.e. because they are all expressed in heat equivalents). A simple example illustrates that this cannot be a viable approach. Assume that sulfur dioxide and any stratospherically reactive chlorofluorocarbon have, by Kümmel's (1989) postulation, the same heat equivalents[25]. Regardless of their entropy production, one can clearly note that their long-term effects on the biosphere are quite different.

3.3 How best to use Entropy in Economic Growth Models with Technological Change

The previous sections show that anthropomorphic interpretations of entropy in terms of disorderliness are problematic. Thus, one wants to avoid the use of the term 'entropy' outside the thermodynamic framework that only has the word itself in common with the original concept. The previous sections also shows that quantitative measures of entropy production from resource use, the use of entropy as measure of economic value or the measure of entropy as an index of pollution all fail to provide a realistic aggregate measure for environmental damage. Approaches that impose absolute constraints on economic growth seem to be too pessimistic. Therefore what is the ideal isomorphism between economics and entropy? Do we need one?

Section 2.3.4 concludes that because human activity contributes about 0.008% to 0.012% of the total entropy production of the Earth, anthropogenic contribution to overall entropy production rates on Earth is trivial. Schwartzman (1996) goes further to state that (1) any change in the Earth's entropic flux in itself gives us no information about actual impacts of global warming, for example, which are outcomes of fossil fuel consumption, and (2) that sustainable societal self-organization on Earth is only limited by the low-entropy solar flux, "a limit with no practical consequences far into the future". Although Earth's entropy flux provides little information about impacts of global warming, the production rate of entropy and its export to the environment is, nevertheless, an important factor for the stability of complex dissipative structures[26]. If one considers several complex dissipative structures coexisting in the same local environment, they will compete for the same energy resources and for the ability to export

[25] Kümmel's (1989) postulation is as follows: "… the proposal is to "weight" pollutants by the indicator "entropy production". This is the (unavoidable additional) heat one generates if, when using an energy carrier, one prevents the emission of all material pollutants (like CO_2, SO_2, NO,) by appropriate technological means."

[26] A dissipative system is a thermodynamically open system which is not in thermodynamic equilibrium. Examples include Bénard cells and the Belousov–Zhabotinsky reaction.

entropy outside the local environment. As noted by Gößling (2001), the local environment itself, in which the complex structures exist, will also have a limited ability to export entropy to a 'sink environment' or meta-environment. Mathematically, one can express this limitation by first separating, for open systems, changes in energy, E, and changes in entropy, S, into internal, i, and external, e, contributions:

$$dE = d_eE + d_iE \qquad (3.12)$$

$$dS = d_eS + d_iS \qquad (3.13)$$

When the export of entropy by the system exceeds the internal entropy production, then the change in entropy of the system is negative:

$$dS < 0, \text{ if } -\frac{d_eS}{dt} > \frac{d_iS}{dt} \geq 0. \qquad (3.14)$$

Equation 3.14 holds for systems that are far from equilibrium; otherwise, the positive d_iS would be large such that it would dictate the entropy balance and drive the system towards equilibrium. Thus, for the stability of complex dissipative structures that coexist in the same local environment, one sees that the local environment (or system) itself will also have a limited ability to export entropy to a meta-environment (Gößling, 2001):

$$-\frac{d_eS}{dt} \geq \frac{d_iS}{dt} + \sum_j \frac{d_iS_j'}{dt} + \sum_{jk} \frac{d_iS_{jk}''}{dt} + \cdots \leq -\frac{d_eS}{dt} \qquad (3.15)$$

where S = entropy in the meta-environment;

S_j' = entropy in sub-environment, *j*; and

S_{jk}'' = entropy in sub-sub-environment, *jk*.

Although the entropy export rate of the meta-environment is dependent on internal and external parameters, we see, from equation 3.15, that an increase in entropy production of one of the sub-systems reduces the available capacity for entropy export of the other sub-systems. The ability to export entropy may be affected by the activity of one or more of the subsystems, and because dissipative structures are non-linear systems, small variations in one system parameter may lead to large system-wide effects (Gößling, 2001). Overcritical changes in dissipative structure systems from internal or external forces lead the system to look for new patterns[27] of internal structure that enable an enhanced entropy export (Gößling, 2001).

In summary, one can extend the phenomenon of limiting entropy production rates from complex dissipative structures to the economic-biosphere interactions in which they can be viewed as two co-existing and competing, in entropy terms, sub-systems within a large meta-environment, where increases in the entropy production of one of the sub-systems might have detrimental effects on the other sub-system and/or meta-environment. Therefore, given that the current entropy production of the Earth's biosphere is approximately ten times larger than that for civilization's energy system and if one were to assume that every country produced entropy at the same per capita rate and with same energy efficiencies as currently occurs in industrialized countries, then the entropy production rate could approach the same order of magnitude as Earth's biosphere. This result has important implications regarding environmental impact (Rosen and Scott, 2003). Although natural processes account for almost all of Earth's entropy production, civilization's energy system could, in the future, come to have an environmental impact approaching that of life itself (Rosen and Scott, 2003).

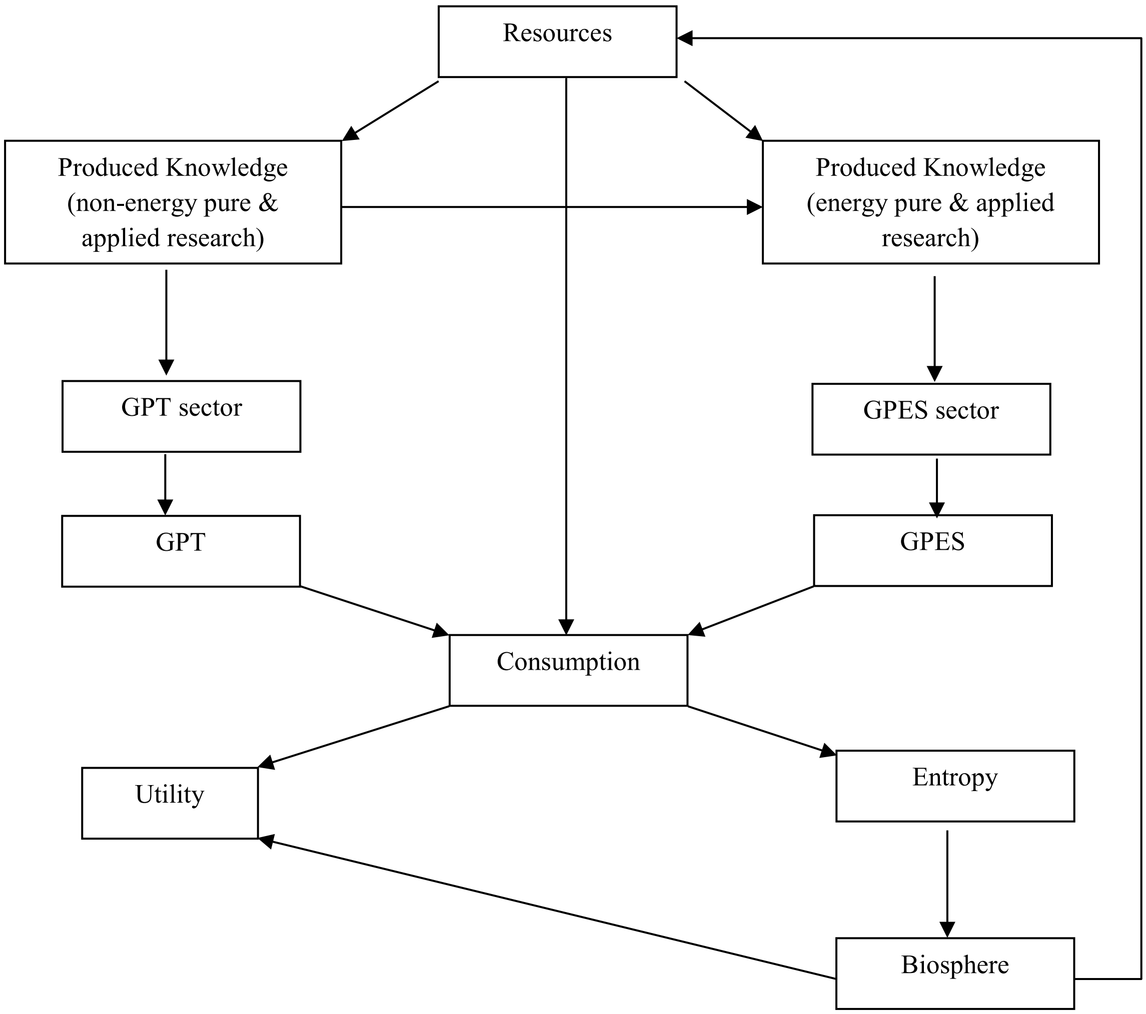
This brings one to this thesis' postulate on the use of entropy in economic growth models. The concept of entropy should be divorced from its association of resource use including energy sources, and entropy should not be seen to be equivalent to pollution. Likewise, it should not be used as either a qualitative or quantitative measure of 'disorder'. Rather, in keeping within a thermodynamic framework[28], for economic purposes, entropy should be interpreted only within qualitative relationships and used as a qualitative measure of waste energy produced in and by any energy conversion process where the waste can take various forms such as heat or pollution such that the increase (decrease) in anthropogenic entropy results in a decrease (increase) in the entropy production ratio of the biosphere to civilization. Decreases (increases) in the biosphere to civilization entropy production ratio decreases (increases) utility. However, it should be clear

[27] Quantifying the critical parameters of a complex dissipative system remains impossible in many cases (Gößling, 2001).
[28] In other word, based on the idealistic assumptions of classical thermodynamics and statistical mechanics.

that the generation of entropy does not need to be a ‘bad’ per se because its generation allows us to consume, build, and develop new technologies. It is only when entropy production rates within a system or sub-system (i.e. economic, in this case) become large enough to rival that of the biosphere that things may go awry.

By using entropy in its thermodynamic framework, one can appeal to environmental or sustainability discourses without loss of clarity. The following chapter details with the incorporation of entropy in an economic growth model that employs GPTs and GPESs as illustrated in Figure 3.3.

Figure 3.3: Graphic Illustration of the Biosphere-Energy-Technology (BET) Model



Technical labour resources contribute directly to the production of energy knowledge, non-energy knowledge and/or GPES pervasiveness, while non-technical labour resources only affect the production of consumption goods directly. Non-energy knowledge and energy knowledge lead directly to the discovery of GPTs and GPESs, respectively, which, in turn, rejuvenate growth of consumption. Increases in consumption increase utility, but generate entropy, which negatively affects the biosphere. A decrease in the level of the biosphere will reduce economic agents' utility and, if severe, can result in the reduction of overall population levels (i.e. labour resources). Therefore, economic agents face a trade-off between increasing consumption and maintaining a suitable biosphere level.

Chapter 4: Modeling the Race between Energy and Technology

This chapter uses the information and arguments presented in Chapters 1 through 3 to build a theoretical biosphere-energy-technology (BET) growth model. The baseline model includes the elements of a GPT, GPES, and entropy and its effects on the biosphere. The model will be provided with various parameter values and growth will be simulated numerically in Section 4.2. Section 4.3 will present simulation results when feedback to allocation of resources from the biosphere is added to the baseline model. Growth will be simulated under two assumptions: (1) perfectly myopic agents who care about current consumption only, and (2) partially myopic agents who care about current consumption and future biosphere levels. Chapter 4 will conclude with a discussion of the applicability of the full model and policy implications that stem from it. The appendix to Chapter 4 will briefly discuss whether an augmented neoclassical (Solow) model could have been used to model the race between energy and technology.

4.1 Outline of the BET Model

The model in this chapter builds on and modifies the model presented in Lipsey *et al.* (2005). The model presented will extend the basic GPT model presented in Lipsey *et al.* (2005) by adding the effect of GPESs and that of entropy production on the biosphere.

The BET model has four sectors:

(1) a consumption sector that produces a single aggregate consumption good;

(2) a GPT sector that uses produced pure and applied knowledge (or, simply 'produced knowledge') from fundamental research and research and development (R&D), respectively, which leads to new GPTs and applications specific to the GPT;

(3) a joint GPT-GPES sector that uses produced knowledge from GPES R&D and the joint interaction of GPT-GPES R&D that leads to the recognition and adoption of new GPESs; and

(4) an environmental sector, called the biosphere, which is vital for human life and has an entropy threshold export capacity that competes with the anthropogenic rate of entropy production that results from the production of the aggregate consumption good.

The first three sectors employ labour resources specific to their sector. The labour resources are constrained by a fixed population size. As such, they are interrelated by their opportunity cost. Furthermore, each of the first three sectors has a production function that displays diminishing returns to the resources that are used.

4.1.1 Law of Motion for the Productivity Parameters in the GPT (Produced Knowledge) Sector

One begins with a pure and applied knowledge (or, simply 'produced knowledge') sector that is equivalent to Lipsey *et al.*'s (2005) two-sector model's applied R&D sector. This thesis adopts a new name to differentiate and avoid confusion from Lipsey *et al.*'s (2005) fundamental knowledge sector in their three-sector model. The BET model does not differentiate between applied and fundamental knowledge for reasons explained below. The produced knowledge sector is essentially a GPT sector that uses knowledge from fundamental research and R&D, respectively, which leads to new GPTs and applications specific to the GPT. Correspondingly to Lipsey *et al.'s* (2005) model, the GPT sector creates knowledge that increases the productivity of resources in the consumer goods sector. Thus, the production function in the GPT sector is

$$A_t = a_t + (1 - \varepsilon_1)A_{t-1} \quad (4.1)$$

$$\text{where } a_t = \upsilon G_t (d_t^G)^{\alpha_1},\ \alpha \in (0, 1) \quad (4.2)$$

The current stock of pure and applied knowledge, A_t, is dependent on the previous period's stock of pure and applied knowledge in the GPT sector, A_{t-1}, but is reduced by an obsolescence factor, ε_1 (Equation 4.1).

The flow of produced knowledge, a_t, is augmented by a productivity coefficient, G_t, which embodies the current period's GPT[29]. An increase in G_t will cause an increase in the marginal productivity in the knowledge sector. This will, in turn, raise the productivity of the resources in the production of consumption output. The flow of produced knowledge from the GPT sector is also a function of the resources devoted to its production, $\mathrm{d}_\mathrm{t}^\mathrm{G}$, the labour-hours spent on developing new ideas related to non-energy, GPT technologies, which is subject to diminishing returns.

4.1.2 Labour Resources

The labour resources enter the production function of each sector with a positive exponent. Restrictions on exponents ensure either diminishing or constant returns to labour inputs. It is also assumed that the size of the population, *N*, is fixed. Thus, Equation 4.3 represents the labour resource constraint:

$$N = n_t + d_t^G + d_t^E \qquad (4.3)$$

where *n* is the labor force producing the aggregate consumption good, and *d*'s are researchers. Specifically, d_t^E is the population or labour-hours allocated to the development of new ideas related to energy technologies and d_t^G is the population or labour hours allocated to the development of new ideas related to non-energy (GPT) technologies.

Similar to Lipsey *et al.* (2005), the key trade-off is between the output of resources devoted to consumption production with a given production function (defined below) and output of the resources that go into the non-energy technology sector and joint GPT-GPES sector (i.e. energy

[29] The parameter, υ, which is ∈ (0, 1] is used to calibrate the model and can be set to one for the baseline simulation model.

sector), respectively, to improve the productivity of the resources that remain in the consumption sector. Thus, marginal returns to labour are equalized across sectors.

4.1.3 Law of Motion for the Productivity Parameter joint GPT-GPES Sectors

I now introduce a second, unique sector in our model: a joint GPT-GPES sector that uses composite knowledge that comes from the produced knowledge (i.e. GPT) sector and the joint interaction of GPT-GPES R&D that leads to the recognition and adoption of new GPESs. This a departure from the Lipsey *et al.* (2005) model in that rejuvenation of growth in the BET model depends not only on exogenous changes in GPT levels, but also on exogenous changes in GPES levels. In a similar fashion to the GPT sector knowledge production function, the production function in the joint GPES-GPT sector uses labour resources and is augmented by a productivity coefficient, G_t^E:

$$a_t^E = a_t G_t^E (d_t^E)^{\alpha_2}. \qquad (4.4)$$

$$A_t^E = f(a_t^E, A_{t-1}). \qquad (4.5)$$

The current stock of pure and applied energy knowledge, A_t^E, is a stock of composite knowledge, and is dependent on the previous period's stock of pure and applied knowledge in the GPT sector, A_{t-1}. The stock of energy knowledge is governed by the flow of produced energy knowledge, a_t^E, which is a function of a_t. Modeling the energy knowledge production function in this manner is unconventional. These two (unconventional) assumptions are justified by noting that energy knowledge is quite different from GPT knowledge. First, the current stock of pure and applied energy knowledge, A_t^E, cannot be dependent on A_{t-1}^E because whereas GPT knowledge accumulates and is usefully transferred from a previous period to the next (even though GPTs can be technologically distinct from each other), energy knowledge, while dependent on technology knowledge, is not necessarily cumulative or dependent on a previous period's accumulated energy knowledge. This is because energy knowledge from period t-1 becomes obsolete in period t. Examples can be used to illustrate this point. For example, the development of successive GPTs like the internet and the motor vehicle depended entirely on previously accumulated knowledge of other GPTs such as the computer and the internal combustion engine, respectively. The development of nuclear energy, however, is not dependent on any previously accumulated energy knowledge from coal or petroleum or wood energy development. In a sense, energy knowledge is similar to tacit knowledge[30]; that is, it is highly contextual and difficult to employ given different applications. Energy knowledge gained in the petroleum sector would be of little use in the hydrogen sector. Relative to GPT knowledge, energy knowledge is embodied knowledge bounded to particular energy sources such as foodstuffs, wood, coal, hydrogen, etc. Thus, spillovers of energy knowledge are limited and the marginal cost of transmitting or employing the knowledge from one application to another would be extremely high. Energy knowledge, relative to and unlike GPT knowledge, is created in one place for one purpose or GPES and is not applicable to a new GPES. Another illustrative example stresses this point. Total power installed in Europe in the early 1800s was mostly in waterwheels, with some in steam engines (von Tunzelmann, 1978). The kinetic energy of flowing water represented the GPES and its use/power generation was confined to specific sites where water flowed. The later widespread adoption of coal as the new GPES to produce steam, whose use and application is completely unlike its predecessor GPES, permitted steam engines to be used anywhere, which also permitted the automation of textile manufacturing and the development of the factory system.

The last example above clearly illustrated that the energy knowledge embodied in flowing water for its use in watermills is independent of the energy knowledge embodied in coal for its use in steam engines. There is no sharing of energy knowledge between successive GPESs. As such, one can represent this 'tacit' characteristic of energy knowledge by rewriting equation (4.5) as equation (4.5a) where the previous stock of energy knowledge is reduced by an obsolescence factor, ε_i[31], equal to unity.

$$A_t^E = f(a_t^E, A_{t-1}) + (1 - \varepsilon_i)A_{t-1}^E. \qquad (4.5a)$$

Although the assumption that energy knowledge embodies a tacitness is a strong assumption and it helps simplify the workings of our model, one can further justify setting the obsolescence factor, ε_i, equal to unity as follows. In a world with intermittent arrivals of new and distinct

[30] Technically, tacit knowledge is bound to an individual with, say, a specific skill that is not generally codified.

[31] The subscript *i* is used to indicate any particular value of obsolescence.

energy sources, a representative individual faces the choice of sticking with an established GPES or moving on to on new (better) one. The trade-off is as follows: switching to a new GPES would allow the agent to employ a more efficient energy source but the agent would lose the composite energy knowledge, the specific human capital accumulated in the old GPES. Essentially, when a new GPES arrives exogenously in time period t, human capital from the energy sector in period t-1, d_{t-1}^{E}, becomes vintage human capital such that it becomes immediately obsolete in the following period[32]. Although the stock of composite knowledge grows in the energy sector every period, it is only dependent on current flow of knowledge in the current period and the stock of knowledge in the GPT sector. Using the notion put forward by Chari and Hopenhayn (1991) of technological diffusion and complementarity of old and new vintage human capital, it is assumed that complementarity between old and new GPES is lost fairly quickly, which implies that stock of human capital in the energy sector also becomes obsolete quickly.

In sum, the stock of energy knowledge is complemented by non-energy knowledge, and depending on the energy source, the two types of knowledge can exhibit a degree of substitution. I adopt a constant elasticity of substitution (CES) functional form to model the abovementioned properties of our stock of energy knowledge (Equation 4.5b below). The CES function allows for greater flexibility (i.e. specifying the degree of complementary or substitution between energy knowledge and non-energy knowledge for the stock of energy knowledge) without compromising the properties of energy knowledge I wish to illustrate:

$$A_t^E = [\varepsilon_2 (a_t^E)^{\omega} + (1-\varepsilon_2)(A_{t-1})^{\omega}]^{\frac{1}{\omega}}, \qquad (4.5b)$$

where $\frac{1}{1-\omega}$ is the elasticity of substitution between the previous period`s stock of technology knowledge and the current period`s flow of composite energy-technology knowledge and ε_2 is the obsolescence factor.

[32] Justifies ε_i= 1.

The second unconventional assumption made was that the flow of produced composite energy knowledge, a_t^E, is a function of a_t. This resulted in the production function (4.4), $a_t^E = a_t G_t^E (d_t^E)^{\alpha_2}$. Substituting (4.2) into (4.4), we get

$$a_t^E = \upsilon G_t G_t^E (d_t^G)^{\alpha_1} (d_t^E)^{\alpha_2}. \qquad (4.4a)$$

Equation 4.4a implies that the flow of energy knowledge is augmented by two productivity coefficients: a productivity coefficient, G_t, which embodies the current period's GPT and another by a productivity coefficient, G_t^E, which embodies the current period's GPES. It also implies that the flow of energy knowledge is a function of both labour resources in the GPT sector and labour resources in the GPES sector, each of which has a different elasticity of output. Inclusion of the two types of resources is justified by noting the arguments presented in Chapter 2: historically, coupling a technology to a new GPES can improve its chances of acceptability and if a GPT and a GPES are related then a GPES or a GPT can represent a precondition for the arrival of one or more GPTs or an improved GPES, respectively.

It is also noted that Equation 4.4a, $a_t^E = \upsilon G_t G_t^E (d_t^G)^{\alpha_1} (d_t^E)^{\alpha_2}$, is a Cobb-Douglas production function. If all the exogenous parameters $\upsilon, G_{t,} G_t^E$ are grouped under a single productivity coefficient, *Z*, one can rewrite Equation 4.4a as

$$a_t^E = Z (d_t^G)^{\alpha_1} (d_t^E)^{\alpha_2} \qquad (4.4b)$$

The production function from in Equation 4.4b is a departure from Lipsey *et al.*'s (2006) production function in that their production functions for flows of knowledge only have one input resource and all exhibited diminishing returns to resources used. The model's flow of composite knowledge, like the Cobb-Douglas production function, is also subject to diminishing marginal returns to each of the labour inputs; however, there is nothing about the historical behaviour of the GPT and GPES sectors that would imply that the function be first order homogenous. While this thesis is in agreement with Lipsey *et al.* (2006) that there is no reason to expect decreasing returns in technology, it takes a different view of composite energy knowledge.

There are two arguments that can be used such that one would not necessarily expect that the production function of composite energy knowledge exhibit at least constant returns to scale. First, one can argue for decreasing returns to scale for the production of composite energy knowledge. The number of new GPESs is finite while the number of GPTs is, relatively speaking, not. Thus, researchers today will have more difficulty in discovering or creating new general purpose energy sources than their predecessors because the simplest discoveries have already been made. Weil (2013) defines this negative effect of past discoveries on the ease of making discoveries today as the fishing out effect. Indeed, Weil (2013) argues that the assumption that the growth rate of technology depends only on the amount of resources devoted to research and development is not justified. It would be an even less appropriate assumption to make for the production of composite energy knowledge. Second, as the effort devoted to research and development in energy sources increases, the effectiveness of each new researcher falls. Nuclear fusion provides for the most extreme of examples for this second argument. Nuclear fusion was one of the most promising energy technologies of the post-WWII era. However, after decades of research and billions of dollars spend on nuclear fusion research, the energy sector still has not been able to produce a controlled fusion reaction that yields a net amount of energy.[33]

In sum, the model shows that, in the absence of a biosphere, the production function for composite knowledge should be modeled with decreasing returns to scale. As long as the individual labour resource elasticities are greater than zero, composite knowledge production function isoquants will be downward sloping and convex. However, to maintain a realistic application to the effects of consumption goods production on the biosphere, when it is included, the production function for the flow of composite knowledge should be modeled with small to moderately decreasing returns to scale (i.e. close to constant returns to scale). Otherwise, when the biosphere is included in the model, entropy (a bad) is produced jointly with the production of consumption goods has no or little effect on the biosphere if the production function for the flow of composite knowledge exhibits highly decreasing returns to scale.

[33] *The Economist* (2002) states that fusion reactors, "are reckoned to be 50 years from commercialization – and have been for most of the 50 years since people first started trying to build them."

4.1.4 Consumption

Consumption output is produced by an aggregate production function[34]:

$$c_t = A_t^E (n_t)^{\alpha_3} \qquad (4.6)$$

Consumption output depends on the non-technical labour resources allocated to the consumption sector, which enter the consumption production function with a positive exponent of less than or equal to unity so that accumulated resources are subject to constant or decreasing returns. Consumption output is also dependent on A^E, the productivity parameter of composite knowledge that is determined in the joint GPT and GPES sector.

4.1.5 Representative Agent Problem

The social planner needs to optimally allocate labour resources so as maximize consumption, given the constraints on the stocks and flows of knowledge and the constraint on labour:

$$\max_{d_t^E, d_t^G, n_t,} c_t = A_t^E (n_t)^{\alpha_3} \quad \text{subject to}$$

$$N_t = n_t + d_t^G + d_t^E \qquad (4.3)$$

$$a_t^E = Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}, \text{ where } Z = \upsilon G_t G_t^E \qquad (4.4b)$$

$$A_t^E = [\varepsilon_2 (a_t^E)^{\omega} + (1 - \varepsilon_2)(A_{t-1})^{\omega}]^{\frac{1}{\omega}} \qquad (4.5b)$$

In the numerical simulation section, it will be shown that energy and non-energy productivity shocks have different impacts on consumption (See discussion in Section 4.2). Here, first order

[34] For simplicity, we have assumed that output, y, is equal to consumption, c.

condition results are used to describe some of the theoretical properties of our model in the absence of entropy and the biosphere.

Consider the state of the economy at time, t. Suppose $\mathrm{A}_{\mathrm{t}-1} = 0$ and, for simplicity, $\varepsilon_1 = 0$. This reduces Equation (4.1) to $\mathrm{A}_{\mathrm{t}} = \mathrm{a}_{\mathrm{t}}$. The consumption function can be rewritten as

$$c_t = a_t^E (n_t)^{\alpha_3} = \varepsilon_2\, Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3} \qquad (4.6\text{ a})$$

and the maximization can be simply stated as follows:

$$\max_{d_t^E, d_t^G, n_t,} c_t = \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3} \text{ subject to } \quad N_t = n_t + d_t^G + d_t^E.$$

From the first-order conditions, it follows that

$$\alpha_1\, n_t = \alpha_3\, d_t^G \qquad \text{(i)}$$

$$\alpha_2\, n_t = \alpha_3\, d_t^E \qquad \text{(ii)}$$

Also, replacing the non-energy and energy technical labour variables in Equation 4.6a with our maximization results above, we can rewrite Equation 4.6a as follows:

$$c_t = \varepsilon_2 Z \left(\frac{\alpha_1}{\alpha_3}\right)^{\alpha_1} \left(\frac{\alpha_2}{\alpha_3}\right)^{\alpha_2} \left(\frac{\alpha_3 d^G}{\alpha_1}\right)^{(\alpha_1+\alpha_2+\alpha_3)} \qquad (4.6\text{b})$$

or equivalently as,

$$c_t = \varepsilon_2 Z \left(\frac{\alpha_1}{\alpha_3}\right)^{\alpha_1} \left(\frac{\alpha_2}{\alpha_3}\right)^{\alpha_2} \left(\frac{\alpha_3 d^E}{\alpha_2}\right)^{(\alpha_1+\alpha_2+\alpha_3)} \qquad (4.6\text{c})$$

The energy and technology shocks, G_t^E and G_t, respectively, enter equation 4.6b(c) symmetrically, via *Z*. Thus, when a shock occurs, there is an increase in the productivity of resources allocated to the production of knowledge. The maximisation of consumption in any one period requires that a marginal reallocation of labour resources out of the consumption sector, which reduces consumption directly, is exactly offset by the indirect increase in consumption brought about by the increased productivity caused by devoting labour resources to the GPT and composite knowledge GPES-GPT sectors, respectively. The latter two sectors increase the productivity of the resources that remain in the consumption sector via the production of composite energy knowledge and non-energy knowledge.

4.1.6 Entropy

The effect of energy use in our model will now be incorporated, via the impact of entropy on the biosphere. To my knowledge, the modeling of energy, entropy and the inclusion of the biosphere has no equivalent in the GPT literature, specifically, or growth literature, in general. The model already presented an unconventional production approach to the stock and flow of composite energy knowledge in the joint GPT-GPES sector. With the inclusion of entropy, however, I seek to establish a more conventional use of entropy than what is currently found in the ecological economics literature. Thus, 'entropy' is used within a thermodynamic framework in order to avoid problems that arise from anthropomorphic interpretations of entropy in terms of disorderliness, as discussed in Chapter 3.

Energy use is implicit in entropy production and the adoption level of a GPES. Although the exogenous shock of a GPES arrival (i.e. G^E) increases consumption, we have argued that increases in consumption are accompanied by a bad, or negative externality, entropy. Entropy, however, is a function of and thus can be mitigated by increases in the adoption level of a new more thermo-efficient GPES, B_t. The stock or level of adoption is raised to a negative exponent with values between 0 and 1 so that increases in the stock or pervasiveness of thermo-efficient energy sources used in the production process result in decreases in entropy. The stock of a new GPES at time t is a result of the accumulation of use-experience of a new more thermo-efficient GPES (also called adoption flow), b_t plus the previous period's adoption level, which is subject to a small abandon factor, ε_3, which occurs when agents begin to look for GPES alternatives[35]:

$$B_t = b_t + (1 - \varepsilon_3)B_{t-1}. \qquad (4.7)$$

[35] In the early stages of adoption of a new GPES, the abandon factor can be zero because (1) alternatives may not exist or (2) the new GPES was originally regarded as the alternative to the previous GPES. In our numerical simulations, values close to zero or zero do not alter the qualitative results in any way.

The adoption flow, b_t, is a function of the energy resources spent on developing new GPES-related ideas (i.e. d_t^E), which is subject to diminishing returns. Furthermore, b_t, is augmented by the productivity coefficient, G_t^E, which is determined in the GPES sector and embodies the current period's GPES. The parameter, θ, can take on any positive value and is used to calibrate the model.

$$b_t = \theta G_t^E (d_t^E)^{\alpha_4} \tag{4.8}$$

While 4.8 looks symmetric to 4.4, it is not a function of a_t, but only of d_t^E and G_t^E because unlike a_t^E (see Equation 4.4b), use-experience, while a form of knowledge, is not composite knowledge. Only when a new GPES arrives will there be any increase in use-knowledge; otherwise, the growth of use-knowledge of any energy source eventually converges to zero, except when there is a temporary shift of resources from the non-technical labour resources to the energy and GPT sectors, which occurs during the exogenous arrival of a new GPT. For example, once gasoline was recognised as a GPES, use-experience, b, only accumulates if agents employ the GPES in various applications in different sectors. The applications can only result from modifications of the GPES that arise strictly from labour resources in the GPES sector. Application of the new GPES and any fuel modification for wider applicability is assumed to be dependent on the resources devoted to the GPES sector, d_t^E. Research in the development of octane numbers for gasoline provides for an effective example. By the 1920s, gasoline was already a GPES, but its pervasiveness in the economy grew from research in (gasoline) fuel efficiencies, such as refining the fuel by focusing on high octane fuels and then various fuel detergents[36]. This research from the GPES sector used the resources devoted to the GPES sector, d_t^E, which lead to a variety of additional applications and thus pervasiveness within society – light and heavy duty fleets, aviation applications, and generally, high-compression engines.

[36] In the mid-1950s, "the American Petroleum Institute (API) Research Project analyzed the pure-component octane numbers (ONs) for over 300 different hydrocarbon molecules, and several reliable correlations relating gasoline composition to ON were developed. The work not only quantified the ON trends with molecular structure and size, it also studied the nonlinear interactions between different molecular types toward ON" (Gosh *et al*., 2006).

4.1.7 Entropy Properties in the GPT-GPES Model

Earth's biosphere is stressed from the past and present growth of economic activity. In the model, this stress is manifest as entropy, S_t, that is created via any production process. This is represented by equation 4.9:

$$S_t = \mu c_t {B_t}^{-\alpha_5}. \tag{4.9}$$

The parameter, μ, which can take on any positive value, controls for the magnitude of entropy production. Note that entropy, S_t, is a flow variable while, B_t, is a stock variable. In an economy with no exogenous shocks, consumption and the adoption level of a GPES grow such that accumulated resources are subject to decreasing returns. Increased use of new thermo-efficient GPESs in the production process results in smaller entropy changes.

4.1.8 The Biosphere

Consumption output uses some energy conversion process where increases in anthropogenic entropy results in a decrease in the entropy production ratio of the biosphere to civilization. Thus, the biosphere, $X_{t,}$, is treated as a complex dissipative structure coexisting in the same local environment as the economy, and they each compete for the ability to export entropy outside the local environment. In competition with the economy, the biosphere has a limited ability to export entropy to a 'sink environment' or meta-environment. The limit of the biosphere's ability to compete with the economy in exporting entropy is S_{max}. The entropy production ratio of the economy to biosphere is the constraint to this ability. In other words, S_{max} is maximum rate of entropy production that the biosphere can accommodate without adverse effects (i.e. loss of biosphere). One can interpret S_{max} as the biosphere's carrying capacity for entropy. Loss of the biosphere can occur should the carrying capacity (i.e. the maximum rate of anthropogenic entropy production) be exceeded in any time period. The loss of the biosphere continues until a minimum is reached. This minimum level of biosphere necessary for human life at which it can no longer regenerate itself is X^*. However, the biosphere is able to regenerate itself at or above X* and, as it does, it increases its ability to compete in exporting entropy. We set the initial capacity of the biosphere to support anthropogenic activity at X_0. Thus, the regenerative rate of biosphere up to a maximum of X_0 and as long as X does not fall below X^* is R_t.

In order to model and justify the dynamics of the biosphere using the specifications above, one must recognise that the biosphere, like any other complex dissipative structure defined in Chapter 3, has a critical threshold where, when a tipping point is passed, the system shifts to another state. In our model, the biosphere's tipping point is defined as X^*. Beyond the tipping point, the new state of the system/biosphere either collapses or is unsustainable. Some large scale complex systems such as the biosphere and a range of ecosystems, including climate are known to exhibit critical tipping points (van Ness and Scheffer, 2007). It is difficult to predict or anticipate the arrival of a tipping point because there may be little change occurring in a system until the critical threshold. Furthermore, the ability to absorb perturbations like increases in entropy without being thrust into another alternative system is an important part of the stability of a system (van Ness and Scheffer, 2007), which we incorporate as S_{max} in our model.

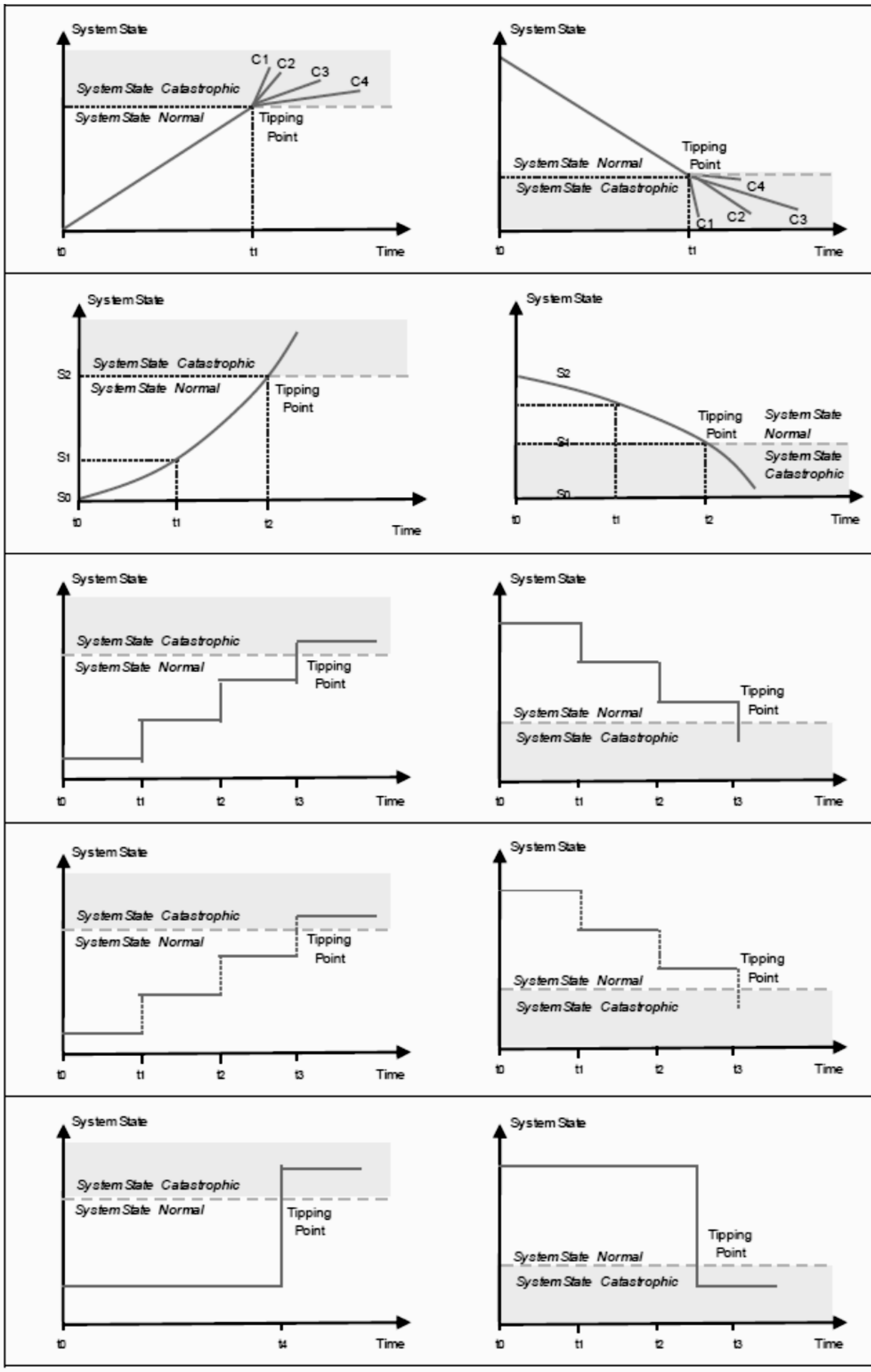
Transition paths describe how a system like the biosphere shifts from life-sustaining to one of collapse. Initially, a system is stable and holds a position between t_0 and t_1. Then, due to some external interfering stress(es), such as entropy, that act upon the system state normal the system reaches a tipping point. If this critical point is passed, the system starts tending away from its stable position (equilibrium), either up or down, as in the case of the biosphere. The moment the system leaves its equilibrium position, it enters the catastrophic state (Mrotzek, 2011).

The goal is to use a simple, generic mathematical form to model the biosphere as system that has three characteristics that define systems that have tipping points:

(1) the ability to absorb perturbations such as entropy,
(2) the ability to return to its initial value via a recovery rate, as long as the system has not passed the tipping point, and
(3) a critical threshold or tipping point that, should it be surpassed, causes the system shift from a 'normal' state to 'catastrophic' state.

According to Mrotzek (2011), there are five generic types of possible catastrophic transition paths. These are depicted in Figure 4.1 (Mrotzek, 2011).

Figure 4.1: Generic Catastrophic Transition Paths



1. Linear
A linear catastrophe transition is a continuous process *without* feedback from the changing system.

2. Reinforcing
A reinforcing catastrophe transition is a continuous process *with* feedback from the changing system.

3. Cascade
A cascade catastrophe transition represents a chain of events where each event *builds up on the previous one*.

4. Multiple Independent
A multiple independent catastrophe transition represents a chain of events where each event *is independent from the other ones*.

5. Bifurcation
A bifurcation catastrophe transition represents *a single shift*.

Linear systems are rare. Systems paths may appear linear because of short time horizons (Sterman, 2000). The other four transition paths for catastrophic events have all been observed in natural systems, but it should be noted that the same catastrophic event can be associated with different types of generic paths depending on one's perception of a system (Wolstenholme, 2003). Mrotzek (2011) uses the example of an avalanche to illustrate this point; that is, an avalanche can be seen as a

1. *Bifurcation* – nothing happens until suddenly the avalanche occurs,
2. *Cascade* – many intervals of snowfall over several week, where at one point in time the avalanche happens,
3. *Linear process* – seeing the whole snowfall as a linear accumulating process,
4. *Reinforcing process* – likeliness of catastrophe rises exponentially, as snow accumulates.

In addition to perception-based determination of transition paths, real systems only present one case history for study (Hastings and Wysham, 2010). That is, every real system is described by different models with alternative stable states and varying complexity. Therefore, predicting critical points before they are reached is extremely difficult. Furthermore, almost all real systems are permanently subject to natural perturbations (Scheffer *et al.*, 2009). However, there are many real complex systems that have tipping points and spontaneous systemic failures. Particularly relevant complex systems that experience catastrophic bifurcations for which our biosphere can be modeled include: asthma attacks, epileptic seizures, abrupt shifts in ocean creaction profileulation or climate, catastrophic shifts in rangelands, fish populations or wildlife populations (Scheffer *et al.*, 2009). As we have seen, for catastrophic bifurcations[37], once a

[37] An example of a bifurcation in an ecosystem provided by Mrotzek (2011) is the extinction of the passenger pigeon. Although the passenger pigeon was the most common bird in North America, it became heavily hunted in the 19th century resulting in a slow, but steady decline in population from 1800 to 1870. This slow decline was followed by an extreme decline between 1870 and 1890, which ultimately lead to the extinction of the passenger pigeon. According to Mrotzek (2001), there were no initial signals of extinction that resulted from the declining population of passenger pigeons. However, when the point of minimum population necessary for reproduction was reached, the killing of one additional passenger pigeon at this critical tipping point lead to a system state shift from 'system state normal' to 'system state catastrophic' such that the extinction of the bird became inevitable. Even though there is a heavy decline in total population, the system is still in the normal system state as the flock size is big enough to recover. Yet, at one point, here at 1890, the critical amount of pigeons is reached and with the decisive kill, the system switches.

threshold is exceeded, a positive feedback propels the system through a phase of directional change towards a contrasting state (Hastings and Wysham, 2010).

In sum, there are numerous mathematical models, with varying degrees of complexity that represent different kinds of catastrophic thresholds. Given that there is no model that describes system shifts for the biosphere as a whole when subjected to entropy perturbation, I develop a simple and generic relationship for the biosphere that, like many real systems, can undergo catastrophic bifurcation (via a piecewise function) and has the three characteristics, outlined above, of a system with tipping points. The model is comparable to and behaves like many real systems. Although the model is a first difference equation, it behaves analogously to single differential equation models that describe natural phenomena. Nutrient cycling in lakes can be used as an illustrative example. One can describe the loss of phosphorus from the top layers of a deep lake and the sudden recycling (when tipping point is reached) if the deeper water becomes anoxic using a relatively simple differential equation (van Nes and Sccheffer, 2007):

$$\frac{dx}{dt} = a - bx + c\frac{x^p}{x^p+1},$$

where a is a nutrient load control parameter, b is the decay rate, c is the maximum recycling rate, p is a constant, and x is the nutrient of interest.

In the same manner, the generic relationship between the biosphere and changes in entropy production, which includes the three characteristics of a system with a tipping point, is as follows:

$$X_t = X_{t-1} - max\{0, S_{t-1} - S_{max}\} + R_t. \qquad (4.10)$$

If $X_0 > X_t \geq X^*$, then $R_t = (X_{t-1} - X^*)\gamma_3$; otherwise $R_t = 0$. (4.11)

S_{max} is the biosphere's carrying capacity, and X* is the minimum level of biosphere necessary for human life at which it can no longer regenerate itself. X_0 is the initial capacity of the biosphere that supports anthropogenic activity, and R_t is the regenerative rate of biosphere as long as $X > X^*$. Regeneration of the biosphere occurs until X_t reaches X_0.

4.1.9 Biosphere Properties and Steady-State Existence

From equations 4.10 and 4.11, it is noted that the biosphere is a function of entropy and a regenerative rate. The regenerative rate, however, is itself a function of the biosphere and no other input. Thus, the regenerative rate is completely determined by the state of the biosphere. The regenerative rate, R_t, is equal to zero when (i) where the biosphere is at its peak capacity, X_0, and, (ii) where the biosphere can no longer regenerate itself, at X^*. In all other instances, the biosphere regenerates itself in every subsequent time period to the period in which it was stressed by entropy production.

4.1.10 Steady-States When Entropy is Accommodated

If the level of entropy production at time t-1 is within the biosphere's ability to accommodate the generated entropy without adverse effects, then $S_{max} > S_{t-1}$ and $max\{0, S_{t-1} - S_{max}\}$ is zero. Therefore, if one substitutes $R_t = (X_{t-1} - X^*)\gamma_3$ and set $max\{0, S_{t-1} - S_{max}\}$ to zero into equation 4.10, then one has

$$X_t = X_{t-1} - max\{0, S_{t-1} - S_{max}\} + (X_{t-1} - X^*)\gamma_3 \qquad (4.10a)$$

$$X_t = X_{t-1} + (X_{t-1} - X^*)\gamma_3$$

$$X_t = (1 + \gamma_3)X_{t-1} - \gamma_3 X^* \qquad (4.10b)$$

In this case, there are two steady-states when $X_t = X_{t-1}$. The first is X_0 and the other, X^*. If the economy starts at the biosphere's tipping point, $X_{t-1} = X^*$, which is an unstable steady-state[38], then any exogenous shock will cause the biosphere to collapse. However, if the economy starts with a biosphere level at or above X^* and the shock is not large ($S_{max} > S_{t-1}$), the biosphere will continually recover with slope $(1 + \gamma_3)$ until it reaches the maximum level of biosphere, X_0. Once X_0 has been reached, there will be no more recovery and thus, $R_t = 0$. When R_t, = 0, $X_t = X_{t-1}$. Figures 4.2a and 4.2b plot the difference equations concerning the biosphere and the corresponding steady-states.

[38] For inhomogeneous difference equations with the form $y_t = ay_{t-1} + b$, for t = 0, 1…, where a and b are constants, the stationary state is $y^{ss} = b/(1-a)$ provided that $a \neq 1$. If $|a| < 1$, then the solution to $y_t = ay_{t-1} + b$ converges to the equilibrium state as t approaches infinity and thus, y_t is globally asymptotically stable. If $|a| > 1$, then the solution to $y_t = ay_{t-1} + b$ does not converges to the equilibrium state as t approaches infinity. The absolute value of a^t tends to infinity as t approaches infinity. In our model, the level of the biosphere does not tend to converge to infinity; rather it converges to X_0 because we have defined upper and lower bounds for the biosphere. While in many economic applications and modeling it is desirable and even necessary to have stable steady-states in order to avoid non-convergence or explosive oscillations around an equilibrium state, the existence of an unstable steady-state reflects the natural state of complex dissipative structures. We do, however, avoid non-convergence or explosive oscillations in our model by having upper and lower bounds for X_t.

Figure 4.2a: Plot of Difference Equations and Biosphere

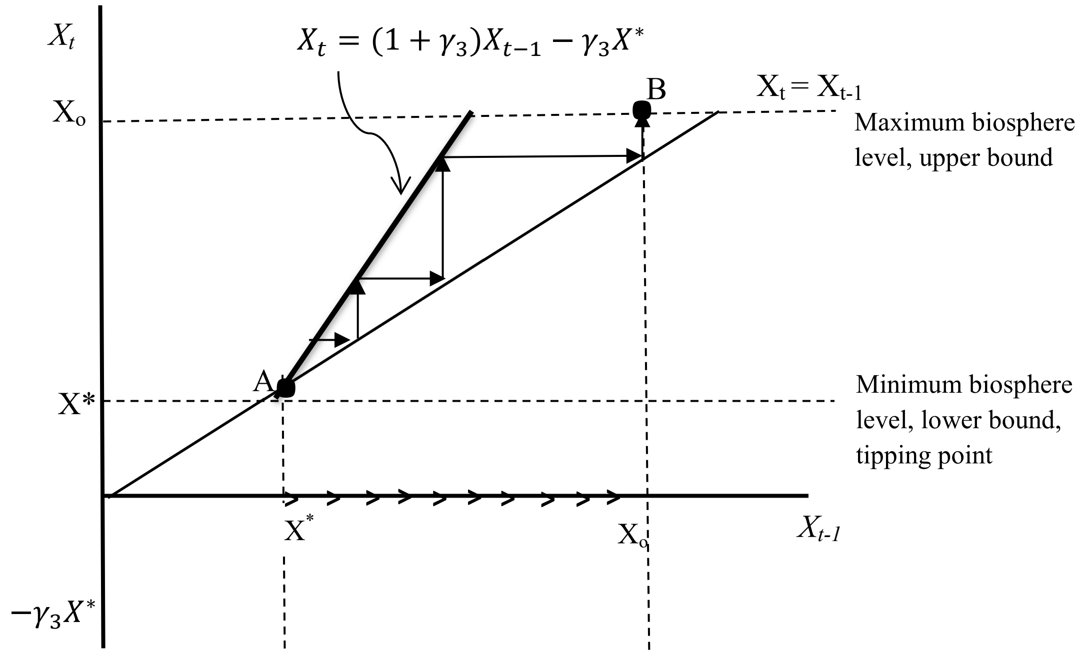
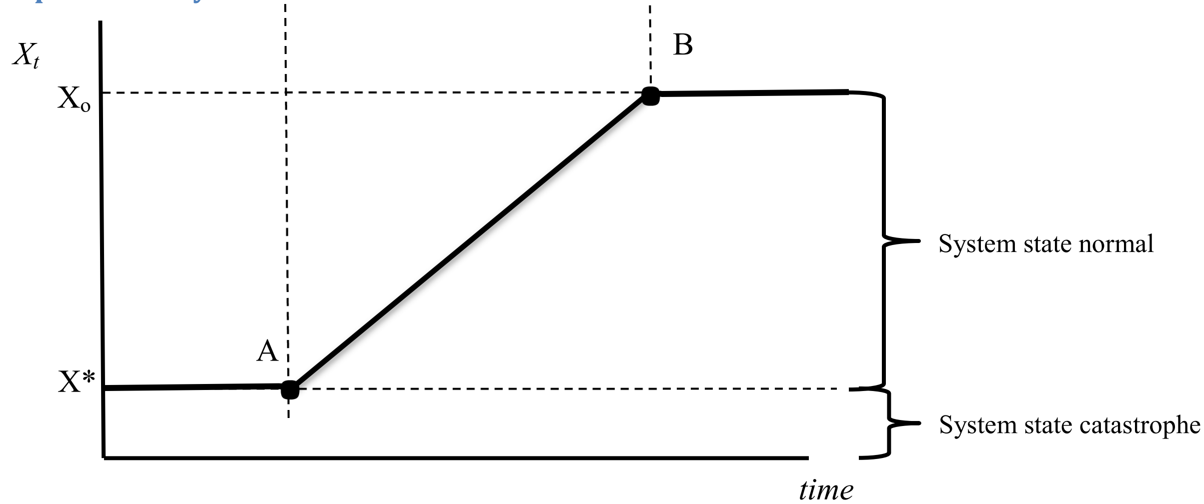


Figure 4.2b: Biosphere and System State



In Figure 4.2a, the economy starts at Point A, which is close to, but above the biosphere's tipping point, X^*. The equilibrium state, X^*, is unstable because X tends to move away from X* (since $\left|\frac{dX_t}{dX_{t-1}}\right| > 1$; see also footnote 28). The biosphere sequence or growth converges to X_o, or Point B, its upper bound. Once X_0 has been reached, there will be no more recovery and thus no more biosphere growth (Figure 4.2b). If the biosphere was not bounded from above (Point B), it would tend to grow to infinity as t approaches infinity, which is an unrealistic characteristic. As long as the biosphere does not fall below X*, it avoids a system state catastrophe.

4.1.11 Steady States when Entropy Production Exceeds Biosphere's Assimilation Capacity

The following is a situation where the level of biosphere is above the minimum level necessary for anthropogenic activity, but below that of maximum capacity. That is, $X_0 > X_t \geq X^*$ such that $R_t = (X_{t-1} - X^*)\gamma_3$. If the level of entropy production at time t-1 exceeds the biosphere's ability to accommodate the generated entropy, then $S_{max} < S_{t-1}$ and $max\{0, S_{t-1} - S_{max}\}$ is positive. If $R_t = (X_{t-1} - X^*)\gamma_3$ is substituted into equation 4.10, then $X_t = X_{t-1} - max\{0, S_{t-1} - S_{max}\} + (X_{t-1} - X^*)\gamma_3$, which can be rearranged to

$$X_t = (1 + \gamma_3)X_{t-1} - S_{t-1} + (S_{max} - \gamma_3 X^*) \text{ , where } (S_{max} - \gamma_3 X^*) > 0. \quad (4.10c)$$

$-S_{t-1} + (S_{max} - \gamma_3 X^*)$ is negative because $S_{t-1} > S_{max}$. As before, one has X_0 as a steady-state. The other steady-state can be found by letting $X_t = X_{t-1}$ in equation 4.10c. Thus,

$$0 = \gamma_3 X_{t-1} - S_{t-1} + (S_{max} - \gamma_3 X^*)$$

$$\gamma_3 X_{t-1} = S_{t-1} - S_{max} + \gamma_3 X^*$$

Since $S_{t-1} - S_{max} > 0$, the right hand side of the above equation is positive. Therefore the steady-state is found at: $\frac{S - S_{max}}{\gamma_3} + X^*$. Note that the biosphere is in a system state normal as long as $X^* < X \leq X_0$. When $X < X^*$, the biosphere is in a system state catastrophe: Figure 4.3

Figure 4.3: Tipping Point Illustration when X<X*

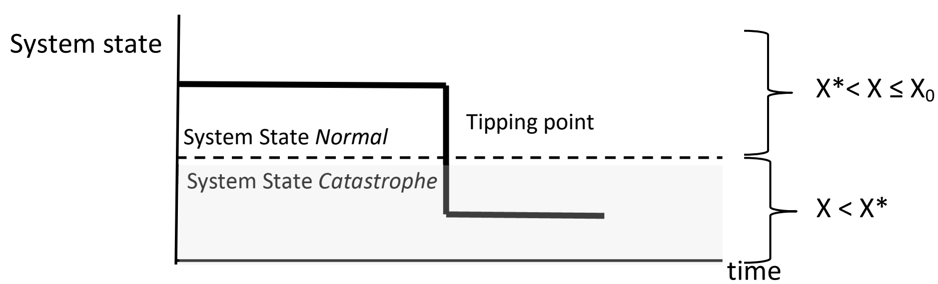


Figure 4.4a plots $X_t vs X_{t-1}$. The existence of an unstable steady-state reflects the natural state of complex dissipative structures that was introduced and described in Chapter 3.

Figure 4.4a: Unstable Steady State Plot

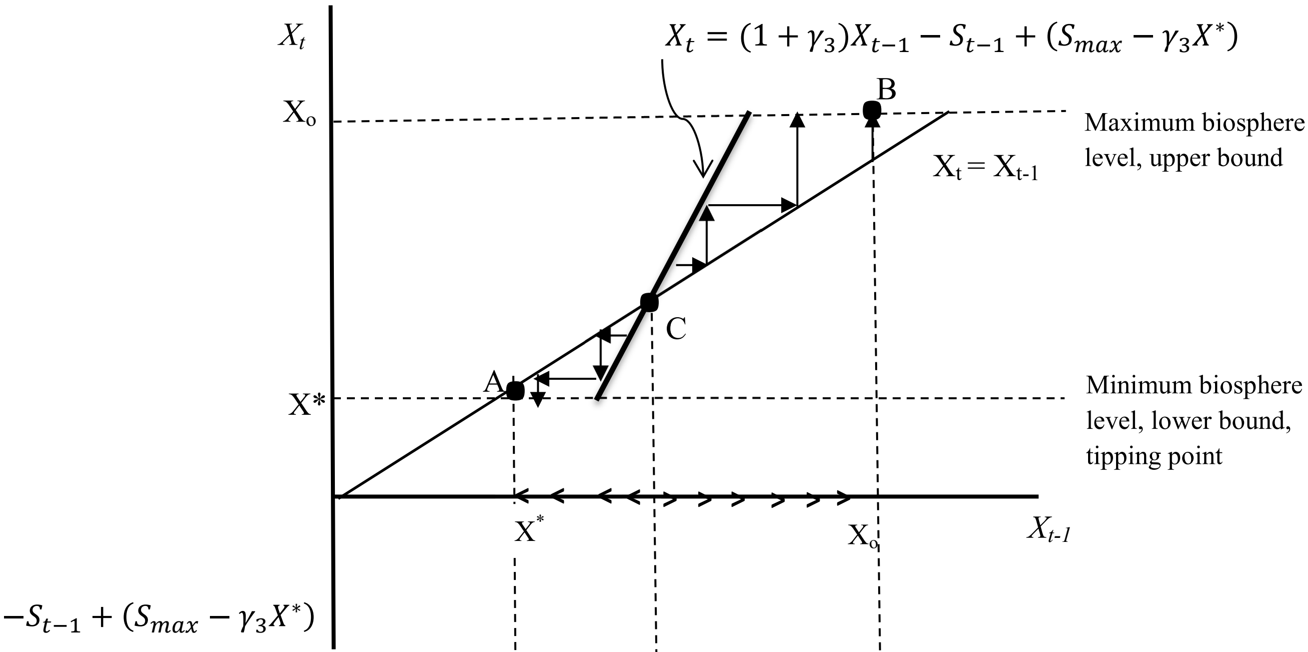
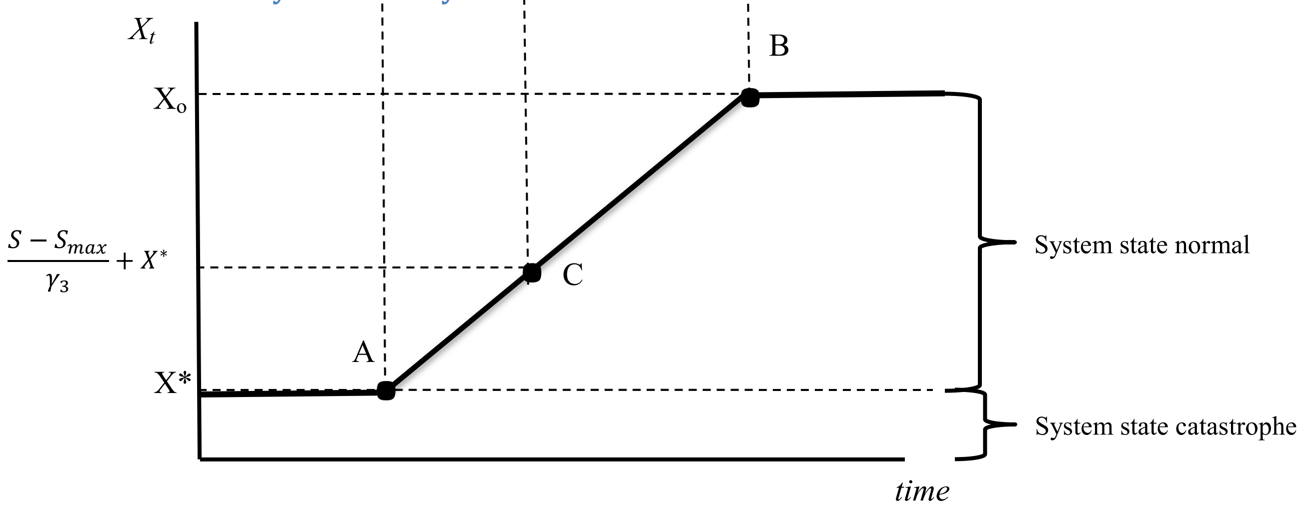


Figure 4.4b: Unstable Steady State and System State



In Figure 4.4a, the economy starts at Point C, which is a steady state. The steady-state is unstable. If the level of entropy production in the next time period exceeds the biosphere's ability to accommodate the generated entropy, then the biosphere will degrade and move towards point A. Any further stress will move the biosphere into a system state catastrophe (Figure 4.4b). If entropy production in the next time period is below the biosphere's carry capacity, the biosphere will regenerate moving it from Point C to Point B. As before, the biosphere sequence or growth converges to X_o, or Point B, its upper bound. Once X_0 has been reached, there will be no more recovery and thus no more biosphere growth (Figure 4.4b).

4.1.12 Utility

Utility is affected by changes in consumption or in biosphere size. The utility function exhibits decreasing marginal utilities with respect to each good – consumption goods and the biosphere. The marginal measure of social preferences over the biosphere versus consumption is γ. It takes on positive values between zero and one. One can further restrict, without loss of qualitative results, our utility function to be homogenous of degree one and thus represent homothetic preferences. With a homothetic utility function, it is assumed that economic agents in our model consume consumption goods and the (services of) the biosphere at a constant ratio with changing income levels; and, they prefer more of both as income grows[39].

When economic agents maximize their utility, they will do so under two different assumptions. The first set of numerical simulations when the biosphere, X, is included will operate under the assumption of perfectly myopic agents who care about current consumption and biosphere only. The second set of numerical simulations will operate under the assumption of partially myopic agents who care about current consumption, and future biosphere levels. Thus, they are maximizing the following homothetic utility function:

$$U(c_t, X_{t+1}) = {c_t}^{\gamma} X_{t+1}^{1-\gamma}. \quad (4.12)$$ [40]

[39] Provided that the marginal utility is greater than zero.

[40] One can also state the social preference parameters as follows: $\gamma = \gamma_1$ and $1 - \gamma = \gamma_2$.

4.1.13 Total System Maximization

As with Carlaw and Lipsey (2006), the maximization problem is simplified by allowing the stocks of produced knowledge to have immediate impact in the production of the aggregate consumption good. Therefore, the period-by-period optimization problem is:

$$\max_{d_t^E, d_t^G, n_t,} U(c_t, X_{t+1}) = {c_t}^{\gamma} X_{t+1}^{1-\gamma} \text{ subject to}$$

$$a_t = \upsilon G_t (d_t^G)^{\alpha_2} \qquad (4.2)$$

$$N_t = n_t + d_t^G + d_t^E \qquad (4.3)$$

$$a_t^E = Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}, \text{ where } Z = \upsilon G_t G_t^E \qquad (4.4b)$$

$$A_t^E = [\varepsilon_2 (a_t^E)^{\omega} + (1-\varepsilon_2)(A_{t-1})^{\omega}]^{\frac{1}{\omega}} \qquad (4.5b)$$

$$c_t = A_t^E (n_t)^{\alpha_3} \qquad (4.6)$$

$$B_t = b_t + (1-\varepsilon_3) B_{t-1} \qquad (4.7)$$

$$b_t = \theta G_t^E (d_t^E)^{\alpha_5} \qquad (4.8)$$

$$S_t = \mu c_t {B_t}^{-\alpha_4} \qquad (4.9)$$

$$X_t = X_{t-1} - max\{0, S_{t-1} - S_{max}\} + R_t \qquad (4.10)$$

If $X_0 > X_t \geq X^*$, then $R_t = (X_{t-1} - X^*)\gamma_3$; otherwise $R_t = 0$ (4.11)

4.1.14 Summary of Economic Trade-Offs

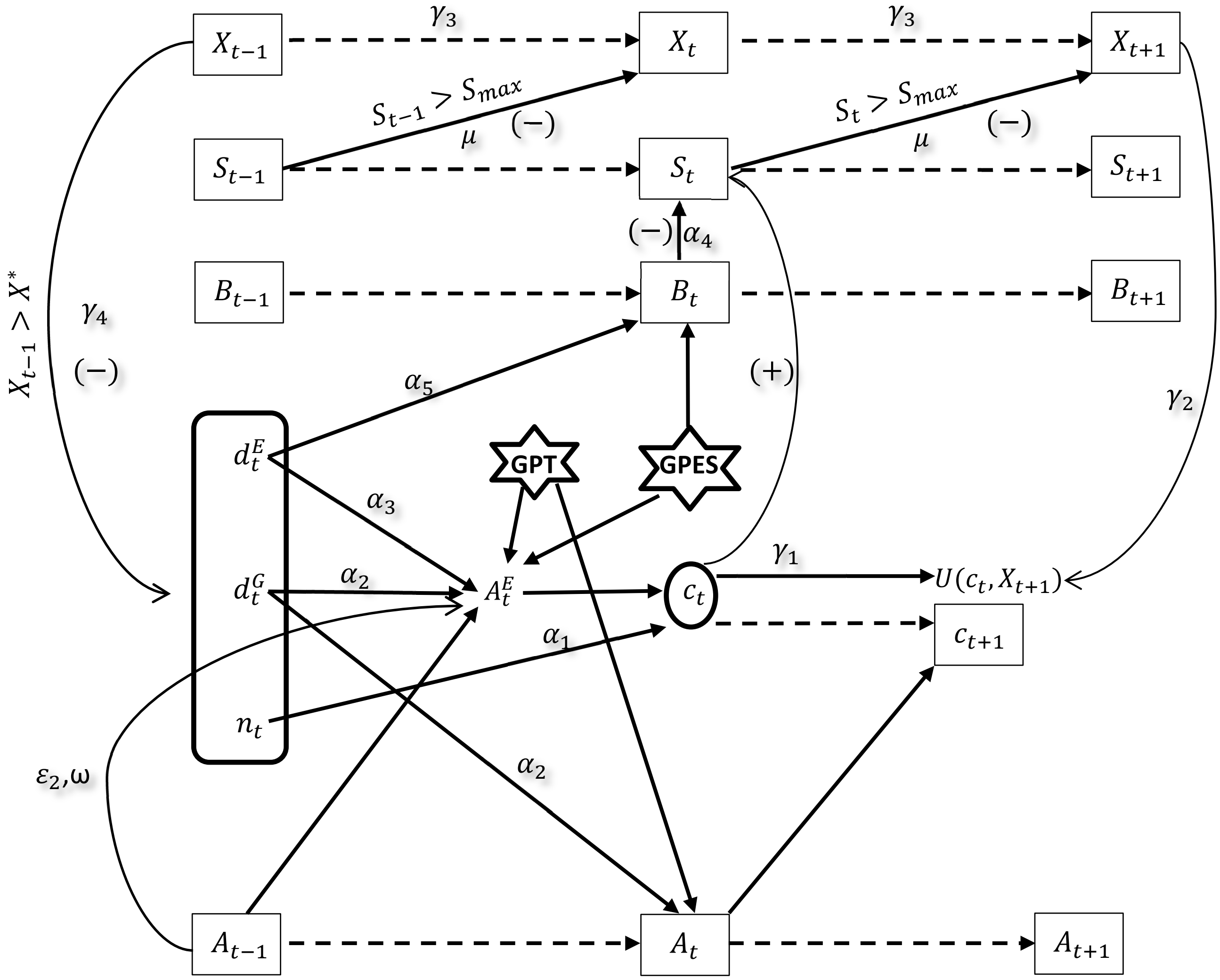
The economic trade-offs that occur in the maximization above can be summarized and represented diagrammatically. Chapter 3 discussed the incorporation of entropy, albeit qualitatively, in an economic growth model that employs GPTs and GPESs. Figure 3.3 illustrated the energy-technology model graphically. Returning to that illustration, it is revised in Figure 4.5 below, to include the defined variables and associated parameters.

In Figure 4.5, labour resources, d_t^G and d_t^E, enter the production functions for energy knowledge, non-energy knowledge and GPES pervasiveness, while only labour resources, n_t, enter the consumption function directly. The key trade-off is between the output of resources devoted to consumption production and output of the resources that go into the non-energy technology sector and energy sector to improve the productivity of the resources that remain in the consumption sector via A_t^E. Productivity increases in the consumption sector can occur with increases in any of the three types of labour resources, with larger marginal changes occurring through increases in the stock of composite energy knowledge. A marginal reallocation of labour resources from the consumption sector to the non-energy and energy sectors directly reduces the production of consumption goods, but indirectly raises the productivity of those labour resources remaining in the consumption sectors by augmenting the output of energy and non-energy knowledge.

In the absence of exogenous changes that affect the productivity of the energy and non-energy sectors, the system asymptotically approaches a steady-state. When a shock occurs via the arrival of a new GPT or new GPES, there is an increase in the productivity of resources allocated to the production of knowledge. As illustrated in Figure 4.5 the arrival of a new GPT increases the productivity of resources allocated to the production of energy knowledge and non-energy knowledge. Thus, productivity grows in the consumption sector and labour resources shift back to the consumption sector. The arrival of a new GPES initially only increases the productivity of resources allocated to the production of energy knowledge. Consequently, productivity grows in the consumption sector to a relatively smaller extent and a smaller portion of labour resources shift back to the consumption sector. Since only a portion of the labour resources actually shifts back to the consumption sector under a GPES shock, this implies that there must be a permanent movement of resources to the energy sector after the arrival of a new GPES. This is an important feature of the steady-state equilibrium of the BET model. That is, the optimal allocation of labour is independent of the arrival of a new GPT (i.e. G_t), but is affected by G_t^E because it is assumed that $G_t$has a symmetric effect on all sectors, while G_t^E has an asymmetric effect.

The arrival of a new GPT indirectly increases entropy production as consumption grows (Figure 4.5). The arrival of a new GPES indirectly decreases entropy production. Thus, consumption has a direct and positive effect on entropy production, S_t, which in turn, has a direct and negative effect on the biosphere, X_t. The magnitude of effect is determined by the parameter μ. Also, large values of α_1, relative to the shares of technical and energy knowledge (α_2 and α_3), could generate too much entropy for the biosphere to accommodate without adverse effects ($S_t > S_{max}$). If the biosphere cannot accommodate increased entropy levels, then the future level of the biosphere is diminished. Given that agents care about current consumption and future biosphere levels, there exists a trade-off between current production and future levels of biosphere. Agents that care about future biosphere levels and current consumption level will equate their marginal utilities such that the ratio of $\gamma_1$to γ_2 equals that of current consumption, c_t, to future biosphere levels, X_{t+1}. If consumption (and thus entropy) is not reduced to levels that are environmentally sustainable by, for example, failing to adopt new GPESs that have a direct and negative effect on entropy (via B_t), then biosphere levels risk falling below some life-sustaining threshold, X*. If the biosphere, a complex dissipative structure, falls below X*, labour resource levels also begin declining exponentially at a rate determined by γ_4. Hence, we have a competitive equilibrium when (1) agents maximize their utility at the optimal allocation of labour resources n_t, d_t^G and d_t^E and (2) entropy production from consumption output equals the biosphere assimilation capacity (so that $X_t = X_{t+1}$). From Figure 4.5, the parameters α_1, α_2, α_3, α_4, α_5, and μ ensure that a steady-state exists.

Figure 4.5: Economic Trade-Offs in the BET Model



4.2 Numerical Simulation

In order to simulate the model, parameter values must be specified. Different parameterizations were tested to check the sensitivities of the model and to assess the robustness of the qualitative results to see whether our basic assumptions about GPTs, GPESs and entropy are satisfied. The following four simulations use the same initial conditions, whose parameters values (see Annex 3) where chosen so that

(1) growth in the consumption sector converges to zero without any exogenous shocks (i.e. converges to a steady-state),

(2) the consumption sector production function exhibits at least constant returns to scale, (i.e. $\alpha_1 + \alpha_2 + \alpha_3 \geq 1$) as described in Section 4.1.3,

(3) the composite knowledge production function exhibits decreasing returns to scale by limiting the sum of $\alpha_1$and $\alpha_2$to less than one, which ensure that (a) exogenous shocks do not cause unrealistic jumps in consumption that lead automatically to biosphere collapse and (b) the model shows decreasing effectiveness of new energy researchers,

(4) $\alpha_3$values do not approach unity, which would lead to unrealistic early collapse of the biosphere, and

(5) all sectors and resources eventually reach a steady-state level and remain there, including utility, in the absence of shocks.

We run the simulations for 500 periods, which allows time for the economy to reach new steady-states after the arrival of GPT and/or GPES shocks. A complete description of parameter value effects and the combination thereof is provided in Section 4.2.3.

4.2.1 Simulation 1A: The Effect of Shocks on the Steady-State under Perfectly Myopic Conditions

In this simulation, the arrival of a new GPT occurs after growth in consumption is in steady-state. Independently, the arrival of new GPES is examined and its effects are compared to and contrasted with the arrival of a new GPT. Both of these exogenous shocks affect the steady-state. The arrival of a new GPT increases the productivity parameter, G_t, of the production function for pure and applied knowledge in the technology sector. The introduction of a new GPES is accomplished by increasing the productivity parameter, G_t^E, of the production function for pure and applied knowledge in the joint technology-energy sector. For the moment, the effect of entropy on the biosphere has been shut down.

The arrival of a GPT increases the productivity of resources allocated to the production of knowledge. Consumption subsequently increases until it reaches a new steady-state. This results in a diversion of resources away from the consumption sector into the technology and joint technology-energy knowledge sectors. As productivity grows in the consumption sector, the resources shift away from the knowledge sectors back to the consumption sector (Figure 4.6a).

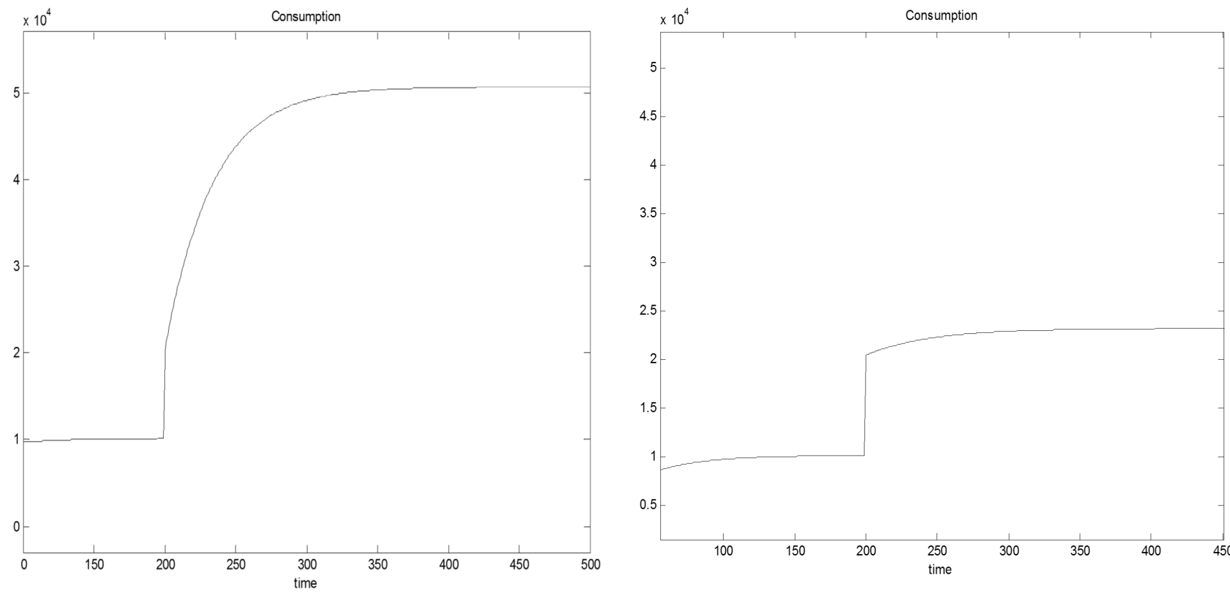
As with the introduction of a GPT, the arrival of a new GPES increases the productivity of resources allocated to the production of knowledge and thus, a diversion of resources away from the consumption sector occurs. However, unlike the introduction of a GPT, there is a permanent movement of resources out of the consumption goods sector to the technology and energy sectors, which maintains lower changes in entropy than would otherwise occur (Figure 4.6b). The permanent movement of labour resources out of the consumption sector will always occur with the adoption of the GPES. Productivity still grows in the consumption sector and some of the resources shift away from the pure and applied knowledge sectors back to the consumption sector, but the introduction of a GPES now makes the resources in the knowledge sectors more productive relative to the consumption sector such that it is advantageous to forgo current consumption to generate increases in future consumption.

The arrival of a GPT increases the change in entropy production as consumption grows (Figure 4.6c). This results in a decrease in the entropy production ratio of the biosphere to civilization.

The arrival of GPES also causes a small increase in entropy production in the short term due to increases in productivity of the knowledge sectors, which cause a level jump in consumption. However, because the arrival of a GPES also increases the adoption level of more thermo-efficient energy, over time, the change in entropy production decreases even as consumption continues to increase. The change in entropy production settles at a higher production level than before any exogenous shocks occurred, but at a lower level than would otherwise be the case after the arrival of a new GPES. That is, entropy's increase after the arrival of a GPT is tempered by the subsequent arrival of a new GPES. This is an important point to stress, which carries policy implications. While technology increases consumption and entropy production, new GPESs can reduce the undesirable effects of technology on the biosphere while itself increasing consumption.

Figure 4.6a: Consumption in the BET Model with Independent GPT and GPES Shocks

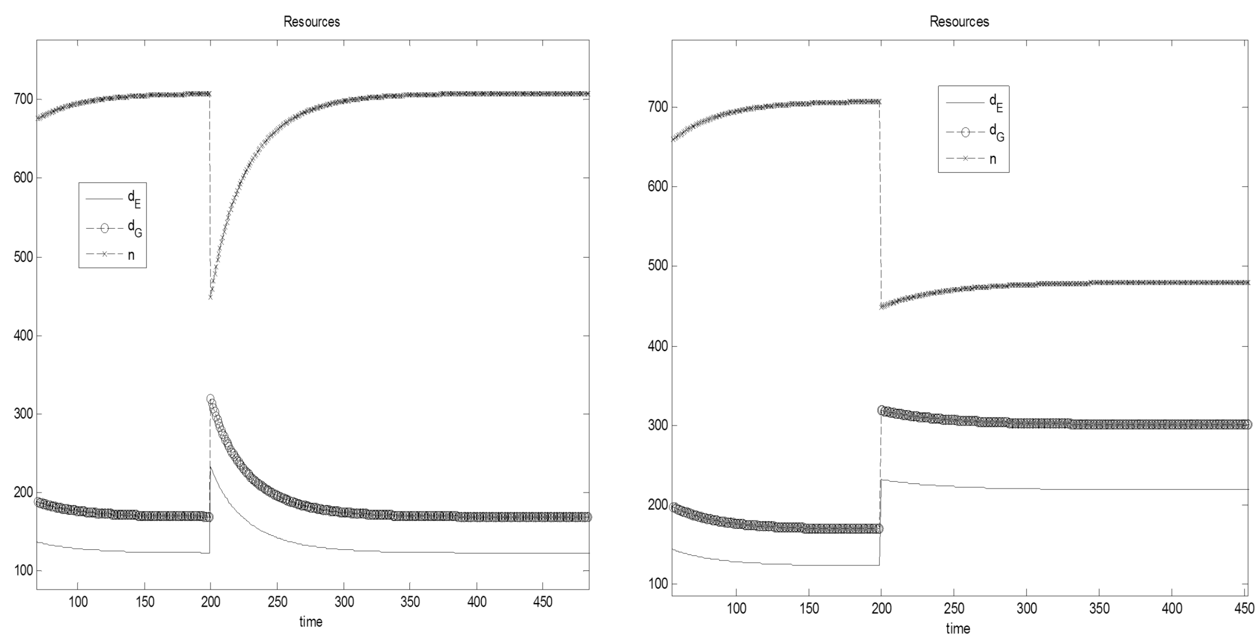
GPT Arrival GPES Arrival



Exogenous arrivals of a GPT and GPES's, respectively, result in increases in the productivity of resources allocated to the production of knowledge. Growth in consumption is rejuvenated.

Figure 4.6b: Resource Allocation in the BET Model with Independent GPT and GPES Shocks

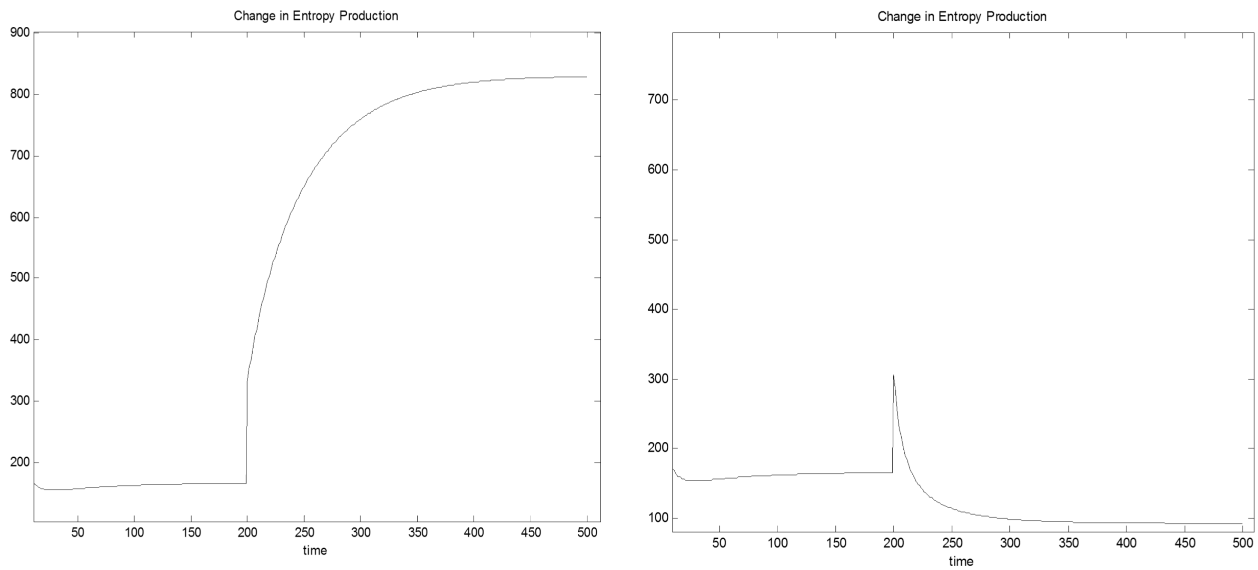
GPT Arrival GPES Arrival



The introduction of a GPT, in the first panel, causes a temporary diversion of resources away from the consumption sector occurs. The introduction of a GPES, in the second panel, causes a permanent movement of resources out of the consumption goods sector.

Figure 4.6c: Change in Entropy Production in the BET Model with Independent GPT and GPES Shocks

GPT Arrival GPES Arrival



The arrival of a GPT increases the change in entropy production as consumption grows (left panel). The arrival of GPES causes a small increase in entropy production in the short term, but the concomitant increase in the adoption level of more thermo-efficient energy, over time, decreases the change in entropy production in the long-run (right panel).

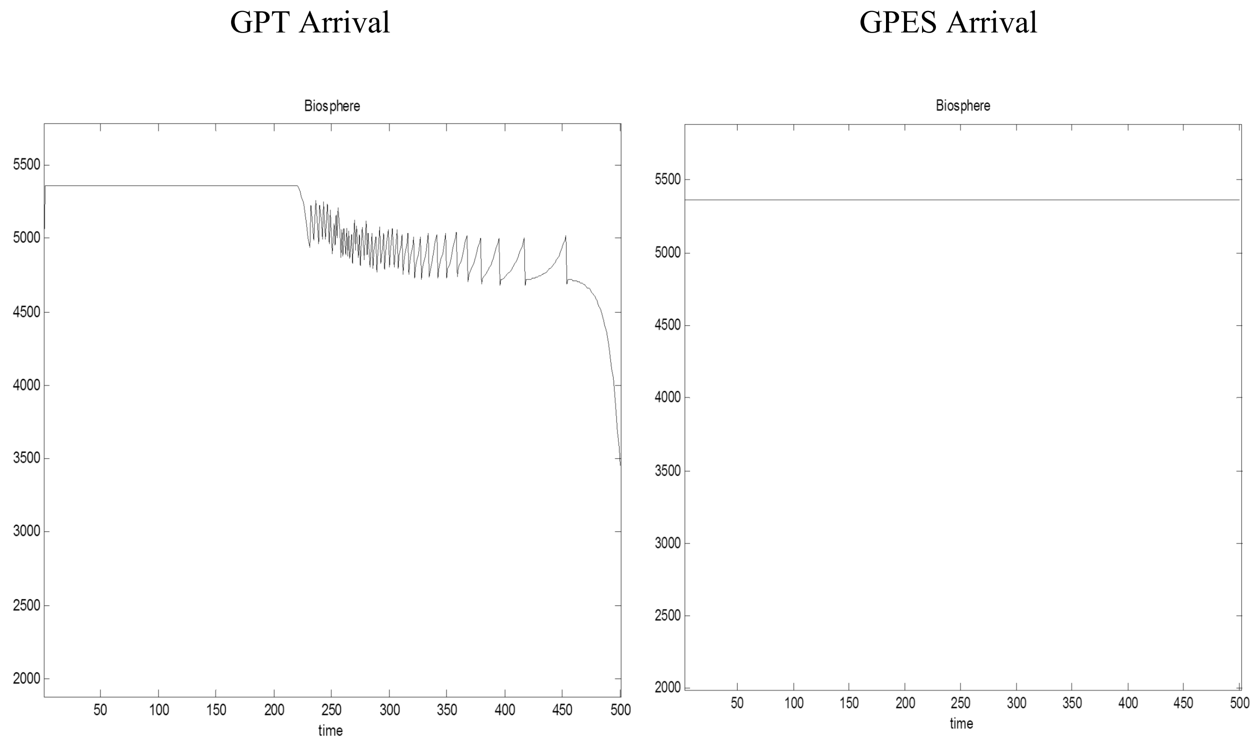
The parameter values for size of the GPT and GPES shocks are equal in the simulations. However, the effects of the two shocks are not necessarily the same. Given identical initial parameters, growth in consumption in our model declines until a steady-state is reached at about 10,000 units. If the economy experiences only an exogenous GPT shock by changing the G_t parameter value from 1 to 5 at any time period (with no GPES shock), then growth in consumption is rejuvenated and increases until a new level is reached at approximately 50,000 units. Similarly, if the economy, with the same initial parameter values, experiences only an exogenous GPES shock by changing the G_t^E parameter value from 1 to 5 (with no GPT shock), then growth in consumption is also rejuvenated and increase until a new level is reached at approximately 23,500 units. In isolation, a technology shock has a bigger effect on the level of consumption than an energy shock because a technology shock increases the productivity parameters for both composite (energy) knowledge and non-energy knowledge. A GPES shock only increases the productivity of composite knowledge. However, an economy that experiences a GPT shock followed some time later by a GPES shock, of the same magnitude, experiences a final growth level that exceeds the sum of the individually isolated GPT and GPES exogenous shocks. Thus, an energy shock amplifies the effects of a technology shock[41]. This is because each successive shock increases an already larger productivity coefficient of the production function of composite knowledge.

It is noted that if one were to allow ε_2 to also approach unity, then, in the absence of exogenous GPT or GPES shocks, consumption would settle at a much lower level than otherwise would be the case. In addition, labour resources would necessarily shift permanently from the non-technical consumption sector to the GPT and GPES sector to maximize consumption output. With the arrival of exogenous GPT and/or GPES shocks, allowing ε_2 to also approach unity causes stepwise level changes in consumption output rather than a gradual increase to a new, higher steady-state. Since both of these outcomes would be unrealistic, we avoid setting ε_1 close to one in our numerical simulations.

If one were to allow the independent shocks to affect the biosphere, one sees an asymmetric effect (Figure 4.6d). Depending on their size, GPT arrivals shocks have the potential to destabilize the biosphere through their positive effect on entropy (via increased consumption). GPES arrivals, however, temper entropy effects on the biosphere and affect consumption indirectly. In isolation, a GPES shock has no effect on a biosphere at steady-state.

[41] The reverse is also true.

Figure 4.6d: Biosphere Level Effects with Independent GPT and GPES Shocks



GPT shocks have the potential to destabilize the biosphere through their positive effect on entropy (left panel). In isolation, a GPES shock has no effect on a biosphere at steady-state (right panel).

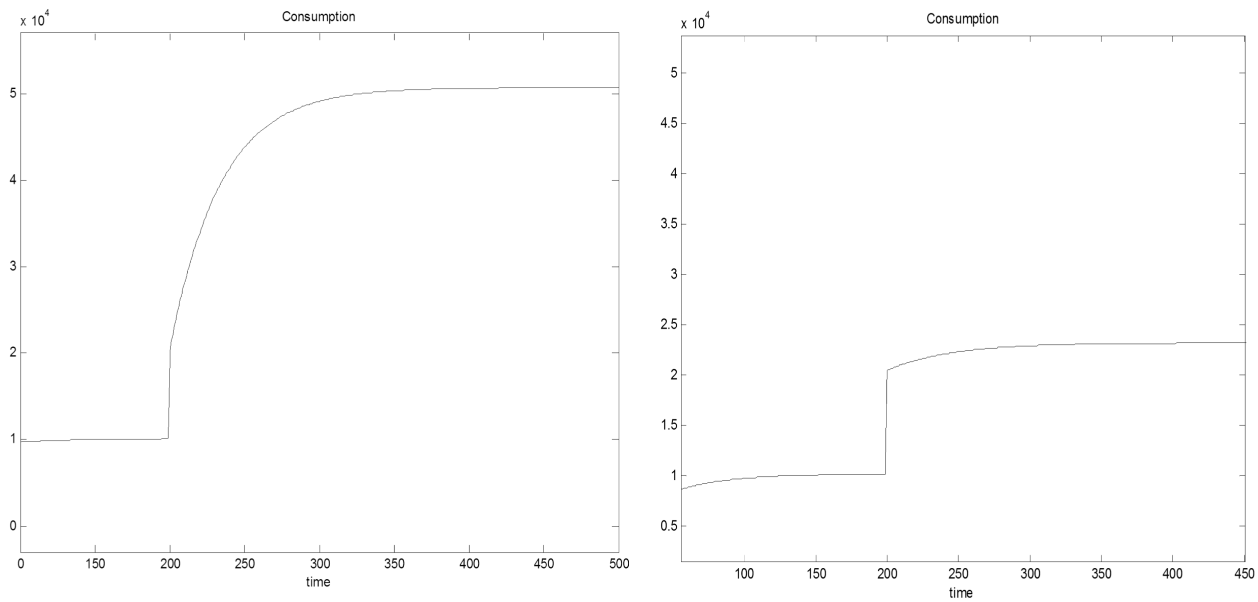
4.2.2 Simulation 1B: The Effect of Isolated GPT and GPES shocks under Partially Myopic Conditions

One can extend Simulation 1A to examine the effect of independent GPT and GPES shock effects on consumption, the biosphere, resource allocation and GPES pervasiveness under partially myopic conditions. In order to compare the effects under partially myopic conditions with those of perfectly myopic conditions, Simulation B uses the same parameters as those in simulation 1A.

Figures 4.6e and 4.6f illustrate the arrival of shocks on consumption and entropy production, respectively, under partially myopic conditions. The effect is analogous to that in Simulation A. In essence, the effect and magnitude of GPT and GPES shocks on consumption and entropy production do not differ under partially myopic conditions for a given range of parameter values.

Figure 4.6e: Consumption in the BET Model with Independent GPT and GPES Shocks under Partially Myopic Conditions

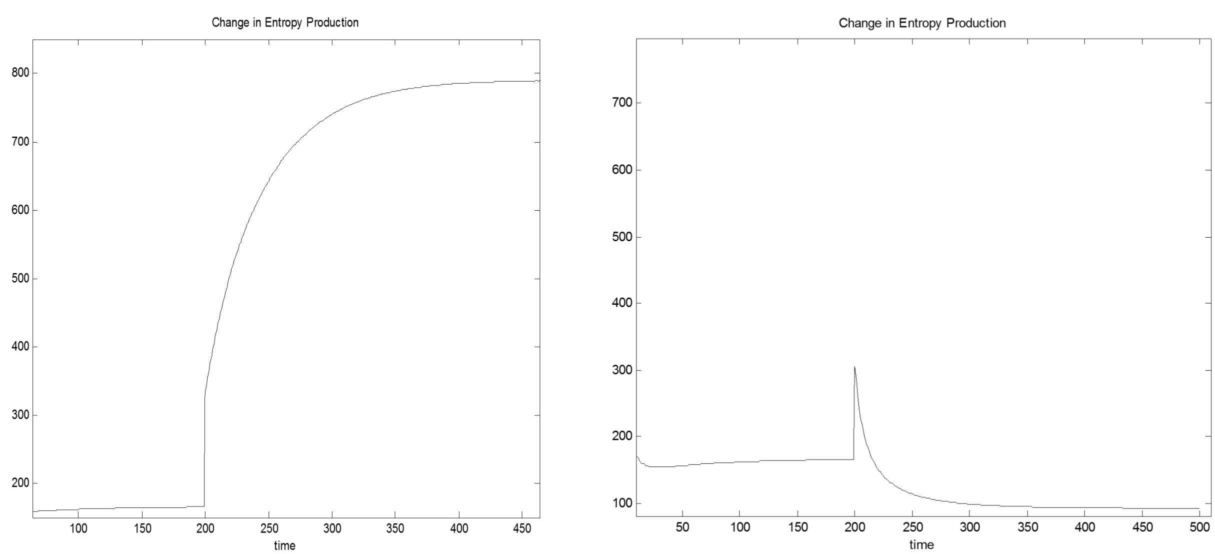
GPT Arrival　　　　GPES Arrival



GPT and GPES shocks on consumption under partially myopic conditions have analogous effects to those under perfectly myopic conditions.

Figure 4.6f: Change in Entropy Production in the BET with Independent GPT and GPES Shocks under Partially Myopic Conditions

GPT Arrival　　　　GPES Arrival



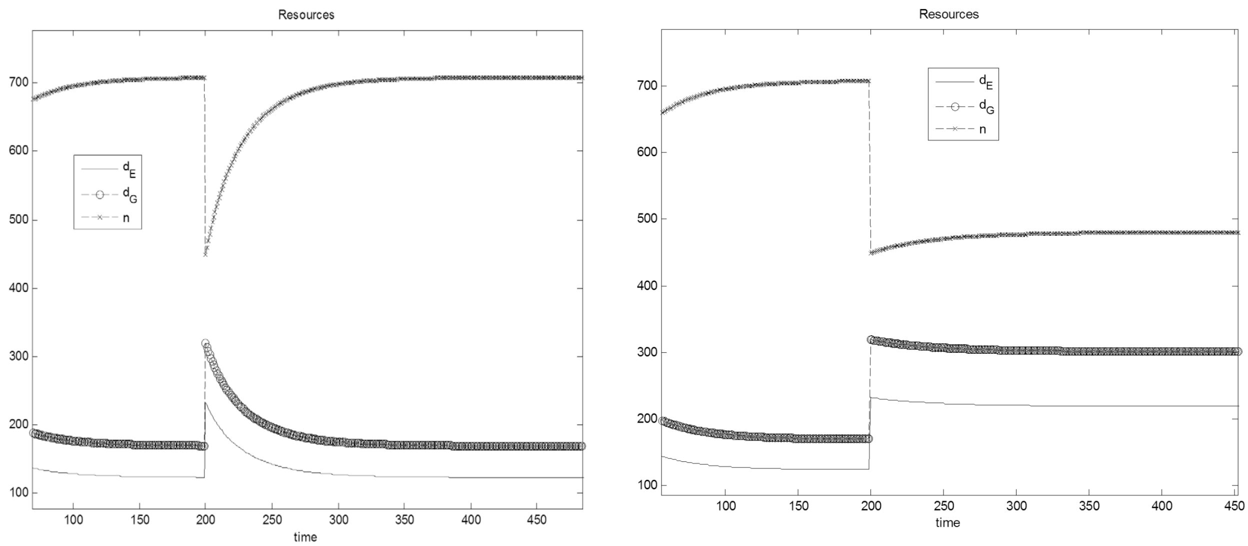
GPT and GPES shocks on the level of entropy production have analogous effects to those under perfectly myopic conditions.

Figure 4.6g illustrates resources allocations in a partially myopic setting after shocks occur. It seems from Figure 4.6g that resource movements under partially myopic conditions mirror those under perfectly myopic conditions. That is, with the introduction of a GPT, there is an increase in the productivity of resources allocated to the production of knowledge and thus, a diversion of resources away from the consumption sector. With the introduction of a GPES, there is a permanent movement of resources out of the consumption goods sector to the technology and energy sectors. However, a comparison of the effect of GPT shocks under partially myopic conditions with that under perfectly myopic conditions (Figure 4.6h), shows a small, but permanent loss of resources from the consumption sector to the knowledge sectors. The resources that return fully to the consumption sector after a GPT shock under perfectly myopic conditions settle at a lower steady-state under partially myopic conditions.

Under perfectly myopic conditions, labour resources in the consumption sector move back to their original steady-state level, at above 700 units. Under partially myopic conditions, labour resources in the consumption sector move back to their original steady-state level, but below the 700-unit level. Thus, we have a trade-off under partially myopic conditions: with less resources devoted to consumption production, one would expect lower entropy levels. Lower entropy levels would, in turn, result in less stress on the biosphere.

Figure 4.6g: Resource Allocation in the BET Model with Independent GPT and GPES Shocks under Partially Myopic Conditions

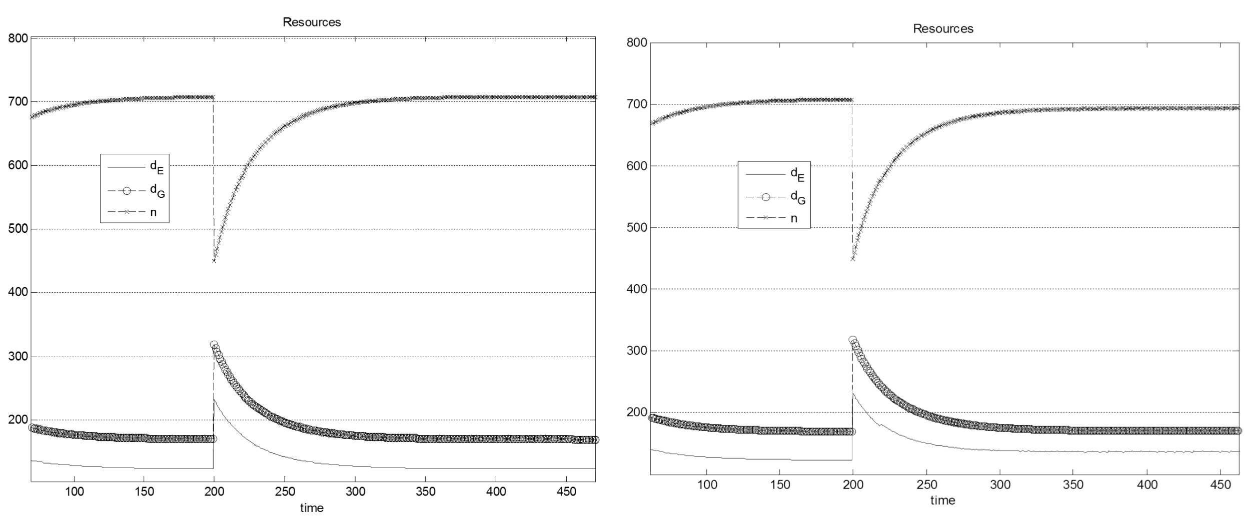
GPT Arrival | GPES Arrival



As with the case of perfectly myopic conditions, the introduction of a GPT, in the first panel, causes a temporary diversion of resources away from the consumption sector occurs. The introduction of a GPES, in the second panel, causes a permanent movement of resources out of the consumption goods sector.

Figure 4.6h: Comparing Steady-States for Resource Allocation following a GPT Shock under Perfectly and Partially Myopic Conditions

GPT Arrival (Perfectly Myopic) | GPT Arrival (Partially Myopic)



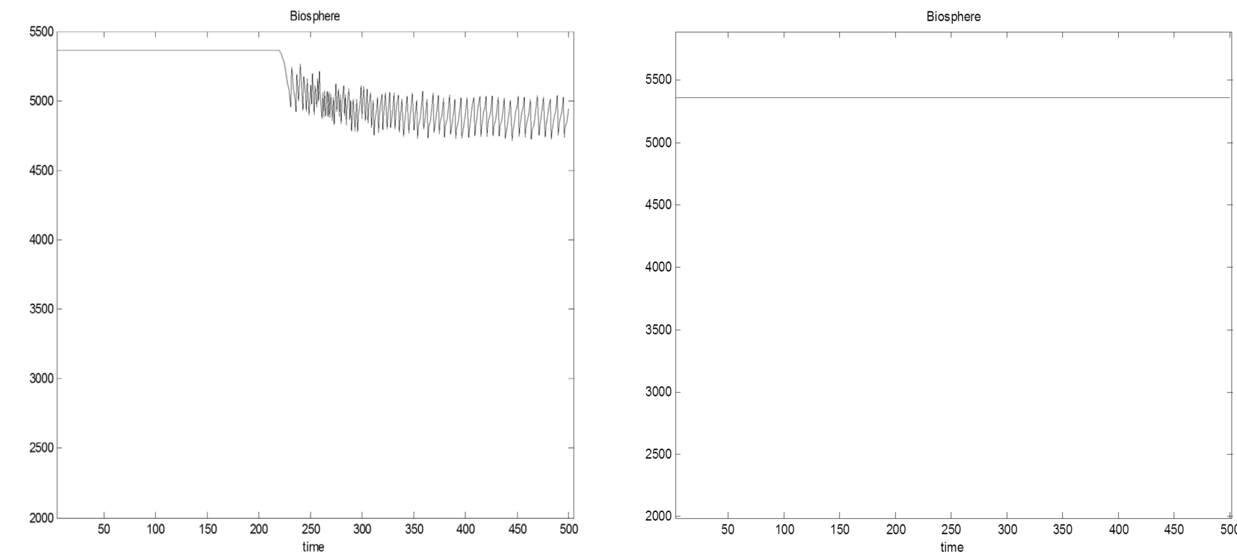
Under partially myopic conditions there is small, but permanent loss of resources from the consumption sector to the knowledge sectors. The resources that return fully to the consumption sector after a GPT shock under perfectly myopic conditions settle at a lower steady-state under partially myopic conditions.

Figure 4.6i shows that the effects of GPT and GPES shocks on the biosphere under partially myopic conditions are asymmetrical. In isolation, a GPES shock has no effect on a biosphere at steady-state. GPT shocks stress the biosphere as a result of their positive effect on entropy. GPT shocks under partially myopic conditions are tempered and do not cause biosphere collapses unless the shocks are very large. The biosphere shows no signs of large losses or collapse in Figure 4.6j, which contrasts with the declining biosphere levels in Figure 4d (which shows the effect of a GPT under perfectly myopic conditions). A comparison of entropy changes for perfectly myopic and partially myopic conditions illustrates that the stable biosphere levels in Figure 4.6i are due to increased GPES pervasiveness under partially myopic levels. In an economy where agents care about future biosphere levels, one will see an increase the level of GPES pervasiveness (by moving more labour resources out of the consumption sector) in order to have a smaller change in entropy production.

Under partially myopic conditions, a GPT shock causes the level of GPES pervasiveness to reaches a new steady-state at 11,000 units (Figure 4.6j). Under perfectly myopic conditions, a GPT shock causes the level of GPES pervasiveness to reaches a new steady-state at 10,000 units (Figure 4.6j).

Figure 4.6i: Biosphere Level Effects with Independent GPT and GPES Shocks under Partially Myopic Conditions

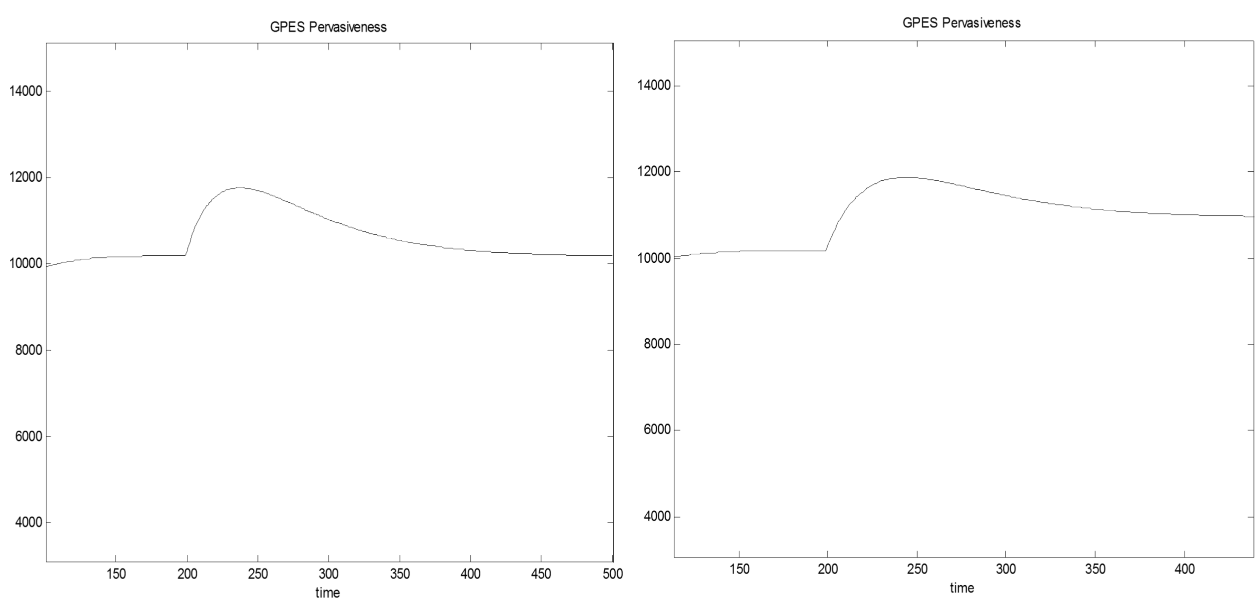
GPT Arrival GPES Arrival



The effects of GPT and GPES shocks on the biosphere under partially myopic conditions are asymmetrical. In isolation, a GPES shock has no effect on a biosphere at steady-state (right panel). GPT shocks stress the biosphere as a result of their positive effect on entropy (left panel).

Figure 4.6j: Comparing GPES Pervasiveness following a GPT Shock under Perfectly and Partially Myopic Conditions

GPT Arrival (Perfectly Myopic) GPT Arrival (Partially Myopic)



Under perfectly myopic conditions, a GPT shock causes the level of GPES pervasiveness to reaches a new steady-state at 10,000 units (left panel). Under partially myopic conditions, a GPT shock causes the level of GPES pervasiveness to reaches a new steady-state at 11,000 units (right panel).

4.2.3 Simulation 2: Effects of Sequential GPT and GPES Shocks under Perfectly and Partially Myopic Conditions

In this section, the effects of sequential GPT and GPES shocks on the biosphere, resource allocation and utility are examined under perfectly and partially myopic conditions. The same initial conditions are used under both conditions. The parameters are the same as those in Simulation 1A, and the value of the parameter μ, which is the calibration parameter that controls the size of the change in entropy production, is keep at least at 8 in order to illustrate the effect of entropy on the biosphere. The introduction of a new GPT and new GPES occurs at t=200 and t=300, respectively. Entropy is allowed to affect the biosphere. The difference between the two independent simulations is that in the second simulation, agents maximise their utility subject to the same restrictions as those that are fully myopic except that the labour resources levels that maximise utility have to be such that future biosphere levels are maximised.

Under partially myopic conditions, slightly less labour resources are devoted to the GPT sector while more labour resources are devoted to energy technologies when a GPT shock occurs at t=200 (Figure 4.7a). When the second shock occurs under partially myopic conditions, there is a greater reallocation of labour resources devoted from the consumption sector to the energy sector so as to reduce consumption-generated entropy. This results in faster GPES pervasiveness and high biosphere levels. Thus, when the biosphere is at risk of large losses or collapse in the next time period an important trade-off occurs: agents sacrifice current consumption to gain future increases in the biosphere. By allocating more resources to the GPES sector, entropy increases are limited.

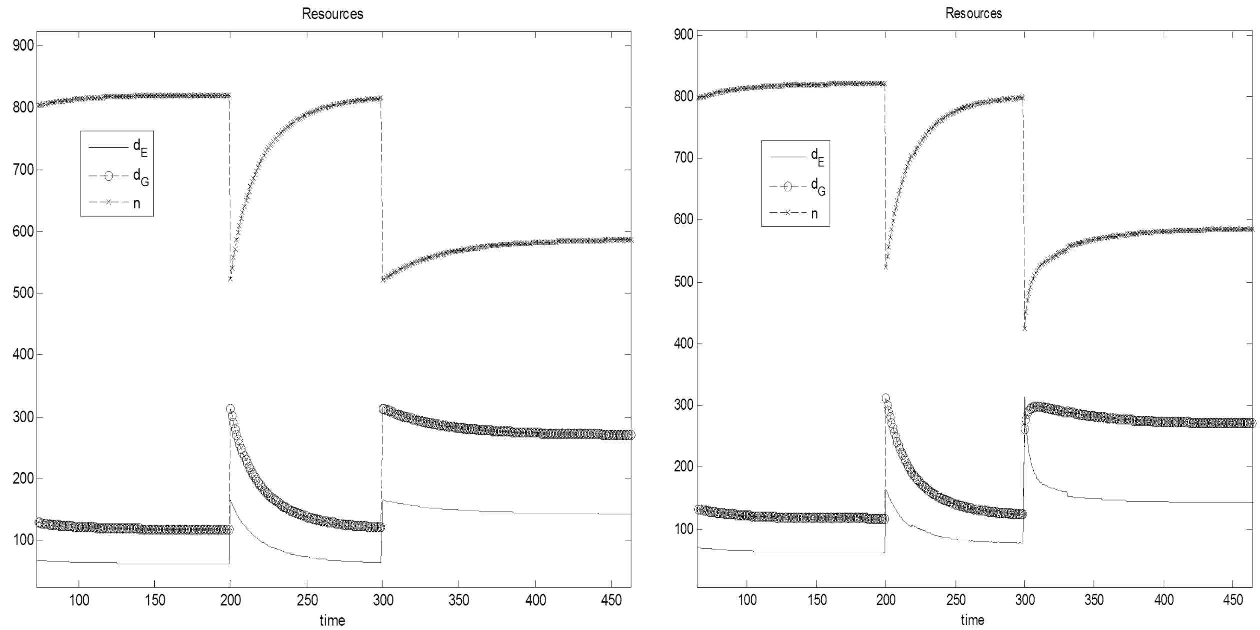
Under perfectly myopic conditions, the arrival of a GPT at t=200 shows a small, oscillating loss of biosphere, but a larger loss occurs immediately after the arrival of GPES (Figure 4.7b). This is a result of a larger sudden increase in entropy production that occurs after the adoption of the new GPES. This relatively larger spike at t=300 seems counter-intuitive; however, upon the adoption of a new GPES, marginal productivities in the knowledge sectors increase to a large extent such that consumption levels are far higher than before the adoption of the new GPES. At first, the economy-wide adoption level of the GPES does not fully compensation for the increase in entropy caused by the increase in consumption. However, over the medium-term, as more of the GPES diffuses into all sectors of the economy, entropy decreases and the biosphere follows the recovery pattern described in the steady-state discussion sections of the biosphere (Sections 4.1.10 and 4.1.11).

Under partially myopic conditions, in order to maximise utility, the future biosphere level change (i.e. decrease) cannot be as drastic as it was under perfectly myopic conditions. Consumption level jumps must be reduced. This allows for (1) small increases in entropy (and (2) sharper declines in entropy levels after the initial increase, which, in turn, result in a faster growth rate of consumption period after the second shock relative to the growth rate of consumption under fully myopic conditions.

Under partially myopic conditions, agents care about future biosphere levels instead of current levels, so their reduction in consumption, which leads to measurable differences in entropy production, results in far smaller losses in biosphere. After the two exogenous shocks, the biosphere level never falls below 4000 units (Figure 4.7b). This results in continuous increases in utility. That is, given the same conditions as the perfectly myopic case, agents operating under partially myopic conditions will never experience major declines in utility after exogenous shocks (Figure 4.7c). Utility is affected by increases in consumption, but the magnitude of the effect of the biosphere is dictated by the value of the parameter, γ. Setting γ_2 to higher values amplifies the effect of the changes in the biosphere on utility and the drop in utility after t=250 is accompanied by the drop in the biosphere level, but increases again as the biosphere recovers and consumption increases (Figure 4.7b). The range for γ_2 (or 1- γ), which allows for the best visible results of the effects of the biosphere on utility is [0.6, 0.95].

Figure 4.7a: Resource Allocation with Independent GPT and GPES Shocks

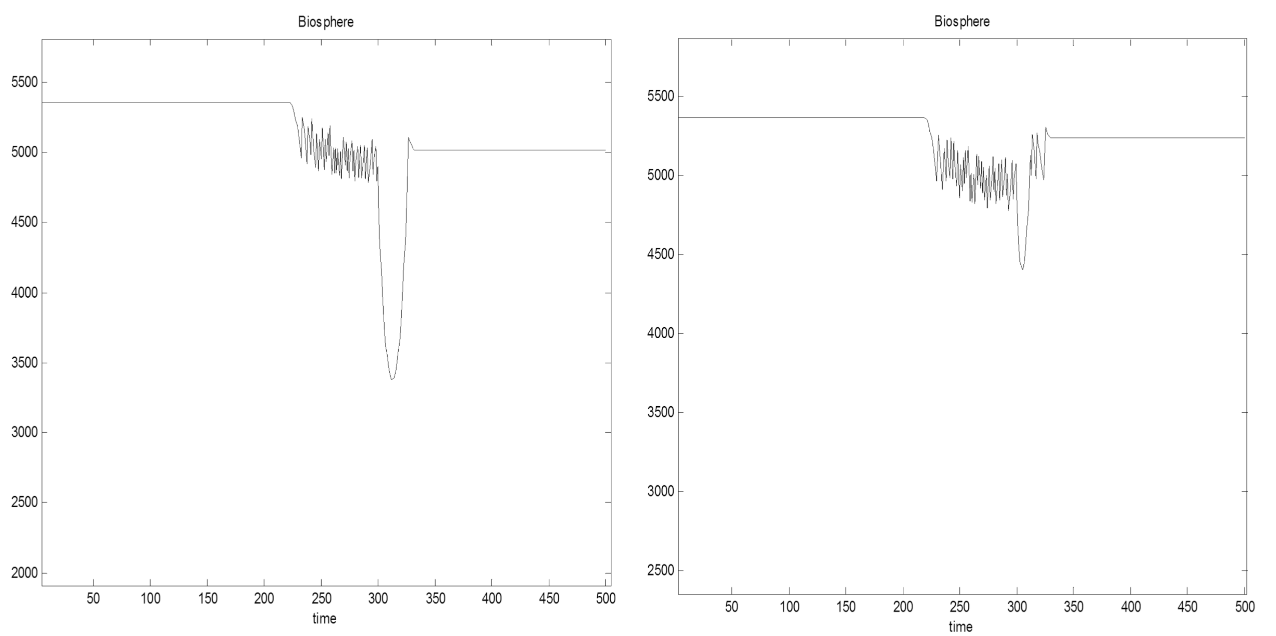
Perfectly Myopic | Partially Myopic



Under partially myopic conditions, less labour resources are devoted to the GPT sector while more labour resources are devoted to energy technologies when a GPT shock occurs at t=200.

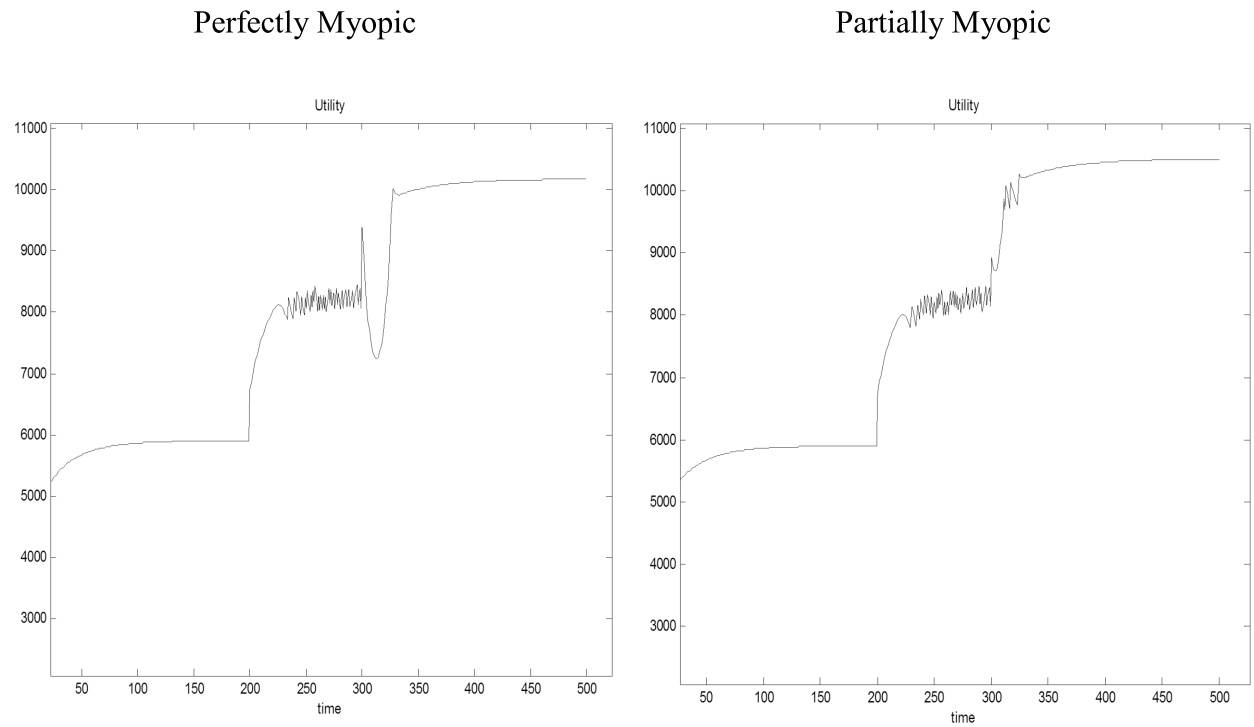
Figure 4.7b: Biosphere Levels with Independent GPT and GPES Shocks

Perfectly Myopic | Partially Myopic



Under perfectly myopic conditions, the arrival of a GPT at t=200 shows a small, oscillating loss of biosphere, but a larger loss occurs immediately after the arrival of GPES (left panel). This is a result of a larger sudden increase in entropy production that occurs after the adoption of the new GPES.

Figure 4.7c: Change in Utility with Independent GPT and GPES Shocks



Agents operating under partially myopic conditions will not experience major declines in utility after exogenous shocks.

4.2.4 Key Parameters that Control the effects of GPES shocks and the biosphere

The arrival of a GPT stresses the biosphere, via increased consumption, such that there is continual loss until either all the biosphere disappears or settles at a new lower level. Key parameters that dictate the degree to which the arrival of a new GPT results in biosphere loss or full/partial recovery are μ, which increases or decreases the effect of entropy, and γ_3, which affects the magnitude of the regenerative rate of the biosphere.

In the absence of any new GPES adoption, it is noted that as long as the shock of a new GPT arrival is relatively large (G_t>5), the biosphere, after a series of decreasing number of recoveries and increasingly longer periods for recovery, will completely collapse. That is, if technology (GPT shocks) is pervasive enough in the economy with many spillovers that lead to relatively large increases in consumption, then GPTs alone will eventually lead to unsustainable growth in consumption. GPTs will rejuvenate growth in consumption, but unlike Lipsey *et al.* (2006), in the absence of GPESs, they will eventually bring about the collapse of the biosphere.

Simulations where a GPES shock does not follow the arrival of a new GPT predict long-term biosphere collapse.

Various combinations, with ranges of [0.5, 15] for μ and [0.05, 0.25] for γ_3, were used to illustrate recovery and loss of the biosphere. This is done to allow for the determination of the conditions under which the biosphere dies out given the ranges of each individual parameter. In addition, it was shown that it is inappropriate to have equation 4.8 as a function of a_t^E. Thus, α_4 is restricted to values between 0 and 1. However, the numerical simulations indicate that the marginal product of energy labour resources need to be large enough (i.e. values of $0.7 \leq \alpha_4 < 1$) to compensate for entropy growth caused by increased consumption production; otherwise, the biosphere collapses very quickly after consumption growth rates increase from exogenous GPT shocks. Table 4.1 summarises the effects/robustness of the parameter values and the model effects they control in my model. The following section describes the race between the arrival of a GPT and the adoption of a GPES and how timing plays a critical role.

Table 4.1: Summary of Model Parameters and Their Effects

Parameter	Effect	Range of Values Tested
α_1, exponent on GPT labour force	This exponent should not be set too close to 0 or to unity; otherwise, there will be no discernible effect of consumption on the state of the biosphere, which is unrealistic, or the GPT and GPES labour will move to zero in the short run such that consumption drops to zero almost immediately, respectively. The production function for the flow of composite knowledge should be modeled with small (close to constant returns to scale) to moderately decreasing returns to scale with the condition that the exponent on GPES labour force should be restricted. Otherwise, when the biosphere is included in our model, entropy has no or little effect on the biosphere if the production function for the flow of composite knowledge exhibits highly decreasing returns to scale.	[0.05, 0.95]
α_2, exponent on GPES labour force	Values close to 0 have no effect on biosphere. Values close to 1 reduce GPT and GPES labour forces to zero in the short run, consumption drops to zero. Our simulations indicate that, under perfectly myopic conditions this should be restricted to less than or equal to 0.55; otherwise values above 0.55 cause early collapse of the biosphere, when the biosphere is included in our model.	[0.05, 0.95]

Parameter	Effect	Range of Values Tested
α_3, exponent on labour force producing consumption goods	Large values (usually above 0.33, depending on the size of exogenous shocks) cause early collapse of biosphere under perfectly myopic conditions	[0.05, 0.95]
α_4, exponent on level of GPES pervasiveness	Values less than 0.7 have a strong negative impact on the biosphere, even prior to the first GPT shock; Larger values exceeding 0.7 reduce the recovery time of the biosphere and decrease entropy increases that occur after a GPES shock; any values close to or exceeding 0.9 eliminate any negative effects of increases in consumption on the biosphere (these levels would however be unrealistic)	[0.05, 0.95]
α_5, exponent parameter for GPES labour force in the of GPES pervasiveness function, *b*	A range of values can be used, but values less the 0.7 give too much weight to GPT resources. Thus the ratio of labour resources GPT:GPES, where GPT is >> GPES causes consumption to grow too fast and leads to early collapse of the biosphere under perfectly myopic conditions.	[0.1, 0.9]
γ_1 and γ_2, exponent parameters on consumption and biosphere variables for the utility function	A wide variety of values can be used such that qualitative results are unchanged, but γ_2 should be kept above 0.6 if one wants changes in the biosphere to be reflected in utility	[0.1, 0.95]
γ3, the parameter that affects the magnitude of the regenerative rate of the biosphere	Values below 0.12 generally show poor biosphere recovery performance that tends to lead to biosphere collapse	[0.05, 0.25]

Parameter	Effect	Range of Values Tested
ν, the calibration parameter on the variable a_t, which is the flow of produced knowledge in the GPT sector	Values greater than unity allow consumption values to become too high, thereby prematurely causing the biosphere to collapse	[0.5, 2]
μ, the calibration parameter that controls the size of the change in entropy production, is critical in controlling the effect of entropy on the biosphere.	A wide range of values can be used resulting similar qualitative results. Higher values (>8) need to be used under partially myopic conditions to see the effects of entropy on the biosphere.	[0.5, 20]
ω, the substitution parameter in the CES function in the numerical simulations.	Labour resources remain at their initial levels, regardless of shocks, when the limit of ω approaches zero.	(0, 1)
ε_2, the distribution parameter that relates the share of output (i.e. stock of energy knowledge) to the inputs, the flow of energy knowledge and the stock of energy knowledge at period t-1.	Allowing ε_2 to also approach unity causes stepwise level changes in consumption output rather than a gradual increase to a new, higher steady-state. Since both of these outcomes would be unrealistic, I avoid setting ε_2 close to one in our numerical simulations.	[0, 1]
θ, calibration parameter for the discovery or production rate of GPES	Values close to unity reduce the magnitude of B, thereby making entropy increases larger than they would be otherwise, which can cause collapse of the biosphere.	[1, 20]

Parameter	Effect	Range of Values Tested
X^*, minimum level of biosphere necessary for human life and at which it can no longer regenerate itself S_{max} , maximum level of entropy that the biosphere can accommodate without adverse effects (i.e. loss of biosphere) R, regenerative rate of biosphere up to a maximum of X_0 and as long as X does not fall below X^*	See section 4.2.6 for full discussion on value validation	

4.2.5 Simulation 3: We are not *all* dead in the long-run, but those that are left are very unhappy: The Importance of Timing

Here, the question of what would happen in the event that the adoption of a GPES took place much later after new steady states establish themselves following the arrival of a new GPT is explored (see Figures 4.8a – 4.8d).

The parameters remain unchanged from those used in the previous simulations and the initial conditions are the same for both simulations[42] under perfectly and partially myopic conditions.

Under perfectly myopic conditions, the GPES shock causes a loss of biosphere immediately after the adoption of GPES (Figure 4.8a). This result is true for any GPES arrival that is delayed by similar time lags. It is not necessary for all of the variables to reach their steady-state. As long as the adoption of the GPES is much removed from the GPT shock so that entropy increases significantly, one will see a drastic decline in the level of the biosphere.

[42] The same initial conditions are used to compare the perfectly myopic case to the partially myopic case, except that there is a further increase in the time interval between the two exogenous shocks and increase the value of the calibration parameter, μ, to highlight the very different resource allocations that occur under partially myopic conditions. Under partially myopic conditions, the simulation includes the adoption of a new GPES, at t = 300, rather than at t=150, when all the variables have reached their respective steady-states. This increased time interval between the two exogenous shocks also highlights the difference between partially and perfectly myopic maximization. Under perfectly myopic conditions, long time lags lead to a total system collapse. For example, an arrival of a GPES shock at t=230 would be too late for biosphere recovery and abatement of entropy increases, which were caused by increases in consumption that, in turn, were triggered by a GPT arrival at t=70. Initial conditions:
alpha = [0.5 0.55 0.4 0.7 0.7]; omega = 0.85; gamma = [0.3 0.7 0.12 -0.005 0.001]; v = 1; mu = 10.3; theta = 7; epsilon = [0.02 0.6 0.02]; N = 1000; X_o = 5000; S_{max} = 500; $X^* = 0.4(X_o)$; n_o = 800; $d_o^G = d_o^G$ =100.

Normally, the economy-wide adoption of the new GPES does not initially fully compensate for the increase in entropy caused by the increase in consumption, which negatively affects the biosphere, but over the medium-term, as more of the GPES diffuses into all sectors of the economy, entropy decreases and the biosphere recovers. The recovery of the biosphere, as one would expect, DOES NOT happen when the introduction of a GPES occurs much later after the introduction of a GPT under perfectly myopic conditions. Why? Because, the longer the economy waits for a new GPES adoption from its initial GPT shock, the more the change in entropy production grows towards a new higher steady-state. The closer entropy gets to its new steady-state, the greater is the decrease in the entropy production ratio of the biosphere to civilization. This causes irreversible damage to the biosphere such that the GPES shock accelerates the biosphere decline. This is because marginal productivities in the energy and technology sectors increase to a large extent such that consumption levels are far higher than prior to the GPES arrival, and the biosphere eventually settles at much lower level. Consequently, utility is much lower than prior to the GPES arrival. The prolonged arrival of a GPES will actually do more immediate biosphere harm than having no GPES shock, but it will prevent the total collapse of the biosphere in the long-run.

This simulation illustrates that relying on technology only for an extended period without the adoption of a new GPES will sustain high levels of consumption for a long time (Figure 4.8b). This long-term, high level of consumption and sustained biosphere with a decreasing entropy production ratio of the biosphere to civilization is deceptive. Eventually, under perfectly myopic conditions, the biosphere will collapse. However, the long-awaited adoption of a new GPES will cause a short-run large decrease in the biosphere (and utility[43]), but will avoid the ultimate long-run complete collapse of the biosphere (Figure 4.8a). Therefore, the adoption of a new GPES that comes much later after the arrival of a new GPT will prevent an economy from dying in the long-run, but will leave agents wholly unsatisfied[44].

[43] For a wide range of parameter values for the case where a GPES shock follows a GPT shock, we generally get sustained growth in consumption. The unsustainability is manifest on utility. This is a result of myopic preferences. If individuals cared about the future, one would get a feedback effect from the biosphere to allocation of resources and consumption and collapse of growth.

[44] GPES shocks that arrive *before* the arrival of a new GPT have also been simulated. Qualitatively, the results are similar to those described in the text. That is, regardless of whether or not the GPES arrives before or after the GPT, eventually, a GPT needs to be followed by a GPES if one wants to avoid biosphere collapse.

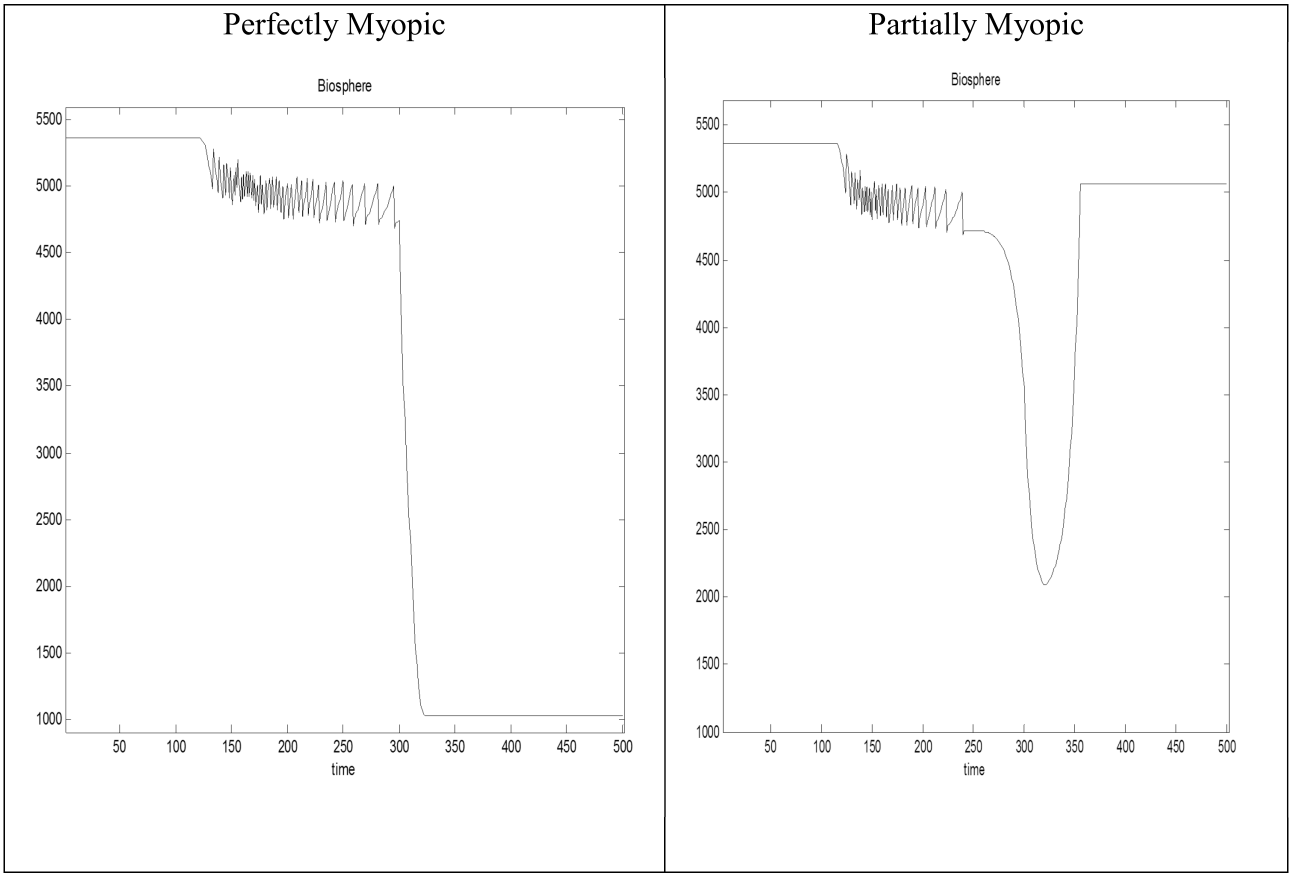
Note that μ, the calibration parameter, controls the size of the change in entropy production, and thus is critical in controlling the effect of entropy on the biosphere. One can illustrate that given GPT and GPES shocks, smaller values of μ can result in biosphere recoveries back to their approximate initial levels even when the GPES shock lags extensively that of a GPT shock.

Under partially myopic conditions, inter-temporal trade-offs between future biosphere levels and current consumption allows for greater time lags between GPT and GPES shocks. Thus, biosphere collapse is delayed allowing the allocation of more labour resources to the energy sector, which would contribute to the discovery or the further adoption of a new GPES (i.e. increase GPES pervasiveness within an economy).

In Figure 4.8c, there are two reallocations of labour resources. The first, at t=100, allowing the allocation of more labour resources to the energy sector and away from consumption goods production to avoid a collapse of the biosphere, and then again at t=300 to initiate biosphere recovery and increase GPES pervasiveness.

When there is no inter-temporal trade-off between current consumption and future biosphere levels, the long-awaited adoption of a new GPES will cause a large decrease in utility and ultimately, utility settles at a much lower level after the exogenous technology shocks (Figure 4.8d). When inter-temporal trade-offs exist under partially myopic conditions, utility also declines, but the decline is temporary. In the long-run, utility settles at a higher level after the exogenous technology shocks (Figure 4.8d).

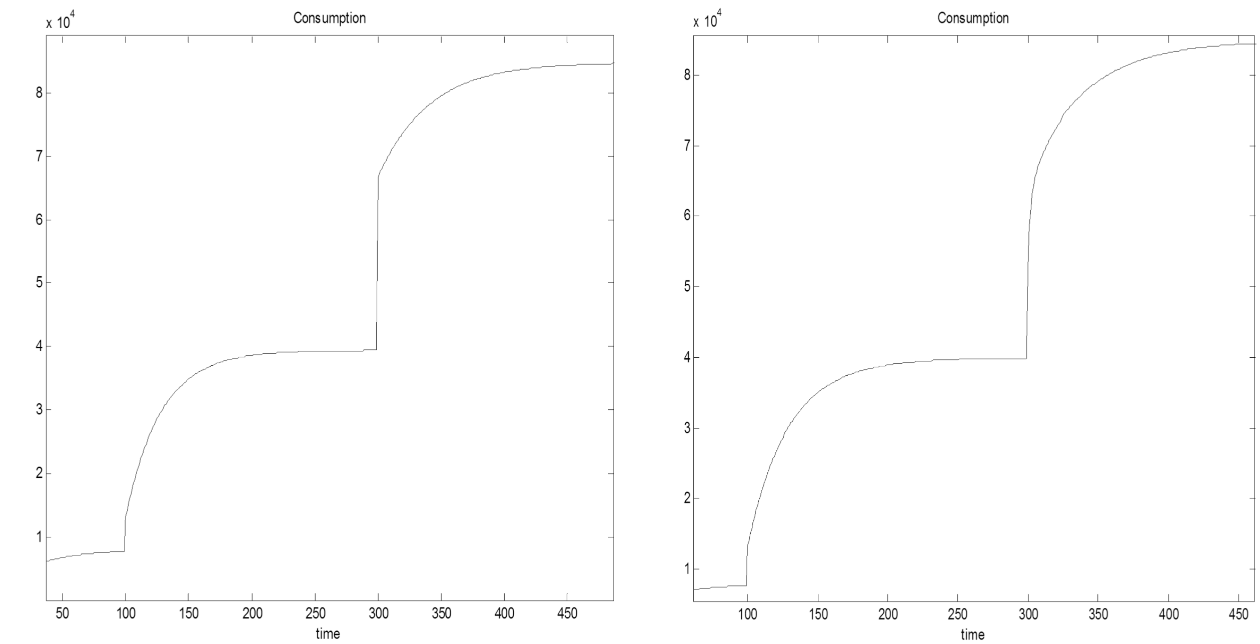
Figure 4.8a: Biosphere Levels and Long time Lag between GPT and GPES Shocks



Under perfectly myopic conditions, the GPES shock causes a loss of biosphere immediately after the adoption of GPES. Under this condition, any GPES arrival that is delayed by long lags causes large losses in the biosphere.

Figure 4.8b: Consumption and Long time Lag between GPT and GPES Shocks

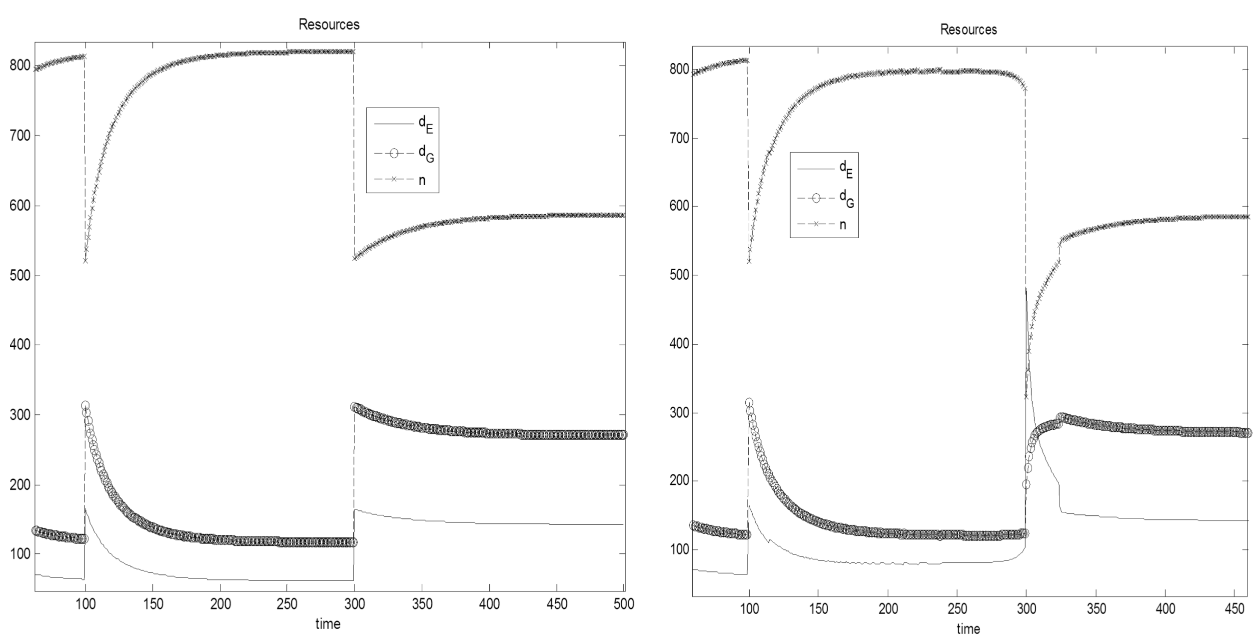
Perfectly Myopic | Partially Myopic



Under perfectly myopic conditions, relying on only technology for an extended period without the adoption of a new GPES will cause high levels of consumption, but will also cause the biosphere to collapse.

Figure 4.8c: Resource Allocation and Long time Lag between GPT and GPES Shocks

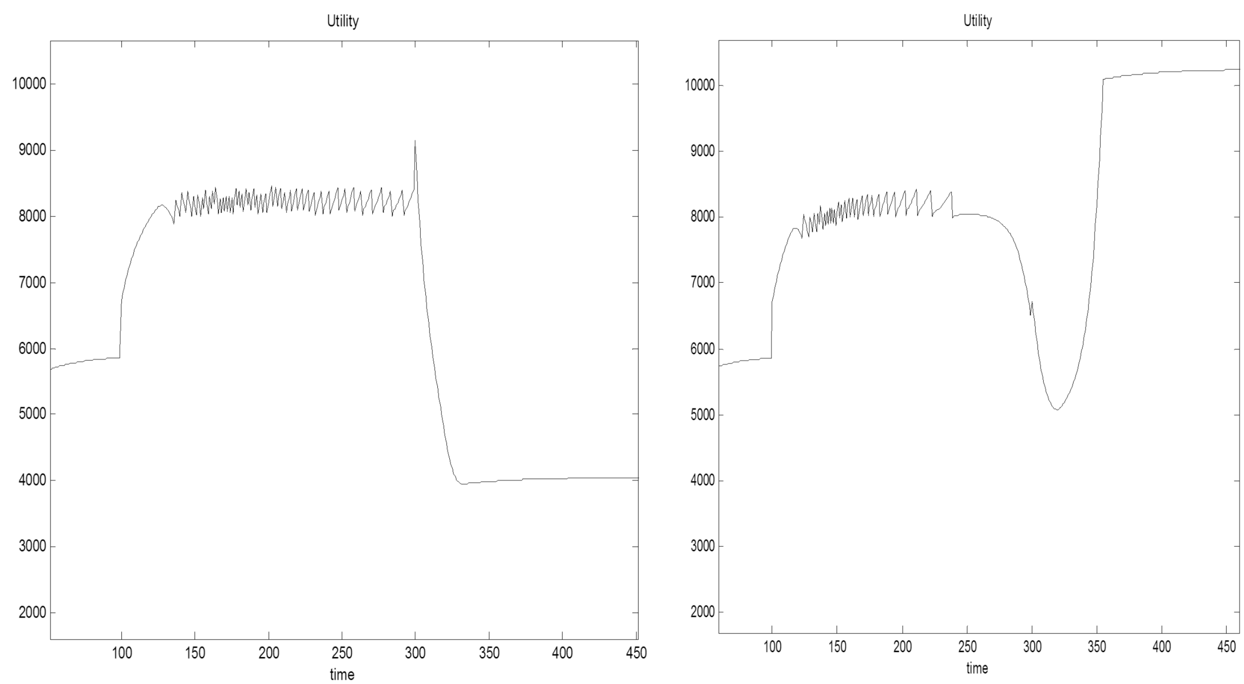
Perfectly Myopic | Partially Myopic



With two shocks, there are there are two reallocations of labour resources. The first, at t=100, allowing the allocation of more labour resources to the energy sector and away from consumption goods production to avoid a collapse of the biosphere, and then again at t=300 to initiate biosphere recovery and increase GPES pervasiveness. The trade-off under partially myopic conditions helps avoid a biosphere collapse (right panel).

Figure 4.8d: Change in Utility and Long time Lag between GPT and GPES Shocks

Perfectly Myopic | Partially Myopic



Relying on technology only for an extended period without the adoption of a new GPES will sustain high levels of consumption for a long time. Eventually, however, under perfectly myopic conditions, the biosphere will collapse leading to lower utility levels (left panel).

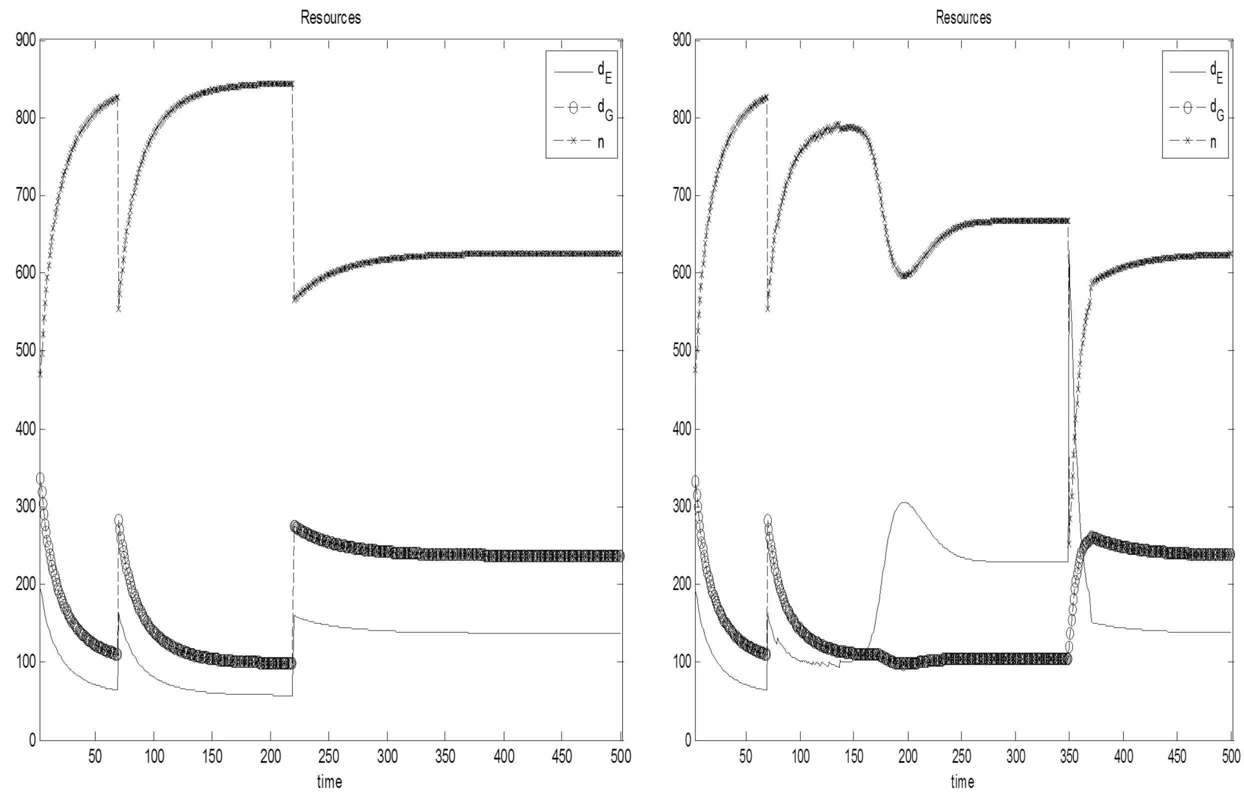
4.2.6 Another Time Lag Effect

Another example underscores the behavioural differences of economies under perfectly and partially myopic conditions. It is now assumed that after an economy is returning to a new steady-state from t=0 to t=70, a GPT arrives before the new steady-state is reached. A new GPES then arrives after a lag at time t=220. In Figure 4.8e, there are two reallocations of labour resources. The first, at t=160, allowing the allocation of more labour resources to the energy sector and away from consumption goods production to avoid a collapse of the biosphere, and then again at t=350 to initiate biosphere recovery and increase GPES pervasiveness. One will also note that the first reallocation results in a trade-off: consumption levels peak at t=160 and then growth becomes negative before settling at a slightly lower level allowing the biosphere to sustain life (Figure 4.8f).

Figure 4.8e: Resource Allocation with a 150-period time Lag between GPT and GPES Shocks

Perfectly Myopic

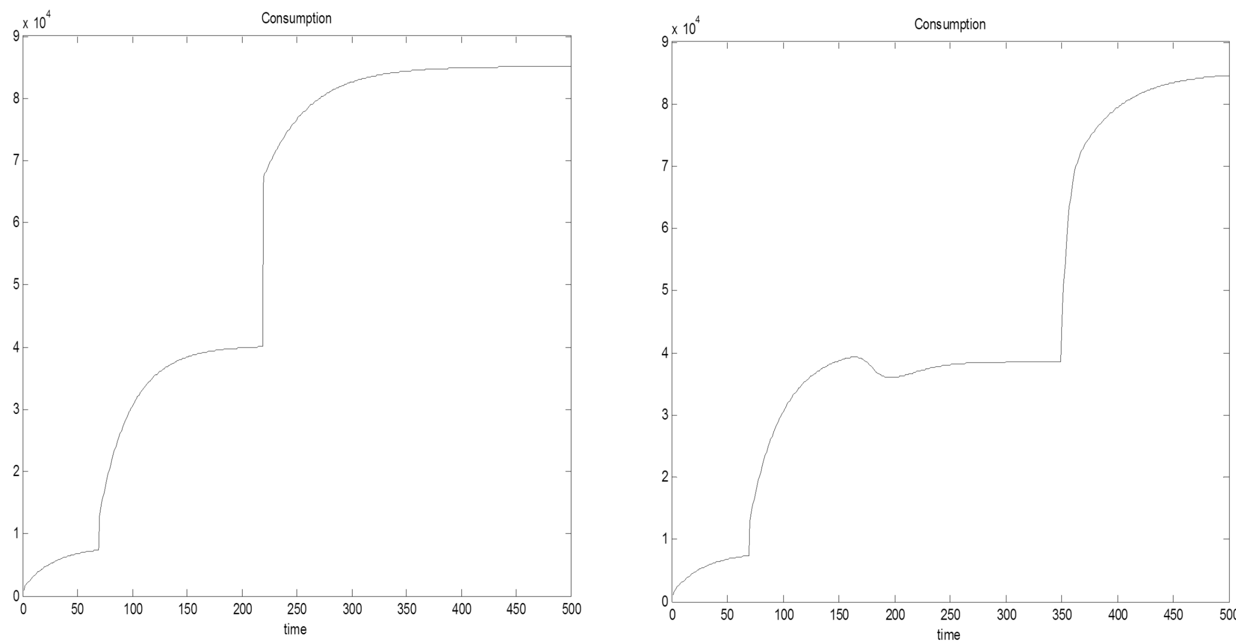
Partially Myopic



A new GPES arrives after a lag, which results in one reallocations of labour resources at t=220 under perfectly myopic conditions (left panel). Under partially myopic conditions, there are two reallocations of labour resources (right panel). The first, at t=160, allowing the allocation of more labour resources to the energy sector and away from consumption goods production to avoid a collapse of the biosphere, and then again at t=350 to initiate biosphere recovery and increase GPES pervasiveness.

Figure 4.8f: Consumption with a 150-period time Lag between GPT and GPES Shocks

Perfectly Myopic　　　　　　　　　　Partially Myopic



The two reallocation of resources in the right panel of Figure 4.8e results in a trade-off: consumption levels peak at t=160 and then growth becomes negative before settling at a slightly lower level allowing the biosphere to sustain life (right panel). There is no such trade-off under perfectly myopic conditions (left panel).

4.2.7 Biosphere Recovery Dependent on Calibration Parameter, μ

Apart from timing, consumption levels and entropy production, and the size of exogenous shocks, the calibration parameter, μ, is critical in determining how well (or badly) the biosphere response to exogenous shocks. In the preceding simulation, the adoption of a GPES takes place much later after the arrival of a new GPT. When this occurs, one risks that, in the long-run, the biosphere settles at a point below which it cannot sustain life. However, if one were to run simulation 3 with all the same parameter values, except replacing μ with a smaller value, one would note two changes in the economy. The first, the biosphere is more resilient and thus recovers at a higher level than that seen in simulation 3; albeit at a lower level than its initial value. The second, utility levels settle at much higher levels after the arrival of GPT and GPES shocks because the biosphere avoids collapse.

4.2.8 Determining the Biosphere Parameters

Simulations 1 and 3 illustrated the collapse of the biosphere when an economy fails to adopt a new GPES after the arrival of a new GPT under perfectly myopic conditions. To be sure, even under partially myopic conditions, the collapse of the biosphere depends on the parameter values used, as illustrated in Table 4.2, and given certain parameters, the adoption of a GPES that occurs much after a GPT's arrival can also make it too late to reverse the loss of the biosphere. So, why does the biosphere react in this manner – seemingly stable for long periods of time and then, even after the entropy production ratio of the biosphere to civilization stabilises, it collapses? Furthermore, are these sharp drops in the biosphere realistic? Is this modeling phenomenon merely a matter of arbitrarily chosen (biosphere) parameters or can the chosen parameters be validated via empirical (biological) evidence?

It is well documented in the literature that biological systems can shift rapidly from an existing state to a radically different state and, these states are neither steady nor in equilibrium, but are defined by characterized range of deviations from a mean condition over a prescribed period of time (Barnosky *et al.*, 2012). There are two effects that can cause a biological state to shift from one state to another: a 'threshold' and 'sledgehammer' effect. The latter can be easily anticipated because it can be caused, for example, by a massive oil spill in a concentrated ecosystem or it can be caused by the mechanical clearing of a forest. The former 'threshold' effect, however, can be difficult to anticipate because the critical threshold is reached as incremental changes accumulate and the threshold value generally is not known in advance (Barnosky *et al.*, 2012)[45]. In both cases, the biological state shift is relatively abrupt and results in new mean conditions outside the range of fluctuation evident in the previous state. This is manifest in our model of biosphere collapse when a new GPT is neither trailed by the adoption of a new GPES or, when a new GPES is adopted, it is done so with a very long lag. It is important to note that once a critical transition[46] occurs, it is extremely difficult or even impossible for the system to return to its previous state (Barnosky *et al.*, 2012).

[45] See also the previous discussion on tipping points.

[46] Threshold-induced state shifts, or critical transitions, can result from 'fold bifurcations' and can show hysteresis. Fold bifurcations occur when changes in a system's underlying parameters alter the number of its steady-states

The range of model parameters chosen for the biosphere keeps this notion of biological state shifts and critical transitions in mind. I have also modeled a 'recovery rate' for the biosphere and specified the minimum level of biosphere necessary for human life at which it can no longer regenerate itself (i.e. X^*). Here, too, the chosen parameters are validated according to the established literature. That is, while it is not presently known how much land, for example, would have to be anthropogenically transformed before a planetary state shift were to be impending, according to Barnosky *et al.* (2012), landscape-scale studies and theory suggest that the critical threshold may lie between 50% and 90% and this would imply that "once a sufficient proportion of Earth's ecosystems have undergone transformation, the remainder can change rapidly, especially because emergent, larger-scale forcings (for instance, changes in atmospheric and ocean chemistry, nutrient and energy cycling, pollution and so on) multiply and interact to exacerbate local forcings". Furthermore, landscape-scale observations and simulations infer that the expected percentage of Earth's ecosystems that actually have to be transformed to "new states by the direct action of humans for rapid state changes to be triggered in remaining 'natural' systems can be as low as 50% or even lower if the interaction effects of many local ecosystem transformations cause sufficiently large global-scale forcings to emerge" (Barnosky *et al.*, 2012).

4.3 BET Model Extension: Population Feedback

The role of the biosphere in our model is to act as a gauge allowing one to understand the conditions under which an economy can sustain growth in consumption. As seen under various parameter values and timing, growth in consumption can be sustained in the long-run or lead to a system collapse. The biosphere allows one to understand how entropy, which changes with different output and technology/energy levels, affects the ability of the biosphere to sustain itself and its contribution to utility. The allocation of resources are maximized with respect to, among

---

(solutions to the system that stay constant over time). If the prevailing steady-state is destroyed, then the whole system may need to rapidly reconfigure to a different equilibrium. Once a biological state shifts large reverse changes, if any, to the regulating parameters may be needed, to return a system to its original steady-state. Examples used in the biological literature include desertification of scrubland following grazing by cattle, and the collapse of fish stocks due to overfishing.

others, the carrying capacity of the biosphere, which in turn, is a function of entropy, which is a function of d^E , the labour force in the energy (GPES) sector.

The model's purpose is to explore the manner in which exogenous technology and energy shocks cause environmental damage and recovery all the while trying to rejuvenate economic growth. The biosphere is an integral component of the BET model, but it has not up to now displayed direct feedback to resource allocation. As such, this section adds feedback to the allocation of resources from the biosphere. This is accomplished by allowing the biosphere to determine labor productivity. That is, population in an economy is a function of the biosphere. If the quality of the environment falls enough, the population declines. As biosphere recovers, so does the population. This is similar to a Malthusian idea of population growth being a function of consumption.

Thomas Malthus theorised that socioeconomic development is limited by the pressure that population growth exerts on the availability of food. Malthus assumed that the world's population tends to increase at a faster rate than its food supply. However, Malthus' population decline prediction does not hold for industrialized countries when one considers the importance of education and parents' investment in their children's quality rather than in their quantity, which can account for lower fertility rates. Our BET model exhibits a type of neo-Malthusian perspective with regard to the relationship between population and the biosphere; that is, excess burden on the biosphere as a result of decreases in the biosphere to civilization entropy production ratio can lead to population collapse. Our model's neo-Malthusian relationship would apply to both poor and rich countries.

In a myopic setting, one does not care about future biosphere levels. Therefore, in any setting that does not alter its resource allocation or population size, but waits until the biosphere declines to X^*, there will be population collapse. Since X^* is the minimal level of biosphere necessary for human life, population starts to decline automatically below X^* (because the biosphere cannot regenerate itself below X^*, population will forever decline alongside the biosphere). This case would be the least interesting to examine. However, in forward-looking or even partially myopic conditions, adjustments to population size can be made so as to reduce consumption levels and entropy production when biosphere levels approach X^*. Any reduction in the population size can be reversed once biosphere levels recover to some acceptable level.

One of the simplest systems that can be used to model a breeding population in which generations do not overlap is to use a first-order difference equation:

$$N_t = F(N_{t-1}) \qquad (4.12)$$

Equation 4.12 describes many natural populations and describes how the population in period t + 1 relates to the magnitude of the population in the preceding time period. For biological populations, there is a tendency for N to increase from one generation to the next when N is small and a tendency to decrease when N is large. A specific example and often used population model in ecology is the logistic difference equation: $N_t = aN_{t-1}(1 - N_{t-1})$. Its main advantage is that it is a simple nonlinear difference equation. However, it attains a maximum value of a/4 at N = ½ and thus possess non-trivial dynamical behavior only if a<4 (May, 1976).

Another population model that is found frequently in the biological literature is one that displays exponential growth at low population density and exponential decline at high exponential density: $N_t = N_{t-1}e^{[a(1-N_{t-1})]}$, where a controls the steepness of the behavior[47].

The BET model assumes a fixed, maximum size for population, N. However, if one were to extend the model to include changing population size, while maintaining a fixed, maximum size, then population would be model as follows:

$$N_t = F(N_{t-1}, X_{t-1}) \qquad (4.13)$$

The current size of the population depends on the magnitude of the population and the level of the biosphere. One can use either the logistic or exponential difference forms above to model simple population behavior in the BET model. The results would not differ qualitatively. There

[47] This equation can be used to model a single species population which is regulated by an epidemic disease at high population density (May, 1976).

are two changes that are required for either the logistic or exponential difference forms in our BET model. There first, is adjusting the population model so that it is a function of the biosphere (i.e. Equation 4.13). The second relates to our assumption of a fixed, maximum size for N_t. Both the logistic and exponential difference population forms model population increases when N is small and decreases when N is large.

The BET model, in its simplest assumption under partially myopic conditions, only needs to incorporate population dynamics when N fulfills three conditions: (1) population is below its maximum, (2) the biosphere is recovering, and/or (3) the biosphere approaches X*. Thus, one can write Equation 4.13, the law of motion for population[48], as follows:

$$if\ X^* < X_{t-1} < aX^*, then\ N_t = N_{t-1}(1 + \gamma_4)$$

otherwise $$if\ N_{t-1} < N_0,\ then\ N_t = N_{t-1}(1 + \gamma_5) \qquad (4.14)$$

otherwise $$N_t = N_0,$$

and where γ_4 and γ_5 are population growth rates and a is an exogenously determined parameter, with a value greater than one, which dictates when population levels adjust to biosphere losses under partially myopic conditions.

Note that equation 4.14 is simply one way to introduce the feedback to allocation of resources from the biosphere. The point here is to illustrate the interaction of an economy and its population after the arrival of shocks to avoid collapse of the biosphere.

[48] A linear equation as well as an exponential equation or a combination of both can be used for the regeneration and collapse rates. The qualitative results are the same. We can also specify the regeneration or collapse rates symmetrically for the biosphere and the population, but it is unclear whether this approach is supported by the biology/ecology literature. We can reasonably assume that the conditions are such that both the biosphere regeneration and collapse rates are higher than the population regeneration and collapse rates. We defend this position by recalling the discussion on biological threshold effects in Section 4.2.6.

Note that productivity or growth in knowledge is not modeled as a function of labour resources so as the avoid “scale effects”, which implies that doubling the number of scientists engaged in R&D should result in the doubling of per capita growth rate of output in the steady state. According to Jones (1995), almost all R&D-based models in the literature share a prediction of "scale effects", but empirical evidence provides little support to this prediction.

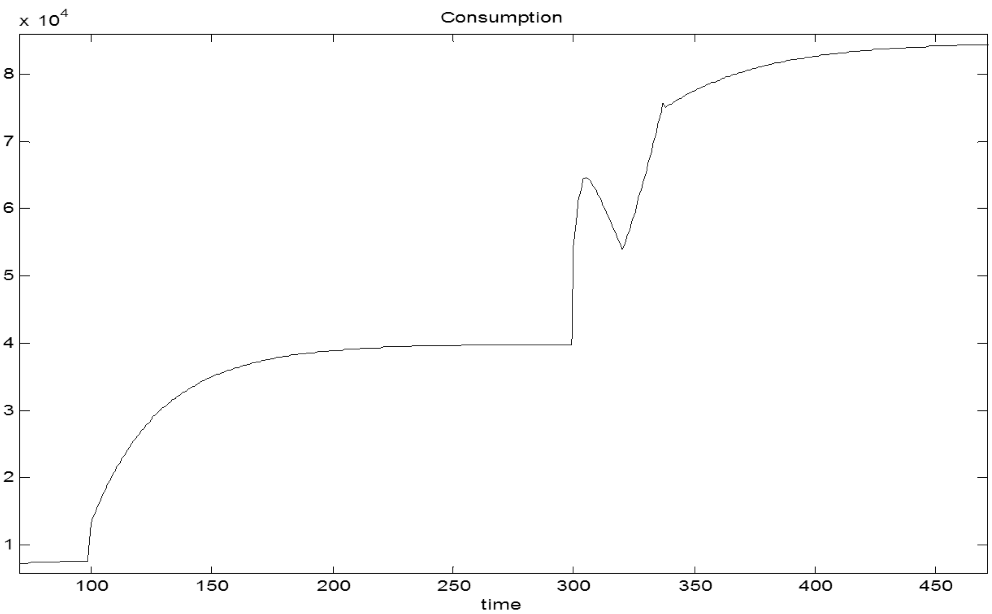
4.3.1 Simulation 4: Feedback to Labour Resources

In this simulation, the case where the level of biosphere approaches that of X* level is illustrated. Simulating the case where the biosphere does not recover is consistent with a myopic setting; however, one can imagine that when the biosphere is getting close to, but not below X* (the minimum level required for its regeneration), population decline begins to occur (e.g. because of planning), which reduces consumption. This reduction in consumption leads to a significant reduction in entropy production, which allows the biosphere to recover and avoid complete collapse. Once the biosphere recovers away from this “danger zone”, population starts to increase. Population growth that occurs from the time the biosphere recovers until it is back to its initial N=1000 level. However, the point here is really to show that less myopic agents can avoid population collapse by early reductions in consumption or hastened adoption of GPESs. Figures 4.9a – 4.9f illustrate the results of consumption growth with feedback to allocation of resources when the biosphere approaches X*[49]. Using similar parameters[50] as Simulation 3, one now includes biosphere feedback to population levels. Exogenous GPT and GPES shocks occur at t=100 and t=300, respectively. As was illustrated earlier, the time lag between these two shocks is considered to be long and would cause biosphere (and population) collapse under perfectly myopic conditions. Under partially myopic conditions, biosphere collapse can be avoided by increased GPES pervasiveness, reduction in the production of consumption goods independent of

[49] These results can be reached by changing one or many parameter values.
[50] The parameter vectors are as follows:
alpha = [0.55 0.5 0.29 0.7 0.7]; omega = 0.85;
gamma = [0.3 0.7 0.12 -0.005 0.001];
v = 1; mu = 10.77; theta = 7; epsilon = [0.02 0.6 0.02];
N = 1000; X_o = 5000; S_{max} = 500; X* = 0.4(X_o); a = 1.5
n_o = 800; $d_o^G = d_o^G$ =100.

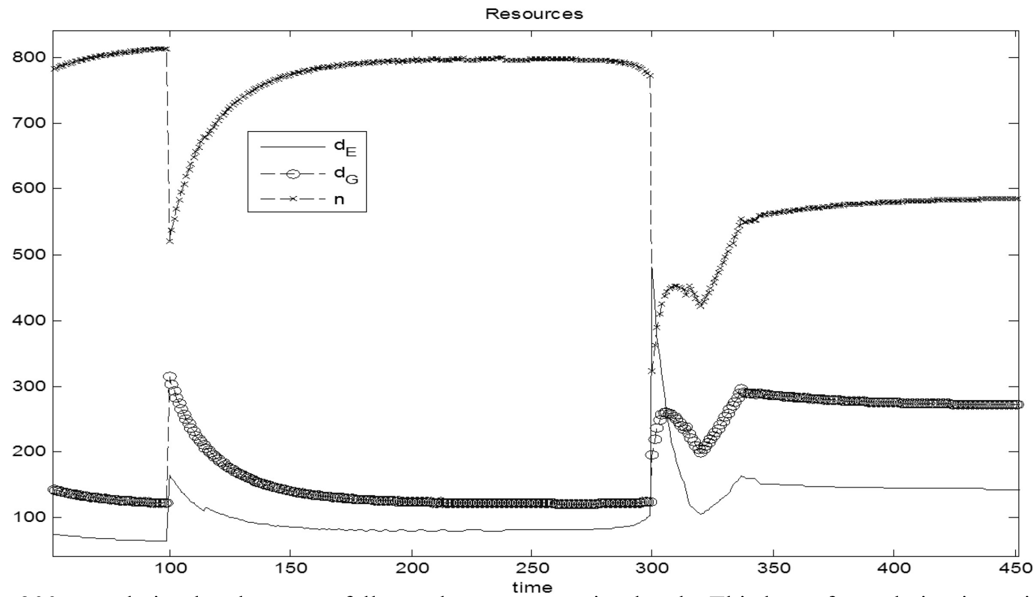
changes in populations, or reduction in the production of consumption goods from a decrease in the population size. Here, one notes the latter case. Once the biosphere falls below an exogenously determined level (around t=300), population levels start to fall in this partially myopic setting. As production resources (i.e. population levels) decline, so do consumption levels and utility. As less consumption goods are produced, changes in entropy-biosphere production ratios begin to decline. The biosphere's decline ceases as entropy production slows down and the biosphere's recovery rate overtakes that of entropy change. As biosphere levels continue to rise, population levels return to their initial levels.

Figure 4.9a: Consumption in the BET Model with Feedback to Resource Allocation



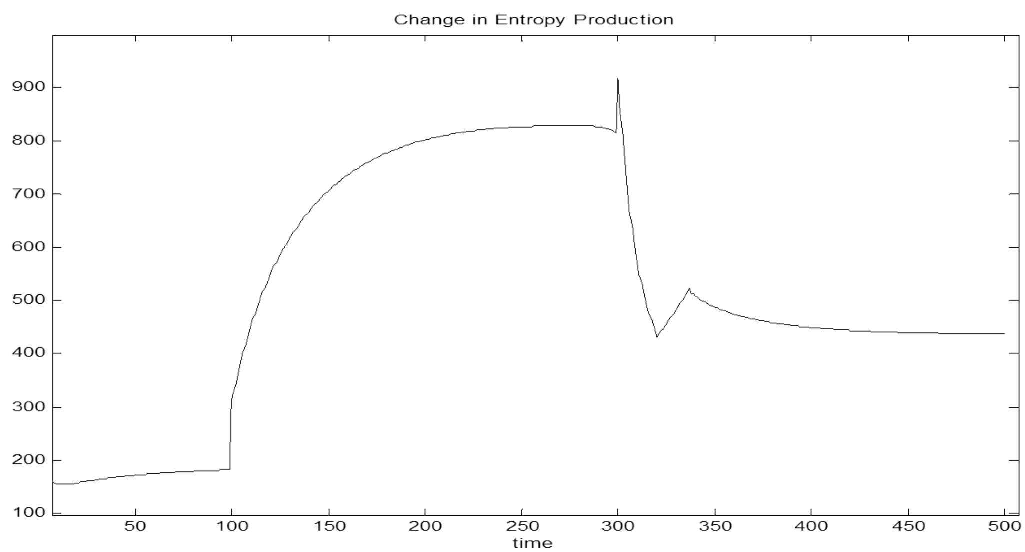
When the BET model includes population feedback, under partially myopic conditions, biosphere collapse can be avoided by a reduction in the production of consumption goods independent of changes in populations, or reduction in the production of consumption goods from a decrease in the population size. Here, one notes the latter case. At t=300, as population levels start to fall, so does the consumption level.

Figure 4.9b: Resource Allocation in the BET Model with Feedback to Resource Allocation



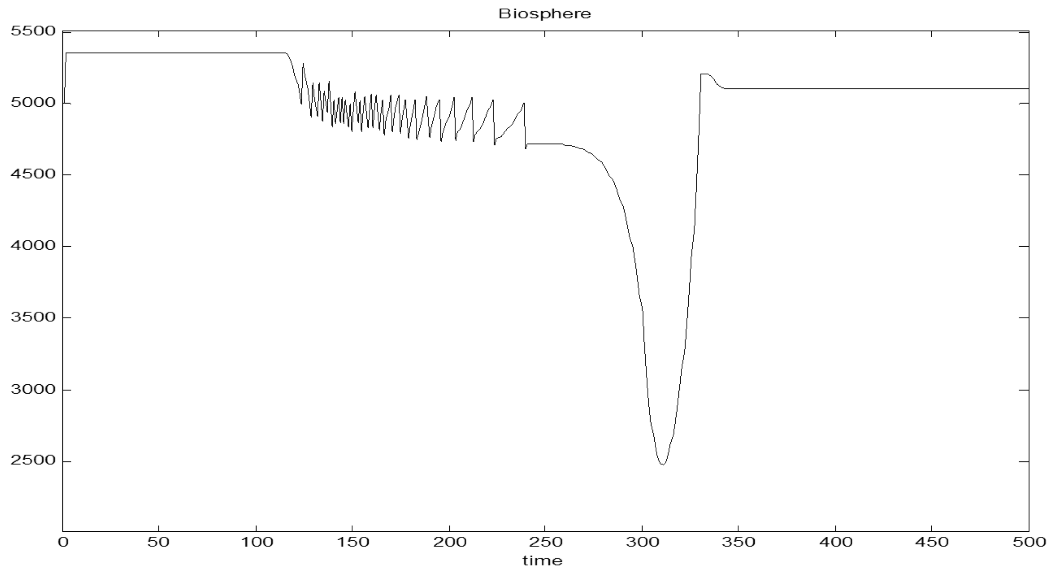
At t=300, population levels start to fall to reduce consumption levels. This loss of population is equivalent to the loss of labour resources. Once the biosphere recovers, population levels also recover at approximately t=320.

Figure 4.9c: Changes in Entropy Production in the BET Model with Feedback to Resource Allocation



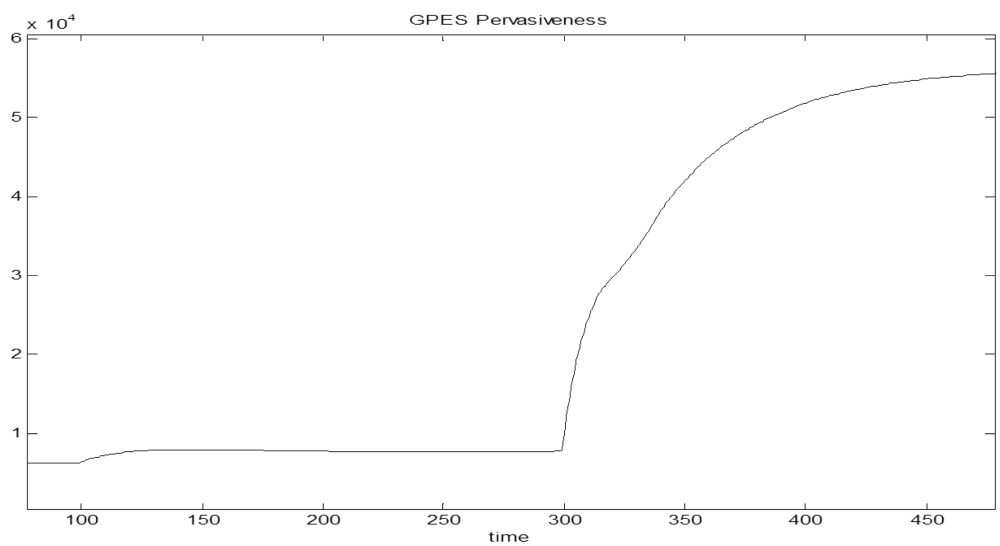
A reduction in the production of consumption goods from a decrease in the population size results in a reduction in entropy production.

Figure 4.9d: Changes in Biosphere Levels in the BET Model with Feedback to Resource Allocation



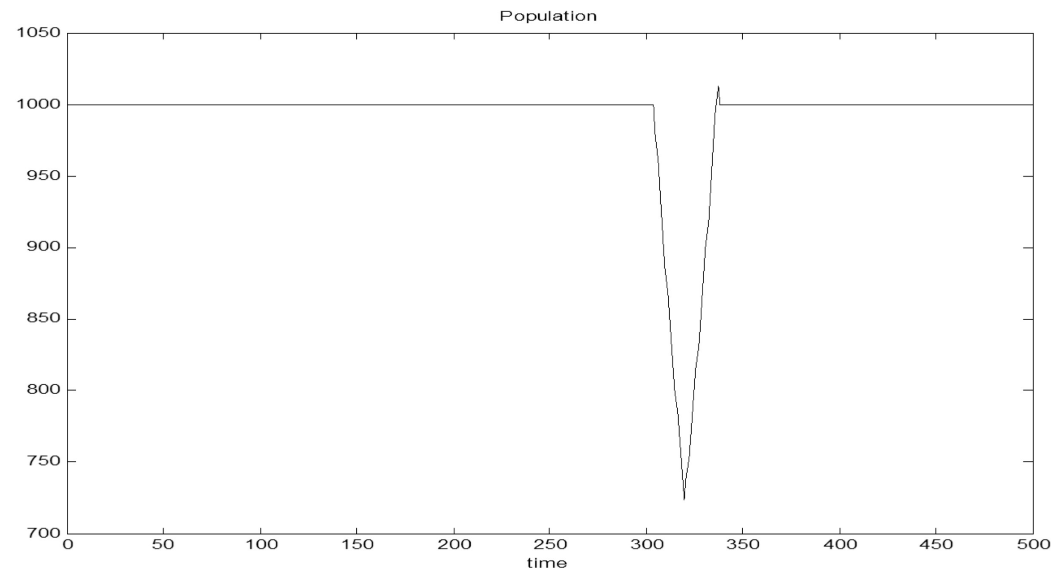
When the BET model includes population feedback, under partially myopic conditions, biosphere collapse can be avoided by a reduction in the production of consumption goods independent of changes in populations, or reduction in the production of consumption goods from a decrease in the population size. These reductions allow for the recovery of the biosphere.

Figure 4.9e: GPES Pervasiveness in the BET Model with Feedback to Resource Allocation



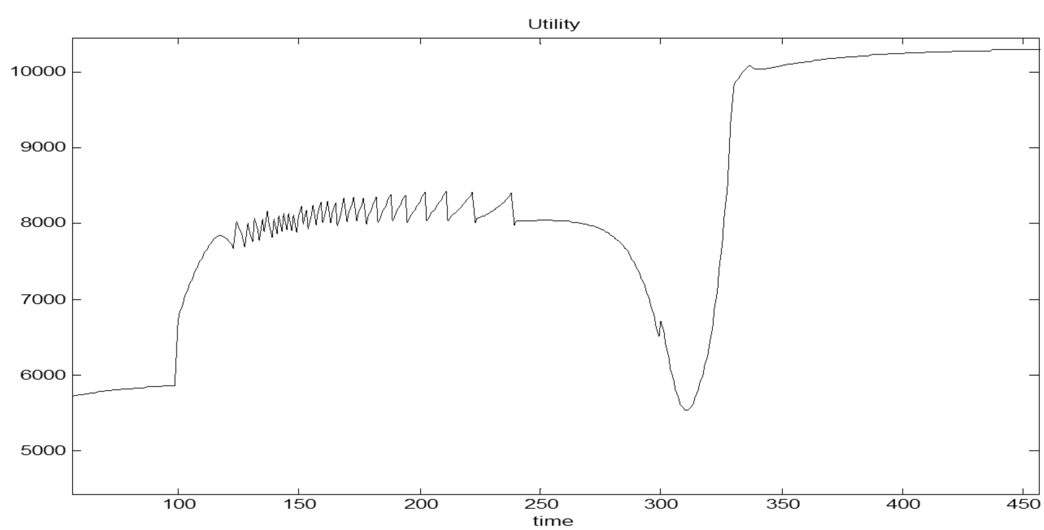
As with any GPES shock, adoption level of new thermoefficient energy sources increases.

Figure 4.9f: Population in the BET Model with Feedback to Resource Allocation



When the BET model includes population feedback, under partially myopic conditions, biosphere collapse can be avoided by a decrease in the size of the population. This reduction allows for the recovery of the biosphere. As biosphere levels continue to rise, population levels return to their initial levels.

Figure 4.9g: Utility in the Model with a Biosphere Collapse and Feedback to Resource Allocation



Reductions in biosphere level result in lower utility. As population and consumption levels decline to initiate recovery of the biosphere, utility levels accompanying the recovery of the biosphere.

4.3.2 History Shows that Technical Innovations are Not Sufficient to Stave off Collapse

The inability of a society to stave off collapse because of an inability to adopt or widely recognize new energy sources even when technologically possible is not without precedent. The energy-technology model can be applied to current and past economies. One can even stretch this argument to argue that the fall of the Roman Empire was due, in part, to overreliance on traditional energy sources: slaves and animals[51]. The fall of the Roman Empire provides well documented historical evidence of the outcome of the winner of the race between energy and technology.

The traditional date for the collapse of the Roman Empire is 476 A.D., when barbaric Germanic tribes sacked the capital and deposed of the last Roman emperor, Romulus Augustulus. It would be simplistic to conclude, however, that the fall of the Roman Empire is solely due to repeated attacks by various barbarian tribes over a number of years. In fact, there have been hundreds of theories that have been put forth to explain the fall of the Roman Empire and some include: outbreak of diseases such as smallpox and the plague, poisoning of the ruling class by lead-tainted drinkware, moral decadence, political corruption, overexpansion, too many slaves, etc. While all of these theorises have their truths and undoubtedly added to the Empire's societal stresses, the Roman Empire, in addition, failed to widely recognise (and adopt) a new GPES in time to save its economy. The Roman Empire, to be sure, was technologically advanced and their technological innovation was, for their period, second to none, but it, at some point, stalled. Although the Romans had developed water-driven grain mills and gravity-driven aqueducts, the empire was locked in a food-based system where its true GPESs were domesticated animal power and slaves.

According to Martin (2012), Rome was the first civilization to develop all the necessary components for the world's first steam engine, but never did build one that could have been of practical use. Roman engineers had the technical knowledge, for example, to build water-powered cylinder-drive pistons. While some Romans, such as Hero of Alexandria, may have recognised that steam could provide for an energy carrier, Roman society never recognized steam as a general purpose energy carrier; likely, because of the plentiful (and cheap, but not

[51] Extractive political institutions also played a major role in Rome's downfall.

endlessly cheap) animal power and slave labour. In essence, similar to our model simulation in Section 4.2.5, Rome's technologies were never followed by a new GPES and economic growth stalled. This and the previously mentioned pressures of war, disease, and bad management contributed to its collapse.

Tainter (1988) explains that "the best key to continued socioeconomic growth, and to avoiding or circumventing declines in marginal productivity, is to obtain a new energy subsidy when it becomes apparent that marginal productivity is beginning to drop". Remarkably, the Roman Empire was able to stall its decline because it was able to acquire its energy subsidies (i.e. slaves and animals) through territorial expansion. Modern economies accomplish this through exploiting fossil fuel reserves and nuclear energy. Once expansion was no longer an option, Rome buckled.[52]

4.3.4 Policy Implications

The BET model can address two opposing views that can be found in the scientific and popular literature: (i) that allocating more resources to knowledge production, which is successful at stimulating further economic growth, will lead only to faster weakening of the environment's ability to cope with anthropogenic activity[53]; and, (ii) that innovative societies will overcome environmental obstacles (because of presumed capital-resource substitutability) and grow forever[54]. We will examine the use of focused policies, which are designed to encourage the

[52] The Roman example can also provide for an illustration on how long lags between technological innovations and GPESs can prevent sustained growth even in the absence of entropy production effects on dissipative structure (sub-)systems. Although it is entirely possible that stressing the environment as well as resources depletion were contributing factors in the decline of Rome as many authors have indicated (see Tainter (1988) for a full discussion), the production of entropy and the applicability of the entropy production ratio of civilisation to the biosphere was a trivial issue for antiquity except for entropy effects on dissipative sub-sub-systems. Environmental critical thresholds were surely exceeded for local environments, but not on large national or international scales. The point here is to highlight the importance of GPES recognition and adoption for modern societies and those of antiquity. Entropy concerns, of course, grow as one approaches the modern era.
[53] This view leads many to call for economic underdevelopment.
[54] According to Tainter (1988), the marginal costs of research and development have grown so high it is questionable whether technological innovation will be able to contribute as much to the solution of future problems

development of specific technologies and particular types of knowledge production. Focused policies can aid in the development of major new technologies or where there is little incentive (e.g. non- patent research) to carry out important research. However, focused policies may prove to be counterproductive in an energy-technology-biosphere context. Focused policies can also have distorting effects on the market. Such policies can be useful in providing assistance to specific technologies where major externalities can be identified, but a focused policy or program whose goal is to support current energy-related technologies to the benefit of a current GPES can result in the crowding out of investment in research for adoption of a new GPES. They can also crowd out technologies that will lead to the adoption of a new more thermoefficient GPES. An example of such a policy that could mimic our model's main finding - that focused policies that support current GPES technologies may crowed out investment in potentially better GPESs - is hydraulic fracturing for petroleum and natural gas.

Although hydraulic fracturing is a relatively old method, multi-stage fracturing is a relatively new technique that has facilitated the development of oil production in many countries with unconventional hydrocarbon resources. If we have a situation where a biosphere is stressed such that the entropy production ratio of the biosphere to civilization is decreasing (i.e. we are approaching S_{max}), and focused polices are designed to support and invest in new technologies (e.g. multi-stage fracturing) for the support of a current GPES (e.g. petroleum), a myopic condition, we may crowd out investments in the adoption for a new GPES or increase the lag between the GPT-GPES shocks. Our energy-technology model predicts that this situation should result in increases in consumption[55], perhaps for many time periods, but sustained growth cannot be possible in the long-run because the biosphere, after a series of decreasing number of recoveries and increasingly longer periods for recovery, will collapse. Given the above, policies seeking new energy sources to maintain economic well-being is a misleading statement. "New" should mean alternate GPESs that are more thermoefficient than current GPESs rather than imply new supplies of the same GPES. In this sense, new GPESs reduce the need for energy policies that reduce the growth rate of energy use, which can reduce long-run growth.

---

as it has to past ones. One the other hand, economic underdevelopment models are unrealistic because they do not represent a rational option (Tainter, 1988).

[55] The effect of multi-stage fracturing on economic growth is reported to be generally positive, but the results of such studies are controversial.

The manner in which the race between technology and energy can be affected is the role human capital promoting institutions play or are encouraged to play by government policy. Human capital formation is dictated by the prevalence of human capital promoting institutions. The assumptions concerning the BET model are such that there are two types of human capital: human capital specific to the technology sector and human capital specific to the energy sector. The absence of significant supply of human capital in the energy sector (relative to the non-energy sector) may provide for limited incentives to invest in and discover a new GPES. Given that knowledge in the energy sector is different than that in the technology sector, an active role by government in creating a larger supply of energy-specific human capital may be necessary.

Appendix I – Chapter 4 - Modeling the Race between Energy and Technology Using an Augmented Neoclassical (Solow) Model

In Chapter 1, it was argued that a co-determinant of growth – energy – should explicitly be incorporated in economic growth models. I specifically chose to build upon the Lipsey *et al.* (2006) GPT model because I find it best suited to explain episodes of fluctuating growth over a large time scale. More conventional models of endogenous and exogenous technological growth have been constructed to explain observed growth in income in the last one to two hundred years, but they cannot be used to describe or account for the highly unstable growth in income before the late 19th century. However, it was also argued that neither the GPT model nor the Solow-type models appreciate the role of the environment in growth. I then incorporated energy, its interaction with technology, and its interaction with the environment into the GPT model. However, aside from the issue of an extended time scale, can the same be accomplished using a neoclassical model?

With neoclassical growth models, economic growth occurs by increasing labour or capital input, technological improvements and/or improved quality of capital and labour inputs. The Solow model illustrates that there is a distinction between economic growth that results from factor accumulation and growth that results from technological progress. The latter results in a shift to a new, higher production function that uses the same amount of inputs to produce more output. The former is subject to diminishing returns. The neoclassical model provides for only a partial view of an economy's true aggregate production function. Aside from labour and capital, other productive variables such as the biosphere and "negative" productive variables such as entropy or, as in most models that incorporate the environment, pollution, are missing. A common argument used is that if natural resources cannot be expanded, then there will be diminishing returns to increases in the other productive factors. To deal with this criticism, Brock and Taylor (2010) added a new dimension to the Solow model that attempts to bridge the environmental gap. Their main departure from the standard Solow model is the assumption that pollution is co-produced with every unit of output and that some fraction of income can be devoted to abatement (Brock and Taylor, 2010). With these assumptions, their "Green Solow" model shows that the production of pollution does not affect growth of output, while the extent of abatement will affect the level of GDP, but not its growth path (Brock and Taylor, 2010).

Brock and Taylor (2010) further demonstrate that the Green Solow model, generates an Environmental Kuznets Curve (EKC) relationship between both the flow of pollution emissions and income per capita, and the stock of environmental quality and income per capita, where the resulting EKC may be humped shaped or strictly declining. The results that generate an inverse-U curve for pollution are based on CO_2 emissions as the indicator of pollution and post-WWII data. As argued in section 3.2.3, it is not appropriate to implicitly assume that the consequences or effects of the various pollutants on the biosphere are equivalent. Some pollutants such as CO_2 may have long-term effects while others such as CFCs have short-term effects. To equate the two and argue, for example, that CFC "emissions" are dependent on GDP growth and would decline after reaching a maximum with increased growth as postulated by the EKC hypothesis is nonsensical. Furthermore, it has not been established that the EKC is U-shaped for all pollutants over all time periods.

An improvement to the Green Solow model, by Van den Berg (2000), avoids using a general pollutant as a negative input variable. Van den Berg's (2000) augmented Solow model uses a *conservation function*. It recognises the need to engage in explicit conservation activities in order to prevent a reduction in nature's capacity to provide renewable services (Van den Berg, 2000). This approach is similar to our use of entropy. Nevertheless, this green-augmented Solow model also makes use of a static equilibrium model and concludes that when the natural environment is included in the Solow model, diverting resources to help mitigate environmental degradation, GDP grows more slowly. Hence, there is always a trade-off between the economy and the environment. This need not necessary need be the case as we have argued through this chapter.

So, models that shift resources towards abatement technologies to sustain the natural environment slow the rate of growth in doing so. There are two inter-related problems with such conclusions. They are a timing issue and a regenerative issue. Abatement technologies usually arrive after there has been some damage to the environment. As such, the natural environment sustains some sort of damage before abatement occurs. However, it is assumed that the damage is generally reversible so that a shift in resources towards abatement technologies will restore the full capacity of the natural environment. These models lack the critical element that characterises the natural environment: that biological systems can shift rapidly from an existing state to a radically different state and, these states are neither steady nor in equilibrium, which can result from threshold effects that are difficult to anticipate, because the critical threshold is reached as incremental changes accumulate and the threshold value generally is not known in advance.

Any green-augmented Solow model will make use of a static equilibrium model and conclude that when the natural environment is included, diverting resources to help mitigate environmental degradation, GDP grows more slowly. A Solow model with stable steady-states cannot be used to illustrate the behaviour of the natural environment – a complex dissipative structure – where GDP growth rates can decrease whether or not an economy diverts resources for abatement of environmental damages. This requires unstable steady-states that are descriptive of complex dissipative structures. Although a Solow model can have multiple steady-states, some of which can be unstable, it would require increasing returns to scale over some range of capital inputs. Thus, for these reasons and those concerning large time scales (as outlined throughout Chapters 1 and 2), I choose to model growth and economy-environment behaviour by building on the GPT model developed by Lipsey *et al.* (2006).

Appendix II – Chapter 4 – Constrained Optimization Derivation

$$\mathcal{L} = \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3} - \lambda[n_t + d_t^G + d_t^E] \qquad \text{(i)}$$

$$\frac{\partial \mathcal{L}}{\partial n} = \alpha_3\, \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3 - 1} - \lambda \qquad \text{(ii)}$$

$$\frac{\partial \mathcal{L}}{\partial d_t^G} = \alpha_1\, \varepsilon_2 Z(d_t^G)^{\alpha_1 - 1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3} - \lambda \qquad \text{(iii)}$$

$$\frac{\partial \mathcal{L}}{\partial d_t^E} = \alpha_2\, \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2 - 1}(n_t)^{\alpha_3} - \lambda \qquad \text{(iv)}$$

$$\frac{\partial \mathcal{L}}{\partial \lambda} = n_t + d_t^G + d_t^E = N_t \qquad \text{(v)}$$

From (i) we get $\alpha_3\, \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3 - 1} = \lambda$, which implies that $\alpha_3\, c_t(n_t)^{-1} = \lambda$ (vi).

From (ii) we get $\alpha_1\, \varepsilon_2 Z(d_t^G)^{\alpha_1 - 1}(d_t^E)^{\alpha_2}(n_t)^{\alpha_3} = \lambda$, which implies that $\alpha_1\, c_t(d_t^G)^{-1} = \lambda$ (vii).

From (iii) we get $\alpha_2\, \varepsilon_2 Z(d_t^G)^{\alpha_1}(d_t^E)^{\alpha_2 - 1}(n_t)^{\alpha_3} = \lambda$, which implies that $\alpha_2\, c_t(d_t^E)^{-1} = \lambda$ (viii).

We set (vi) = (vii) and (vi) = (viii). Therefore,

$$\alpha_3\, c_t(n_t)^{-1} = \alpha_1\, c_t(d_t^G)^{-1}$$

which implies $\qquad \alpha_1\, n_t = \alpha_3\, d_t^G$

and $\qquad \alpha_3\, c_t(n_t)^{-1} = \alpha_1\, c_t(d_t^E)^{-1}$

which implies $\qquad \alpha_2\, n_t = \alpha_3\, d_t^E$

and $\qquad \alpha_2 d_t^G = \alpha_1\, d_t^E$

Appendix III - Chapter 4 –

Table 4.2: Initial Parameters Values used in the BET Model Simulations

Parameter	Baseline Model Value	Justification
α_1, exponent on GPT labour force	0.5	Values close to 0 or to unity will have no discernable effect of consumption on the state of the biosphere
α_2, exponent on GPES labour force	0.4	Values close to 0 have no effect on biosphere. Values close to 1 reduce GPT and GPES labour forces to zero in the short run
α_3, exponent on labour force producing consumption goods	0.55	Large values cause early collapse of biosphere under perfectly myopic conditions
α_4, exponent on level of GPES pervasiveness	0.7	Values less than 0.7 have a strong negative impact on the biosphere, even prior to the first GPT shock
α_5, exponent parameter for GPES labour force in the of GPES pervasiveness function, *b*	0.7	Values less the 0.7 leads to early collapse of the biosphere under perfectly myopic conditions
γ_1 and γ_2, exponent parameters on consumption and biosphere variables for the utility function	0.25 and 0.75	γ_2 should be > 0.6 if one wants changes in the biosphere to be reflected in utility
γ3, the parameter that affects the magnitude of the regenerative rate of the biosphere	0.12	Values below 0.12 generally show poor biosphere recovery performance that tends to lead to biosphere collapse
ν, the calibration parameter on the variable a_t, which is the flow of produced knowledge in the GPT sector	1	Values greater than unity allow consumption values to become too high, thereby prematurely causing the biosphere to collapse

Parameter	Baseline Model Value	Justification
μ, the calibration parameter that controls the size of the change in entropy production, is critical in controlling the effect of entropy on the biosphere.	5 and 10.45	A wide range of values can be used resulting similar qualitative results
ω, the substitution parameter in the CES function in the numerical simulations.	0.85	There is no substitution of labour resources (i.e. they all remain at their initial levels, regardless of shocks) when the limit of ω approaches zero
ε_2, the distribution parameter that relates the share of output (i.e. stock of energy knowledge) to the inputs, the flow of energy knowledge and the stock of energy knowledge at periods t-1.	0.6	Allowing ε_2 to also approach unity causes stepwise level changes in consumption output rather than a gradual increase to a new, higher steady-state
θ, calibration parameter for the discovery or production rate of GPES	7	Smaller values reduce efficacy of GPES pervasiveness on entropy increases
X*, minimum level of biosphere necessary for human life	2000	See section 4.2.6
S_{max} , maximum level of entropy that the biosphere can accommodate without adverse effects	500	See section 4.2.6
X_0, initial biosphere level	5000	See section 4.2.6
Population size	1000	Arbitrary positive real number
GPT labour force	100	Arbitrary positive real number
GPES labour force	100	Arbitrary positive real number
Non-research labour force	800	Arbitrary positive real number

Chapter 5: Predicting the Next GPES

5.1 Predicting GPTs and GPESs

Some technological innovations, such as superconductors, could be argued to have had the potential to become a GPT, but did not. The potential of others, such as information and communication technologies (ICTs), could not have been evident until after their transformative effects on the economy. Still, the ability to identify technological innovations as potential GPTs many years after their initial introduction is useful for policy development with respect to understanding the necessary major economy-wide structural adjustments that accompany GPT diffusion and spillovers. This ability to identify potential GPTs by policymakers should not be restricted to notable changes in productivity. While most neoclassical models imply that changes in technology are only observable by their effects on productivity, differences in productivity between a new GPT and its predecessor may be large or very small (Lipsey *et al.,*2006). These same properties apply to GPESs, with the exception in number of possible GPESs. That is, GPTs do and will outnumber GPESs. Nevertheless, historical reasoning leads us to conclude that GPESs, like GPTs, cannot be predicted with overt confidence.

5.2 Is Hydrogen a GPES Candidate?

A defining characteristic of GPESs is their ability to die out in their (initially) limited use, only to reappear later as GPESs either when their potential use is fully recognised or technology allows for their mass utilisation (e.g. gasoline distillate). Relative to technological innovations, the number of GPESs can be viewed to be constrained. This should, in theory, allow for a more confident prediction of the next potential GPES. Yet, there is no reason to expect that the impact or total number of GPESs should stand in any temporal relation to each other.

The history of GPTs, like that of GPESs, and GPTs' effects on productivity makes the likelihood of identifying the precise evolutionary path which they will follow low, even if a GPT can be identified prior to its full maturity (Lipsey *et al.*, 2006). GPES candidates should be more likely identifiable, but they, too, follow a stochastic evolutionary path. Nuclear energy (via nuclear fission), for example, has all the characteristics of a potential GPES, but its evolutionary path, which includes public confidence erosion in its ability, restricts its applicability to an auxiliary power source, in all countries, except France. Nevertheless, the outcome for nuclear energy has been better than that of steam in the context of the Roman Empire, which was not in that era widely adopted as a GPES. Like steam[56], which was later used for the external combustion engine in the late 18th century, it is possible for nuclear energy to reappear as a true GPES.

To some, the 'ultimate' nuclear GPES is identifiable. It is deuterium (although other compounds are also candidates) used for nuclear fusion. The problem here is that the technology is decades away from creating commercial nuclear fusion for economy-wide adoption. An example of another 'ultimate' potential nuclear GPES is thorium. Both deuterium and thorium are prime examples that illustrate the necessity of technology. Assuming we have recognised our ultimate energy source, we still cannot adopt it as a GPES because of the lack of technology to harness its power. Certainly, with widespread use of nuclear fusion, most would argue that an energy crisis would never exist.[57] Therefore, sustained growth should be possible for a very long time as long as GPTs that support GPESs continue to exist. One can think about a hypothetical scenario: we have coal as a GPES and assume that it does not generate any pollutants or greenhouse gases (i.e. that it is as clean as nuclear fusion) and coal reserves will last for millions of years. As such, we do not worry about climate change or diminishing coal resources. Now, we allow for new technologies but no new GPESs. Will we have sustained growth? Holding GPES constant, at some base period, say 1800, is no different, in terms of outcome, to holding some level of technology constant. The advent of both is required. Even if one were to accumulate at some given rate more physical capital that embodies new technologies, more human capital (more education and more population), but keep coal as the base period GPES, we soon run into the

[56] Note that steam is an energy carrier while nuclear fuel is an energy source. As remarked throughout the text, either can qualify as GPES.

[57] While averting an energy crisis is possible, avoiding an entropy crisis is less straightforward. The supply of deuterium for nuclear fusion would last for millions of years and by-products would be nowhere near as toxic as the nuclear waste we have with today's nuclear fission. Entropy will still be created through any production process, but the lower degree its production using another GPES depends on the energy extraction processes and its effects on the biosphere, the refinement process, the supply process to end-consumers and ultimately the amounted used by consumers relative to alternate GPESs.

problem of technological innovations that cannot be created or at least at the level at which they currently exist because the technologies would depend on next generation GPESs (e.g. petroleum). Some examples of foregone technological innovations if the base period GPES (i.e. coal) is held constant include the modern airplane, petroleum based plastics and medicines, and the modern internal combustion engine.

The above speculation and Section 2.1.4 illustrate that truly holding technology or a particular energy source or carrier constant makes sustained growth impossible. As with Rome, an energy source or carrier needs to be first recognized as a potential GPES. This will, in turn, spur its use by currently existing technologies or will spur the search for externality-producing technology for which to use the energy source or carrier. The latter case applies to hydrogen as a GPES. Hydrogen, like deuterium for fusion reactors and thorium for liquid fluoride thorium reactors, has been purposed as the next ubiquitous energy carrier. Furthermore, a hydrogen economy, in which hydrogen serves as the main energy carrier in the energy supply cycle has been proposed. The term was coined as far back as the 1970s. By 1987, Canada's advisory Group on Hydrogen Opportunities completed a report entitled, "Hydrogen: National Mission for Canada" (Scott, 2007) in which it discerned that electrolytic hydrogen energy supplies can help reduce carbon dioxide emissions to zero. In 2003, the United States announced a $US 1.2 billion "Hydrogen Fuel Initiative" (Sovacool, 2007) program that supports agendas to employ hydrogen as a fuel for powering cars, trucks, homes, businesses and so forth. In 2004, the State of California announced a plan to build a hydrogen highway. Notwithstanding the debate on the viability of a hydrogen economy, the multiple uses and applicability of hydrogen as a fuel currency would be greatly enhanced given appropriate storage materials.

This brings one to ask whether hydrogen is a GPES candidate. Hydrogen meets most of the characteristics described earlier for an energy carrier to be classified as a GPES; namely, hydrogen has the potential to be a generic or all-purpose energy carrier, it is already influencing the development of technologies for its use (e.g. hydrogen storage materials that include metal-organic frameworks (MOFs), microporous organic polymers (MOPs) and microporous hypercrosslinked polymers (HCPs), has had limited, but practical use and is recognised (by many, but not all) as a theoretically pervasive energy carrier. Thus, hydrogen is a potential GPES candidate that has yet to be adopted economy-wide.

5.3 Another Thought Experiment

Whether one considers a myopic or a forward-looking application of our GPES thesis is extraneous. For the purposes of application of the GPES theory, I conduct another, albeit multifarious, mental experiment. First, hydrogen is a GPES candidate given its characteristics. Therefore, let us assume that hydrogen is fully adopted as the next GPES. Will this adoption lead to a spike in growth, some loss of biosphere or recovery of the current biosphere? Will the ratio of anthropogenic entropy production rate to that of the biosphere decrease over time? From our model described in Section 4, one should be able to predict the outcome of adoption of a new GPES. However, it is here where one sees the importance of institutional factors and policy affecting the evolutionary path of a GPES. While supporters of a hydrogen economy predict lower carbon emissions and positive environmental outcomes, not everyone agrees that a hydrogen economy or hydrogen itself as a ubiquitous fuel are efficient and cost-effective means of reducing dependence on fossil fuels. For instance, Shinnar (2004) argues that a national distribution system for hydrogen in lieu of the current infrastructure will result in large efficiency losses. Furthermore, some research on the life-cycle efficiency (well-to-wheel) of vehicles using various alternative fuels (Romm, 2015) concludes that vehicles employing hydrogen internal combustion engines from which the hydrogen derives from natural gas have the lowest overall efficiency. The study on well-to-wheel efficiencies also deduces that carbon dioxide emissions would be higher with such vehicles when compared to hybrid gasoline-electric cars. Conceivably, for the transportation sector, the direct use of electricity produced from non-carbon sources, namely, hydroelectric and nuclear sources, would be more economical than the production and then subsequent use of hydrogen as a fuel. As such, touting hydrogen as a 'green' GPES needs evaluation from many perspectives.

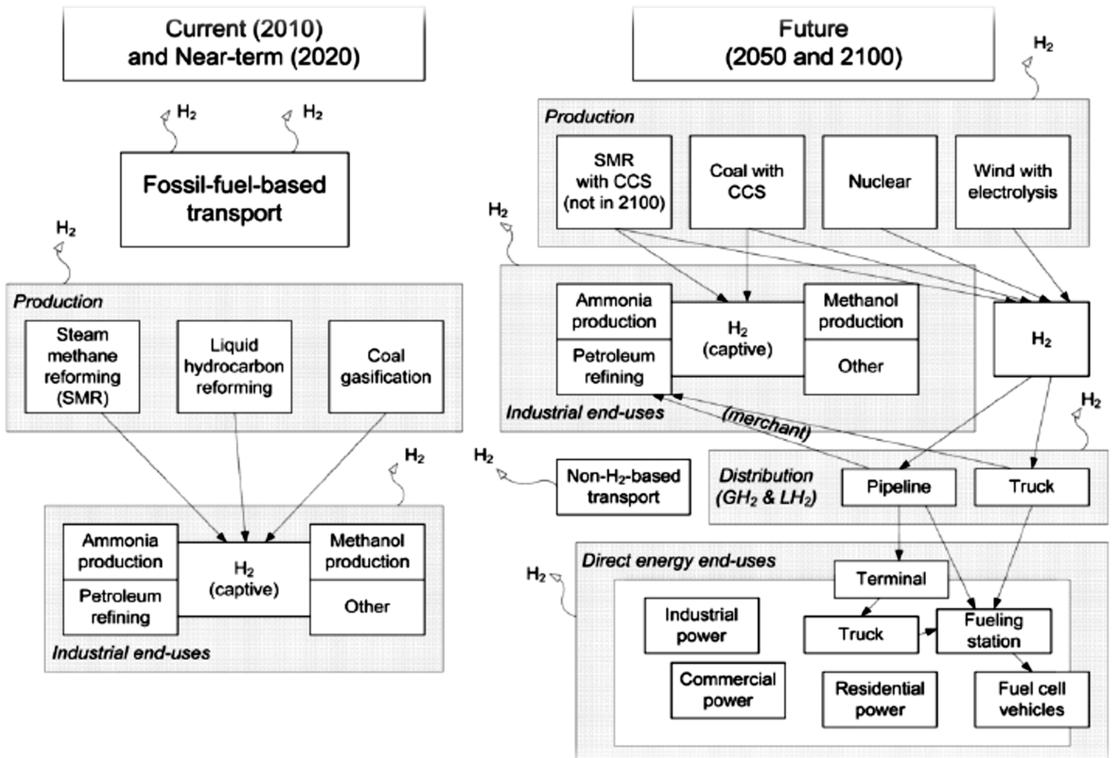
With the BET model in Chapter 4, one expects that, should hydrogen prove to be a true GPES, it will result in an increase in consumption and utility. However, these predictions depend on the magnitudes of various parameters which embody the actions and importance of institutional factors and policy. The magnitude of parameter, θ, which is the calibration parameter for the discovery or production rate of GPES, can easily depend on environmental or testing regulations that may slow or limit the development of hydrogen use. To understand how this is so, consider the development of chlorofluorocarbons (CFCs) as a ‘green chemistry’ analogy to hydrogen. CFCs, which were first introduced in the 1930’s, were thought to be perfect for refrigeration, air conditioning and propellants in aerosol cans because they are non-toxic, stable, non-flammable and can be vaporised at temperatures ideal for use in refrigeration. Decades later, CFCs were identified as a group of compounds that contributed to the deterioration of the ozone layer – a short-term consequence far more devastating than increases in anthropogenic entropy production. Likewise, the adoption of hydrogen as a GPES could be viewed with the policy of minimising environmental harm vis-à-vis the reduction of anthropogenic entropy production and the benefit of sustained growth. Therefore, institutional factors (e.g. government bureaucracy, public policy) may govern the progress of hydrogen becoming a GPES so as to ensure, given for example a risk-adverse public, that hydrogen is adopted without consequences analogous to those of CFCs. That is, the policy of promoting energy-specific human capital, as discussed in Chapter 4, would need to include energy-specific regulatory oversight to anticipate negative consequences of a potential GPES. Chapter 6 of this thesis provides an example of such an oversight for hydrogen during the transitory phase to a hydrogen economy. Thus, Chapter 6 of this thesis explores whether or not hydrogen, a potential GPES, may have adverse atmospheric consequences. Chapter 6 examines the effects of deuterated molecular hydrogen and, by extension, deuterated methane on the kinetic rate constants for a suite of stratospheric radical reactions, and in particular, the rate at which ozone destruction is altered, if at all.

Chapter 6: Potential Kinetic Isotope Effects of Stratospheric Monodeuterated Hydrogen Accumulation during the Transitory Phase to a Hydrogen Economy

Chapter 5 argued that hydrogen is a potential GPES candidate. Chapter 6 will examine potential changes in stratospheric chemistry from adoption of hydrogen as a GPES. Application of the conclusions from these changes will be in the magnitude of parameter, θ, which is the calibration parameter for the accumulation of use-experience of a new more thermo-efficient GPES, b_t. This parameter embodies the actions institutional factors and policy, such as environmental assessment regulations that may slow or limit the development of hydrogen use. In addition, Chapter 6 highlights the need to analyse short-term consequences for new GPESs over long-term increases in anthropogenic entropy production.

The analysis in Chapter 6 will, by necessity, assume that a hydrogen economy exists or will exist sometime in the future. That is, hydrogen, as an energy carrier, is or will be in wide enough use that it is produced commercially in quantities far greater than it is currently. It will consider atmospheric consequences of increased hydrogen use in an economy where future anthropogenic H_2 emissions to the atmosphere will depend on the generation of H_2 from fossil-fuels, production strategies for both industrial processes and direct energy services, leakage and loss rates, and global vehicle numbers and fleet compositions, which is well illustrated by Bond *et al.* (2011) in Figure 6.1.

Figure 6.1: An Illustration of Near-Term H_2 Life-Cycle and Envisaged Future H_2 Economy



The curved arrows represent vehicle exhaust H_2 emissions and losses and leakage along the H_2 production, distribution, and utilization chain. Note that the illustration and caption are a copy extracted from Bond *et al.* (2011).

6.1 Introduction

Estimates of anthropogenic emissions of H_2 vary in the literature, which result in different atmospheric impacts (Schultz *et al.*, 2003; Tromp *et al.*, 2003; Warwick *et al.*, 2004). Thus, it is important that any scenario modeling the impacts of increased hydrogen consider hydrogen production, storage and use leakage rates. This ensures a realistic assumption of atmospheric H_2 concentrations. H_2 is currently the second, only to methane, as the most abundant oxidizable trace gas in the troposphere with an average tropospheric mixing ratio[58] of approximately

[58] The mixing ratio of a gas is defined as the number of moles of the gas per mole of air. It is given in units of volume of gas per volume of air. Mixing ratios of trace gases are commonly given in units of parts per million

5.3×10^{-1} ppm[59] (Ehhalt and Rohrer, 2009) and a high deuterium content (Röckmann *et al.*, 2009). Methane has a mixing ratio of 1.7 ppm. Comparatively, O_2 has a mixing ratio 2.1×10^5 ppm while carbon monoxide has a mixing ratio of 8×10^{-2} ppm. The largest tropospheric source of hydrogen is oxidation of methane by the hydroxyl radical where methane oxidation eventually results in the production of carbon monoxide and a small amount of hydrogen via photolysis of formaldehyde (Ehhalt & Rohrer, 2009):

$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$ (rate limiting step)

$\bullet CH_3 + O_2 + M^{60} \rightarrow \bullet CH_3O_2 + M$

$\bullet CH_3O_2 + \bullet HO_2 \rightarrow CH_3OOH + O_2$

...

$\bullet CH_3O + O_2 \rightarrow HCHO + HO_2\bullet$

The formaldehyde molecule is decomposed by 3 reactions:

$HCHO + \bullet OH \rightarrow H_2O + HCO\bullet$

$HCHO + h\upsilon \rightarrow H\bullet + HCO\bullet$

$HCHO + h\upsilon \rightarrow H_2 + CO$

Another major source of hydrogen includes volatile organic compounds (VOCs) released by land vegetation; with isoprene, monoterpenes ($C_{10}H_x$) and methanol representing the most important VOCs. The VOCs, all attacked by the hydroxyl radical, are highly reactive. They are far more reactive than methane, which does not allow for easy determination of their distribution (Ehhalt and Rohrer, 2009). Nevertheless, hydrogen production from methane is seasonally dependent due to the maximization of [•OH] in the tropics during the summer.

---

volume (ppmv or simply ppm), parts per billion volume (ppbv or ppb), or parts per trillion volume. Note that 1 ppmv = 1x10-6 mol/mol. CO2 concentration, for example, is currently 365 ppmv (365x10-6 mol/mol).

[59] As note in footnote 51, a number of different expressions of concentration for atmospheric gases exist. Here, the concentrations are expressed as ppm (parts per million by volume). Other expressions include concentrations as mg/m^3 (milligrams per cubic meter). All of the concentrations apply only to gases. They are not applicable for liquids. Note that at ambient sea level atmospheric pressure of 101.325 kPa, $ppm = \frac{mg}{m^3}\left(\frac{0.08205T}{M}\right)$, where mg/m^3 = milligrams of gas per cubic meter of air, T = temperature in K, and M = molecular mass of gas (Seinfeld and Pandis, 2006).

[60] M is any species, although usually N_2, that does not itself react, but acts as an energy quencher.

Sink strength for H_2, unlike that of CH_4, is hemispherically asymmetric such that its concentration in the southern hemisphere is higher than that in the northern hemisphere even though the lifecycle for hydrogen is affected by anthropogenic activity (Derwent *et al.*, 2006). Consequently, continental land masses, which are larger in the northern hemisphere, are the resultant major sinks for H_2.

Although H_2 is not removed by uptake on snow, ice, desert or water surfaces, tropospheric H_2 is removed predominately by soils containing organic carbon. According to Conrad (1999), hydrogen uptake by soil is likely mediated by abiontic soil enzymes. The dominance of the soil sink results in a 75% total loss of tropospheric hydrogen or 55-88 teragrams (Tg[61]) H_2y^{-1} (Ehhalt and Rohrer, 2009) and consequently, makes the quantification of the H_2 budget difficult. Unlike CH_4, H_2 loss in the troposphere is not dominated by reaction with •OH. Rather, oxidation by the hydroxyl radical in the sunlit troposphere accounts for 19 +/- 5 Tg H_2 y^{-1} or 25% of total loss (Ehhalt and Rohrer, 2009) via the following reaction: $H_2 + \bullet OH \rightarrow H_2O + \bullet H$.

Hydrogen is also present in the upper troposphere and lower stratosphere, but exhibits a weak vertical gradient. The average vertical distribution, however, in the middle stratosphere is found to be relatively uniform. Hence, the export of H_2 into the stratosphere from the troposphere is limited to approximately 1.9 Tg or 1.8% to 2.6% of annual tropospheric sources (Ehhalt and Rohrer, 2009). Hydrogen production and loss rates in the stratosphere are comparable. Similar to the tropospheric cycle, methane oxidation which first leads to the production of formaldehyde and then H_2 via photolysis is the most significant in situ source of H_2 in the stratosphere.

Reaction with the radicals, •OH and $O(^1D)$, are the main stratospheric sinks of H_2, while reaction with the radical Cl• is a minor stratospheric sink. Oxidation of both methane and hydrogen in the stratosphere lead to the formation of H_2O. Increases in water's mixing ratio in the stratosphere could negatively affect the ozone concentration, albeit that large changes in stratospheric water vapour represent a minor factor in ozone depletion (via cooling and increased polar stratospheric cloud formation) compared to chlorine loading, according to Warwick *et al.* (2004). With hydrogen as a potential future, large-scale energy carrier, unavoidable leaks in the production, storage, delivery and use of H_2, higher atmospheric concentrations of hydrogen

[61] 1 Tg = 10^{12}g.

could have tropospheric effects as well. That is, with an excessively high leakage rate, Warwick *et al.* (2004) find that the tropospheric •OH concentration decreases by 10% in a scenario where the hydrogen mixing ratio is increased from 5.5×10^{-1} ppm to 2.3 ppm, which results from a hydrogen energy economy equivalent to today's fossil fuel consumption. In more modest scenarios (Warwick *et al.*, 2004; Schultz *et al.*, 2003), modeling experiments show that increases in anthropogenic hydrogen have small impacts on tropospheric •OH concentrations and that of ozone.

In spite of potential large-scale production of hydrogen, the literature finds that increases in hydrogen mixing ratios will have only negligible impacts on tropospheric oxidizing potential and stratospheric ozone concentrations. Box model simulations with revised trace gas concentration projections using MECCA (*M*odule *E*fficiently *C*alculating the *C*hemistry of the *A*tmosphere) could add new insight to the current information found in the literature. However, the effects of increases in the D content of stratospheric H_2 via computational primary and secondary kinetic isotope effects (KIEs) have been less studied.

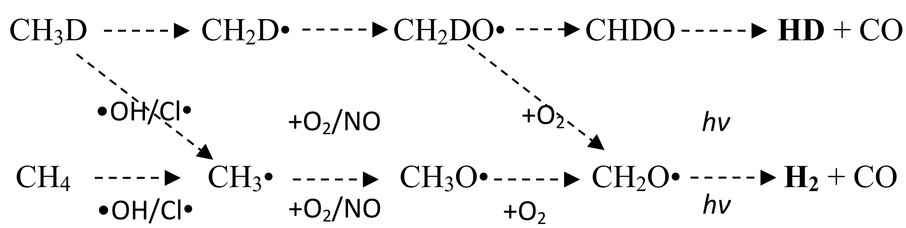
The rise in the D content of stratospheric H_2 is a result of increases in heavy tropospheric methane from anthropogenic activity. In fact, recent D measurements of H_2 indicate an increase in the D content of atmospheric hydrogen, which is believed to be largely a result of an increase in tropospheric CH_4 (Ehhalt and Rohrer, 2009). Photo-oxidation of tropospheric methane would thus result in the production of H_2 with a high D content. The photo-oxidation of methane is slow on the timescale of urban air pollution, and the degradation series of structures that occurs as methane is oxidized in the atmosphere is as follows:

$$CH_4 \dashrightarrow \bullet CH_3 \dashrightarrow \bullet CH_3OO \dashrightarrow \bullet CH_3O \dashrightarrow H_2CO \dashrightarrow HCO \bullet \dashrightarrow CO \dashrightarrow CO_2$$

(Johnston and Kinnison, 1998).

According to Hu *et al.* (2012), the slower consumption of HD over H_2 favors the accumulation of deuterium in the atmosphere, and measurement and modeling convincingly show that the extreme deuterium enrichment could not occur without significant deuterium enrichment during methane oxidation. There are branch points (see Figure 6.2) along this degradation series which lead to further reactions, and the isotope effects in the formation of molecular hydrogen from formaldehyde photolysis have been studied experimentally under various temperature, pressure, and photolysis conditions (Hu *et al.*, 2012). The degree of deuterium enrichment of molecular hydrogen produced from CH_3D is a result of three reactions: (1) the initial methane oxidation by •OH, (2) formaldehyde photolysis, and (3) the reaction of deuterated methoxy radicals (CH_2DO•) with O_2 (Hu *et al.*, 2012).

Figure 6.2: Oxidation Process of CH_4 and CH_3D



Dashed arrows indicate minor paths. The reactions that do not produce molecular hydrogen (e.g., oxidation of formaldehyde by hydroxyl radical) are not shown. Note that the illustration and caption are extracted from Hu *et al.* (2012).

In a full-scale hydrogen economy, the negligible impact of H_2, for example, on tropospheric •OH and ozone from the box models comes from a secondary effect where NO_x emissions are reduced by the replacement of fossil fuels (Denman *et al.*, 2007). In the interim, that is, in the transitory phase where we experience a tethered hydrogen economy – one where hydrogen is produced in far greater quantities than today using steam reforming of methane (SMR) and partial oxidation (POX) of hydrocarbon fuels (discussed in the next paragraph), and where fossil fuels are used at least at current levels and methane emissions from non-biogenic and biogenic sources increase due to increasing world population and worldwide increases in the demand for energy and food – we should experience an increase in atmospheric H_2 with a high D content since the photo-oxidation of increasing levels of CH_4, intuitively, may increase the deuterium content of H_2.

Figure 6.1 above illustrates that a full-scale hydrogen economy is projected in about 100 years. At such time, hydrogen is expected to be produced using a variety of techniques. Currently, however, hydrogen is produced almost exclusively from fossil fuels, with about 48% of the world's hydrogen produced from SMR (Balat, 2008):

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = +206 \text{ kJ/mol}$$

Since the above reaction is endothermic, the process requires high processing temperatures, where the required heat is supplied by burning fossils fuels, notably natural gas. POX of hydrocarbon fuels is another popular method (Balat, 2008) which does not require heat (it is exothermic), but it does release carbon dioxide:

$$2C_8H_{18} + 2H_2O + 9O_2 \rightarrow 12CO + 4CO_2 + 20H_2$$

Given that the impact of anthropogenic H_2 and its isotopes on stratospheric ozone concentration have been less studied via computational methods, I investigate the effects of six stratospherically relevant reactions that involve either H_2 or CH_4 and their isotopes on stratospheric ozone. I also include a seventh reaction, which involves HCl, that is of high relevance to our study on the effects of increased deuterium content from a transitory hydrogen economy. Changes in HCl concentrations can lead to changes in stratospheric ozone concentrations. The seven reactions will be discussed thoroughly in the sections that follow.

It must be noted that the production and loss of stratospheric ozone is complex involving numerous reactive species and catalytic cycles, each with different rates of reactions. The production of ozone naturally occurs from the photolytic decomposition of three O_2 molecules to two ozone molecules. Stratospheric ozone depletion, however, is far more complex and involves a variety of chemical cycles. This thesis will focus on HO_x and chlorine cycles[62] because (1) they play a key role in stratospheric chemistry and, more importantly, (2) they are more likely than the other chemical cycles to have their kinetics altered by anthropogenic increases in deuterated hydrogen and methane concentrations. This thesis postulated that increased hydrogen and

[62] Coupling of cycles, such as HO_x and chlorine cycles or BrO_x and chlorine cycles or HO_x and BrO_x cycles, is also possible.

methane in the stratosphere from a hydrogen economy may compete directly with some of the reactants from these cycles, thereby altering the overall depletion rates of ozone.

The HO_x and chlorine catalytic ozone-depleting cycles, with their respective kinetic rate constants (Seinfeld and Pandis, 2006) are:

HO_x cycle 1:

$$OH\bullet + O_3 \rightarrow HO_2\bullet + O_2$$
$$\underline{HO_2\bullet + O\bullet \rightarrow OH\bullet + O_2}$$
$$O_3 + O\bullet \rightarrow O_2 + O_2 \text{ (net)}$$

HO_x cycle 2:

$$OH\bullet + O_3 \rightarrow HO_2\bullet + O_2$$
$$\underline{HO_2\bullet + O_3 \rightarrow OH\bullet + O_2 + O_2}$$
$$O_3 + O_3 \rightarrow O_2 + O_2 + O_2 \text{ (net)}$$

(Chlorine) ClO_x cycle 1:

$$Cl\bullet + O_3 \xrightarrow{1} ClO\bullet + O_2 \qquad k_1 = 2.3 \text{ x } 10^{-11}\exp(-200/T)$$
$$\underline{ClO\bullet + O\bullet \xrightarrow{2} Cl\bullet + O_2} \qquad k_2 = 3.0 \text{ x } 10^{-11}\exp(70/T)$$
$$O_3 + O\bullet \rightarrow O_2 + O_2 \text{ (net)}$$

The rate constants of any of these reactions involving the production or destruction of ozone may be altered by replacing one or more of a compound's hydrogen atoms by deuterium. Thus, by studying kinetic isotope effects, computationally, I investigate whether anthropogenic increases in deuterated hydrogen and methane have hitherto unknown effects on stratospheric ozone destruction. Where possible, I report the kinetic rate changes that arise from primary isotope effects, which occur when the deuterium bond is formed or broken in the rate determining step, and from secondary isotope effects, which occur when the deuterium bond is not formed or broken in the rate determining step.

6.1.1 Major and Minor Stratospheric Hydrogen Sinks

Methane oxidation in the troposphere which first leads to the production of formaldehyde and then to H_2 + CO and HD + CO would introduce a significant *in situ* source of deuterated molecular hydrogen in the stratosphere. In the stratosphere, the most significant *in situ* source of H_2 is CH_4 oxidation, which can also lead to HD formation from deuterated methoxy radicals (CH_2DO•). Note that the methane mixing ratios are relative large, about 1 to 2 ppm in the lower stratosphere, and they decrease rapidly above 30 km (Burnett and Burnett, 1995). Reaction with the radicals, •OH and O(^1D), are the main stratospheric sinks of H_2, while reaction with the Cl• is a minor stratospheric sink. Furthermore, field studies indicate that the deuterium content of hydrogen produced by methane oxidation varies, in the stratosphere, with altitude (Hu *et al.*, 2012). Thus the three reactions of interest are:

Reaction 1a: $\mathrm{H_2} + \bullet\mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{H}\bullet$
Reaction 1b: $\mathrm{HD} + \bullet\mathrm{OH} \rightarrow \mathrm{H_2O} + \mathrm{D}\bullet\ and\ \mathrm{HOD} + \mathrm{H}\bullet$
Reaction 2a: $\mathrm{H_2} + \mathrm{O(1D)} \rightarrow \mathrm{OH} + \mathrm{H}\bullet$
Reaction 2b: $\mathrm{HD} + \mathrm{O(1D)} \rightarrow \mathrm{OH} + \mathrm{D}\bullet\ and\ \mathrm{OD} + \mathrm{H}\bullet$
Reaction 3a: $\mathrm{H_2} + \mathrm{Cl}\bullet \rightarrow \mathrm{HCl} + \mathrm{H}\bullet$
Reaction 3b: $\mathrm{HD} + \mathrm{Cl}\bullet \rightarrow \mathrm{HCl} + \mathrm{D}\bullet\ and\ \mathrm{DCl} + \mathrm{H}\bullet$

Due to its importance in atmospheric chemistry and photochemical air pollution, the reaction of hydrogen molecules with oxygen atoms has attracted many experimental and theoretical kinetics studies. Presser and Gordon (1984) report experimentally determined rate constants for the reactions of atomic oxygen with H_2, D_2, and HD. However, primary and secondary KIEs for HD at 298 K have not been reported. Of similar importance is the reaction of chlorine atoms with molecular hydrogen. It, too, has received considerable attention both experimentally and theoretically because the reaction and its isotopic variants have served as test models for the transition state theory and the theory of isotope effects (Chen *et al.*, 2002).

While Chen *et al.* (2002) report on the dynamical stereochemistry[63] of Reaction 3a and its isotopic variants, neither they nor Sander *et al.* (2011) report on the rate constants for Reaction 3a at 230 K or the rate constants for Reaction 3b at either 298 K or 230 K. In the study of ozone

[63] Refers to the effect of stereochemistry on reaction rates.

destruction, it is important to use low temperatures for the determination of relevant rate constants because the catalytic destruction of O_3, which is a result of the high concentration of chlorine radicals that form in the polar springtime stratosphere, is only effective at low temperatures approximately below 220 K (Cox, 2012).The only reaction, which reports complete rate constants is reaction 1 include rate constants for reactions with D_2 (Presser and Gordon, 1984); however, not necessarily at 298 K or 230 K.

Computing the transition state structures and evaluating reaction activation barriers for each reaction in our system is essential for the determination of reaction rate constants and kinetic isotope effects. Thus, one objective of this chapter is to obtain theoretical values of primary and secondary KIE for each of these reactions (1 through 3) at room temperature and at a stratospherically relevant temperature. Where possible, the results are compared to experimental and/or theoretically available values.

6.1.2 Stratospheric Methane Oxidation

Reactions 4 through 6 deal with methane oxidation in the stratosphere:

Reaction 4a: $\mathrm{CH_4} + \mathrm{O(1D)} \rightarrow \bullet\,\mathrm{CH_3} + \bullet\,\mathrm{OH}$
Reaction 4b: $\mathrm{CH_3D} + \mathrm{O(1D)} \rightarrow \bullet\,\mathrm{CH_3} + \bullet\,\mathrm{OD}$ and $\bullet\,\mathrm{CH_2D} + \bullet\,\mathrm{OH}$
Reaction 5a: $\mathrm{CH_4} + \bullet\,\mathrm{OH} \rightarrow \bullet\,\mathrm{CH_3} + \mathrm{H_2O}$
Reaction 5b: $\mathrm{CH_3D} + \bullet\,\mathrm{OH} \rightarrow \bullet\,\mathrm{CH_3} + \mathrm{HOD}$ and $\bullet\,\mathrm{CH_2D} + \mathrm{H_2O}$
Reaction 6a: $\mathrm{CH_4} + \mathrm{Cl}\bullet \rightarrow \bullet\,\mathrm{CH_3} + \mathrm{HCl}$
Reaction 6b: $\mathrm{CH_3D} + \mathrm{Cl}\bullet \rightarrow \bullet\,\mathrm{CH_3} + \mathrm{DCl}$ and $\bullet\,\mathrm{CH_2D} + \mathrm{HCl}$

Their study follows naturally from Reactions 1 through 3. Methane oxidation by atomic oxygen is an atmospheric source of hydroxyl radicals. Jursic (2000) uses quantum chemistry calculations to report total energies and activation barriers for Reaction 4a[64] (but not 4b) and for Reaction 5a.

The product of methane's reaction with the chlorine radical is the principal source of solid stratospheric HCl, which is responsible for the depletion of stratospheric ozone. As well, a large

[64] Jursic (2000), albeit, reports methane oxidation with ^3P oxygen.

portion of stratospheric water vapour results from the oxidation of methane by the hydroxyl radical after methane has been transported from the troposphere to the stratosphere. The oxidation of methane in the presence of sufficient concentrations of nitrogen oxides leads to further production of OH and, therefore, can magnify the concentration of HO_x radicals (here: HO_x = •H + •OH + •HO_2), which catalyze ozone destruction cycles, particularly in the upper stratosphere (Gierczak *et al.*, 1997). For these reasons, methane is considered one of the most important constituents of the Earth's atmosphere and its rate coefficient for the reaction of •OH with CH_4 is also has been studied so as to quantify the •OH production in the lower stratosphere (Gierczak *et al.*, 1997). Rate coefficients at stratospherically low temperatures for the reaction of •OH with CH_4 thus need to be defined and Gierczak *et al.* (1997) are the first to report the experimentally determined rate constant for Reaction 5a in the stratospherically important temperature region below 298 K. Truong and Truhlar (1990) carried out quantum chemistry calculations using Møller-Plesset (MP) perturbation theory, scaling all correlation energy in second order (MP-SAC2) with several large basis sets for Reaction 5a in the temperature range from 200 K to 2000 K. Allen *et al.* (2013) investigate the KIE for Reaction 5a and $CD_4 + \bullet OH \rightarrow \bullet CH_3 + HDO$ over the temperature range 200–1000 K using ring polymer molecular dynamics (RPMD) on a full-dimensional potential energy surface. This thesis reports the computed KIE for Reactions 5a and 5b using MP2 perturbation theory within the finite aug-cc-pVTZ.

In a tethered hydrogen economy, one would expect, in addition to increased atmospheric monodeuterated hydrogen concentrations, that anthropogenic methane emissions will increase. Even in the absence of a tethered hydrogen economy, Revell *et al.* (2012) project increases in anthropogenic emissions of the greenhouse gases N_2O and CH_4 through the 21st century. Increases in atmospheric concentrations of N_2O and CH_4 lead to the production of reactive nitrogen species and reactive hydrogen species, which will tend to play an escalated role in determining stratospheric ozone concentrations (Revell *et al.*, 2012). Increasing CH_4 increases the rate of conversion of chlorine to the HCl reservoir (i.e. Reaction 6a: $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$ and thereby slows the chlorine-catalyzed ozone loss cycles throughout the stratosphere. As such, the reaction of the chlorine radical with methane is an important step in the Cl/O_3 destruction chain mechanism in the stratosphere.

The reaction $CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$, and to a lesser extent its reverse reaction, has received substantial theoretical attention including several high level quantum chemistry calculations and various transition state theory calculations where rate constants have been measured in the temperature range of 200 K to 500 K (Yu and Nyman, 1999). Yu and Nymann (1999) calculate the potential energy surface and investigate the quantum scattering dynamics of Reaction 5a, and study the deuterated reaction $CD_4 + Cl\bullet \rightarrow \bullet CD_3 + DCl$. Previously, Truong *et al.* (1989) evaluated the barrier height at the MP2 and MP4 levels and applied the SAC extrapolation method to obtain estimates of basis set and correlation limits. The geometry for the transition state for the reaction has been predicted by using high-level molecular orbital theory at the MP2 level with a large basis set (TZ+2P) by Dobbs and Dixon (1994). Furthermore, Chan and Radom (2006) assessed different computational methodologies for calculating the rate constants for hydrogen abstraction by Cl• for a selection of reactions and found large deviations from experimental rate constants for the conventional approach of calculating higher-level [B2KPLYP/aug'-cc-pV[(T+d),(Q+d)]Z] single-point energies at lower-level [BH&H-LYP/6-31+G(d,p)] stationary point optimized geometries. Chan and Radom (2006) attribute these discrepancies mainly to deviations in the calculated activation energies and the inability of the lower level [BH&H-LYP/6-31+G(d,p)] to adequately locate the transition structures. This thesis reports the transition state structure and thus the KIE for the reaction $CH_3D + Cl\bullet \rightarrow \bullet CH_3 + DCl$ using MP2 perturbation theory within the finite aug-cc-pVTZ.

6.1.3 Source of Stratospheric Chlorine Radical

For the sake of completeness, I investigate the theoretical rate constant for a seventh reaction (i.e. Reaction 7: $HCl + \bullet OH \rightarrow H_2O + Cl\bullet$), which releases the chlorine radical from its HCl reservoir, which is one of the products from Reactions 6a and 6b. Thus, the suite of reactions (1 through 7) and their associated experimentally determined rate constants investigated in our study at stratospherically relevant temperatures is listed in Table 6.1. Of course, many other reactions contribute to stratospheric ozone loss and they depend, in part, on the chlorine radical generated by Reaction 7.

Table 6.1: Stratospheric Second Order Reactions of Interest and Experimentally Determined Rate Constants* ***(*rate constants for T = 298 K are from Sander et al. (2011) while those at T = 230 K are from Röckmann et al. (2003))***

	Reaction	k(298 K)	k(230 K)
		$cm^3 molecule^{-1} s^{-1}$	
1a	$H_2 + \bullet OH \rightarrow H_2O + H\bullet$	6.7 x 10^{-15}	9.2 x 10^{-16}
1b	$HD + \bullet OH \rightarrow$ products	4.0 x 10^{-15}	4.75 x 10^{-16}
2a	$H_2 + O(1D) \rightarrow OH + H\bullet$	1.2 x 10^{-10}	1.1 x 10^{-10}
2b	$HD + O(1D) \rightarrow$ products	n/a	1.1 x 10^{-10}
3a	$H_2 + Cl\bullet \rightarrow HCl + H\bullet$	1.5 x 10^{-14}	
3b	$HD + Cl\bullet \rightarrow$ products	n/a	
4a	$CH_4 + O(1D) \rightarrow \bullet CH_3 + \bullet OH$	1.31 x 10^{-10}	
4b	$CH_3D + O(1D) \rightarrow$ products	n/a	
5a	$CH_4 + \bullet OH \rightarrow \bullet CH_3 + H_2O$	6.3 x 10^{-15}	
5b	$CH_3D + \bullet OH \rightarrow$ products	5.0 x 10^{-15}	
6a	$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$	1.0 x 10^{-13}	
6b	$CH_3D + Cl\bullet \rightarrow$ products	6.8 x 10^{-14}	
7	$HCl + \bullet OH \rightarrow H_2O + Cl\bullet$	7.8 x 10^{-13}	

Reaction 7 is included because hydrochloric acid is the main reservoir for the ClO_x family of compounds. Other reactions that are part of the catalytic atmospheric loss processes, which were mentioned in the introduction, influence stratospheric ozone concentrations via the loss of odd oxygen (i.e. O or O_3). The chain mechanism that simplifies the process of ozone destruction via loss of odd oxygen can be written as follows:

$$X + O_3 \rightarrow XO + O_2$$
$$\underline{XO + O \rightarrow X + O_2}$$
$$O + O_3 \rightarrow 2\,O_2$$

where 'X' is the stratospheric catalytic species and it can be H, OH, Cl, NO, Br, and I.

I focus on the theoretical determination of rate constants using MP2 perturbation theory within the finite aug-cc-pVTZ for Reactions 7, for which (1) no rate constant has been established at a stratospherically relevant temperature, (2) no transition state structure has been investigated[65], and (3) no primary KIE has been determined. Reaction 7 is of high relevance to our study of the effects of increased deuterium content from a transitory hydrogen economy because HCl is the main reservoir for the Cl radical and changes in its concentration can lead to changes in stratospheric ozone concentrations. Computational results for Reaction 7 are compared to, where available, the experimentally determined values. In sum, this thesis investigates the optimized transition state geometry and report the primary KIE for Reactions 7 at 298 K and 220 K using MP2 perturbation theory within the finite aug-cc-pVTZ. This thesis also investigates for the first time the kinetics of the seven reactions in a consistent, unified manner using the same level of quantum chemistry computational theory.

6.2 Computational Methodology

Throughout this study, the quantum chemistry post-Hartree–Fock (HF) *ab initio* method has been used. The geometries of the reactants and products, and each of the transition states have been optimized using second-order Møller-Plesset perturbation theory within the finite aug-cc-pVTZ.[66] Following each geometry optimization, harmonic frequencies were calculated and examined for one imaginary frequency to confirm the nature of the stationary point as a transition structure. All calculations have been carried out using *Gaussian 09* and the molecular structures were constructed and viewed using *Jmol 13.0*. Vibrational frequency modes were visualised using *Gauss View Version 5*. *Gaussian 09* is also used to determine the reaction profile of each of the reactions. The ratio of the rate constant of the unsubstituted reaction to that of the isotopically substituted reaction at a given temperature defines the KIE.

KIEs can be computed either by the standard transition state theory, which uses two points on the potential energy surface, or by more complete formalisms which take account of larger bands of

---

[65] To the best of my knowledge, my literature review did not produce any studies that describe the geometry of transition state for Reaction 7 using MP2 perturbation theory within the finite aug-cc-pVTZ.

[66] "aug" means one set of diffuse functions is added for every angular momentum present in the basis set, while pVTZ refers to polarized-valence triple-zeta . For example, aug-cc-pVDZ for C atom has diffuse s,p,d. The AUG-cc-pVTZ basis places one *s,* one *d*, and one *p* diffuse functions on hydrogen atoms, and one d, one p, one d, and one f diffuse functions on B through Ne and Al through Ar.

the potential energy surface. The latter is more time intensive. The former distinguishes isotope effects as a result of altered zero point vibrational energies (ZPVEs), which are residual amounts of vibrational energies associated with bond stretching. Primary isotope effects are usually governed by the difference in ZPVEs. Given that zero-point energies, and the translational, rotational, and vibrational partition functions all depend on the isotopic masses of the atoms involved in a reaction, a primary isotope effect, usually expressed as the ratio of the rate constants of the lighter isotope to that of the heavier isotope, $\frac{k_{light}}{k_{heavy}}$ or in our case $\frac{k_H}{k_D}$, will be determined for reactions involving deuterated methane or monodeuterated molecular hydrogen. Isotope studies are useful in that they help determine whether a particular bond is involved in the rate-controlling step of a reaction. The isotope effect is larger when there is a bigger relative change in masses of the atom involved.

Transition state theory (TST) benchmarks the performance of the electronic structure method (MP2-aug-cc-pVTZ, in our case) predicting the deuterium KIEs against experiment values and other reported calculations, where available, that use different computational methodologies.

The replacement of any atom such as hydrogen by an isotope does not affect the electronic structure. Thus, the force constant, k_F, related to the inflexibility of a molecular bond is independent of isotopic substitution (Equation 6.1). In other words, the force constant, k_F, does not vary when there is isotopic substitution. Rather, it is determined by the number of electrons and the overall charge. However, the energy of the system is dependent on the mass of the atoms (Equation 6.2). Deuterium, the heavier isotope, would thus have a lower associated ZPVE - the potential energy for bond stretching. The reduction of ZPVE of a deuterated molecule occurs in the isolated state and in the transition state complex. Once the transition state complex has been formed, the vibrational modes of the two reactant subunits somewhat blend together, which results in new vibrational modes that were not present in either of the isolated reactant molecules. These intermolecular modes can be influenced by the substitution of a hydrogen atom by its heavier isotopomer (Tsai and Hu, 2013).

Stretching frequencies, ν, for isotopomers differ because of the differences in mass (Equation 6.1).

$$v = \frac{1}{2\pi}\sqrt{\frac{k_F}{\mu}} \qquad (6.1)$$

Where k_F is the force constant related to the inflexibility or stiffness of the bond, and μ is the reduced mass, m, of the atoms involved in bond stretching ($\mu = \frac{m_1 m_2}{m_1 + m_2}$).

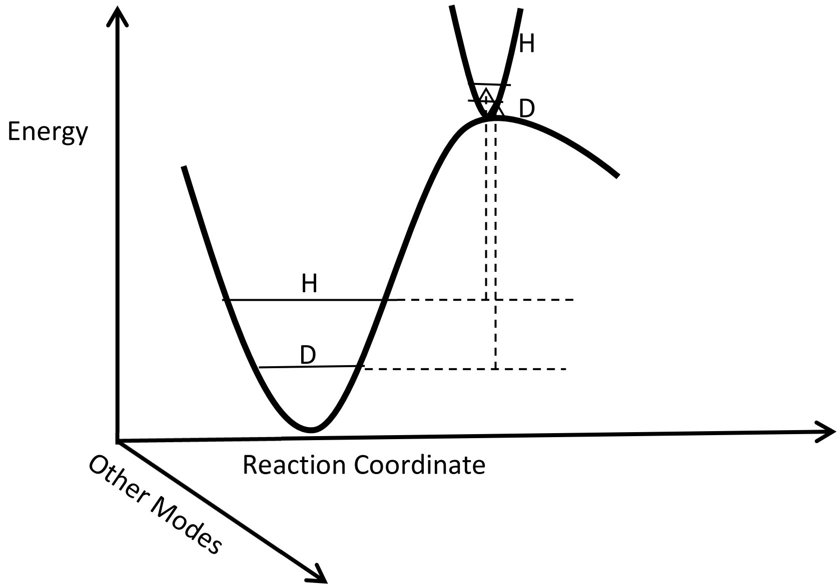
The energy of a system can then be found as follows:

$$E_V = \left(\vartheta + \frac{1}{2}\right) hv = (\vartheta + \frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k_F}{\mu}} \qquad (6.2)$$

where h is Plank's constant, and ϑ is a quantum number.

Hence, the ZPVE is inversely proportional to square root of the reduced mass (i.e. $\frac{v_H}{v_D} = \sqrt{\frac{\mu_D}{\mu_H}}$). Figure 6.3 shows the effect of deuterium substitution on the activation barrier diagrammatically. The vibrational levels are more closely spaced in the transition state than they are in the reactants. For the heavy isotope, the net effect of a lower ZPVE in the reactants, but a similar (although still lower) vibrational level in the transition state is a higher activation energy barrier, and therefore, a slower reaction. A maximum isotope effect occurs when the bond involving the isotope is completely broken in the transition state. In this case, the difference in activation energies is equal to the difference in ZPVEs of the reactants. In other cases, ZPVE differences occur only between the transition states. This leads to a KIE that is less than unity (an inverse isotope effect) because the heavier isotopomer undergoes a faster reaction than the lighter isotopomer.

Figure 6.3: Differences in Activations Energies resulting from Different ZPVEs



ZPVE changes from the ground state to the transition state are due to changes in the force constant, k_F. The magnitude of the KIE is determined by the energy difference between the two ZPVEs.

Given that the isotope effect is completely controlled by the difference in the ground state zero-point energies, the KIEs can be evaluated according to Equation 6.3.

$$\frac{k_H}{k_D} = e^{\frac{-(\Delta ZPVE_H - \Delta ZPVE_D)}{RT}} = e^{\frac{(\Delta G_D^{\ddagger} - \Delta G_H^{\ddagger})}{RT}} = e^{\frac{(\Delta E_a^D - \Delta E_a^H)}{k_B T}} = e^{\frac{h(v_H - v_D)}{2k_B T}} \quad (6.3)$$

where T is the temperature, R is the gas constant, k_B is Boltzmann's constant, $\Delta G^{\ddagger}$ is the difference in free energies between the optimized transition state structure and the optimized reactants structures, E_a is the activation energy, and ΔZPVE is the change in ZPVEs of the transition state and the reactants. The subscripts H and D represent reactions in which only hydrogen is present and where deuterium is present, respectively.

Quantum chemical tunneling is known to play a critical role in obtaining accurate rate coefficients for proton transfer processes, especially at lower temperature, and, will be discussed in the Results and Discussion (Section 6.3). KIEs calculated by computing rate constants using free energy differences[67] from the optimized transition state and reactants structures employ transition-state theory Equation 6.4 (Laidler, 1987):

$$k(T) = \frac{k_B T}{h} e^{\frac{-\Delta G^{0,\ddagger}}{RT}} \quad (6.4)$$

where h is Planck's constant, T is temperature, R is the gas constant, $k_B$is Boltzmann's constant and $\Delta G^{0,\ddagger}$ is the difference in the sum of electronic and thermal free energies between the optimized transition state structure and the optimized reactants structures. Note that rate constants calculated via Equation 6.4 are in s^{-1} units[68]. For the bimolecular case, a conversion factor, $\frac{P}{RT}$, can be used to convert the rate units from s^{-1} to $cm^3molecule^{-1}s^{-1}$:

$$k(T) = \left(\frac{k_B T}{h} e^{\frac{-\Delta G^{0,\ddagger}}{RT}}\right)\frac{P}{RT} \quad (6.4a)$$

---

[67] "Sum of electronic and thermal Free Energies" values from the Gaussian output optimized structures are used.

[68] In order to convert the rate constants to $cm^3molecule^{-1}s^{-1}$ units, one needs to multiply the s^{-1} units by an appropriate conversion factor, which is an approximation of the total concentration of air molecules in $cm^3molecule^{-1}$ at a stratospheric altitude, z, and temperature T. Given that the majority of the atmosphere's ozone is found in the stratosphere layer, z would have a value between 20 and 45 km. More specifically, the majority of the ozone, sometimes referred to as the ozonosphere or commonly as the ozone layer, lies between 25 km and 35 km. Thus, I set our z at 30 km and our temperature at 230 K. One also has the static atmospheric pressure, 12 hPa or 1200 Pa, at 30 km. Thus, the conversion factor for the calculated rate constants, which is also the density, ρ, of air molecules is calculated as follows:

$$\rho_{z=30,T=230K} = \frac{p_{z=30}\, A_v}{RT} = \frac{(1200\ m^{-1}kgs^{-2})(6.02x10^{23}\ molecules)}{8.31\ m^2kgs^{-2}mol^{-1}K^{-1}(230\ K)}$$

$$\rho_{z=30,T=230K} = 3.78x10^{23}\ moleculesm^{-3} = 3.78x10^{17}\ moleculescm^{-3}$$

In sum, the kinetic rate constant in $cm^3molecule^{-1}s^{-1}$ units for reactions at stratospheric altitudes is calculated using Equation 6.5:

$$k(T) = (3.78x10^{17})\frac{k_B T}{h} e^{\frac{-\Delta G^{0,\ddagger}}{RT}} \quad (6.5)$$

6.3 Results and Discussion

6.3.1 Reactions 1-3: Major and Minor Stratospheric Hydrogen Sinks

The computational results are compared with experimental results, where available, with those of Presser and Gordon (1984), Röckmann *et al.*, (2003), and Sander *et al.* (2011), in Table 6.2. Tables 6.2 lists computed and experimental activation energies (E_a) for reactions 1 through 3 and also lists experimental and computed reaction rate constants that were determined free energy differences between products and transition state complexes. Computed values that differ more than a factor of 3 (i.e. >200%) with experimental values, where available, are not reported.

From Table 6.2, computational results for primary isotope effects (i.e. D-abstractions) are seen to be in good agreement with experimental values. Reactions 1b and 2b have small percent differences between theoretical and experimental rate constant values at 298K (and 230K, not listed). It is found that Reaction 1b shows an increasing isotope effect with decreasing temperature that suggests slower reaction rates for deuterated hydrogen with hydroxyl radicals, a main sink reaction for molecular hydrogen in the stratosphere. The reaction profile for Reaction 1 and 1b (primary isotope effect only) indicates a small difference in transition state energies that gives rise to the larger than unity KIE ratio (see Figure 6.4).

Isotope effects (i.e. H-abstraction) for Reaction 1b show, unexpectedly, an inverse KIE effect (albeit very small; KIE = 0.99). Secondary effects are mainly a result in changes in vibrational frequencies in the reactants and activated complexes and one would expect a small positive KIE with$1 < \frac{k_H}{k_D} < 1.68$. In fact, Table 6.2 shows that the computed rate constant for Reaction 1a differs by 51% with the experimentally obtained value. It is likely that, due to the involvement of H, quantum-mechanical tunneling is occurring at these relatively low temperatures, which is not captured in our computational results. One thus expects the experimental KIE to be somewhat larger (at least unity) than the computed value.

Table 6.2: Reaction rate Constants and KIEs Computed from Free Energy[69] Differences for Reactions 1-3 at 298K

Reaction		Ea (experimental) kcal/mol	Ea[70] (computed) kcal/mol	k (experimental) $cm^3 molecule^{-1}s^{-1}$	k (computed) $cm^3 molecule^{-1}s^{-1}$	% difference[71] from experimental	KIE (experimental)	KIE (computed)
1a	$H_2 + \bullet OH \rightarrow H_2O + H\bullet$	3.6	7.4	6.7×10^{-15}	3.97×10^{-15}	51%		
1b (H-abstraction)	$HD + \bullet OH \rightarrow H_2O + D\bullet$	4.3	7.4	n/a	3.98×10^{-15}	n/a		0.99
1b (D-abstraction)	$HD + \bullet OH \rightarrow HOD + H\bullet$	4.3	7.4[72]	4.0×10^{-15}	1.35×10^{-15}	99%	1.68	2.94
2a	$H_2 + O(1D) \rightarrow OH + H\bullet$	≈0	1.1	1.2×10^{-10}	2.4×10^{-6}	-200%		
2b (H-abstraction)	$HD + O(1D) \rightarrow OH + D\bullet$	n/a	1.2	n/a	1.97×10^{-6}	n/a	n/a	1.21
2b (D-abstraction)	$HD + O(1D) \rightarrow OD + H\bullet$	n/a	1.2	n/a	1.97×10^{-6}	n/a	1.00 (at 230K)	1.21
3a	$H_2 + Cl\bullet \rightarrow HCl + H\bullet$	4.5	*[73]	1.5×10^{-14}	8.88×10^{-57}	200%		
3b (H-abstraction)	$HD + Cl\bullet \rightarrow HCl + D\bullet$	n/a	*	n/a	1.17×10^{-37}			<<1
3b (D-abstraction)	$HD + Cl\bullet \rightarrow DCl + H\bullet$	n/a	*	n/a	3.59×10^{-57}			7.59

[69] Note that, approximately, 1 Ha = 2600 kJ/mol = 630 kcal/mol.

[70] Activation energies are included for illustration purposes only. Energies calculated with one quantum chemistry level of theory are not directly comparable to those calculated using a different level of theory.

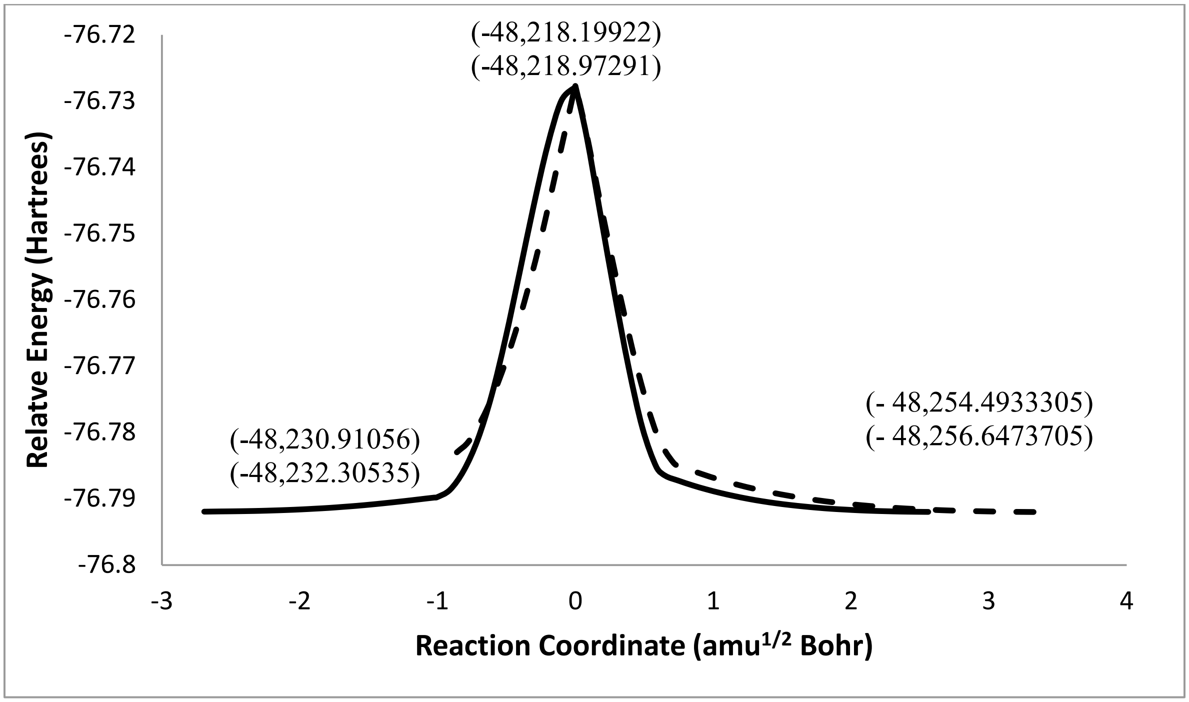
[71] The difference between two values divided by the average of the two values. Shown as a percentage.

[72] Differences in the activation energy values are found at the fifth decimal place.

[73] Computed activation is not reported. Values are too large to reflect accuracy in computational method used.

Figure 6.4: Reaction Profile for Reactions 1a and 1b[74,75]

$H_2 + \bullet OH \rightarrow H_2O + H\bullet$
$HD + \bullet OH \rightarrow HOD + H\bullet$



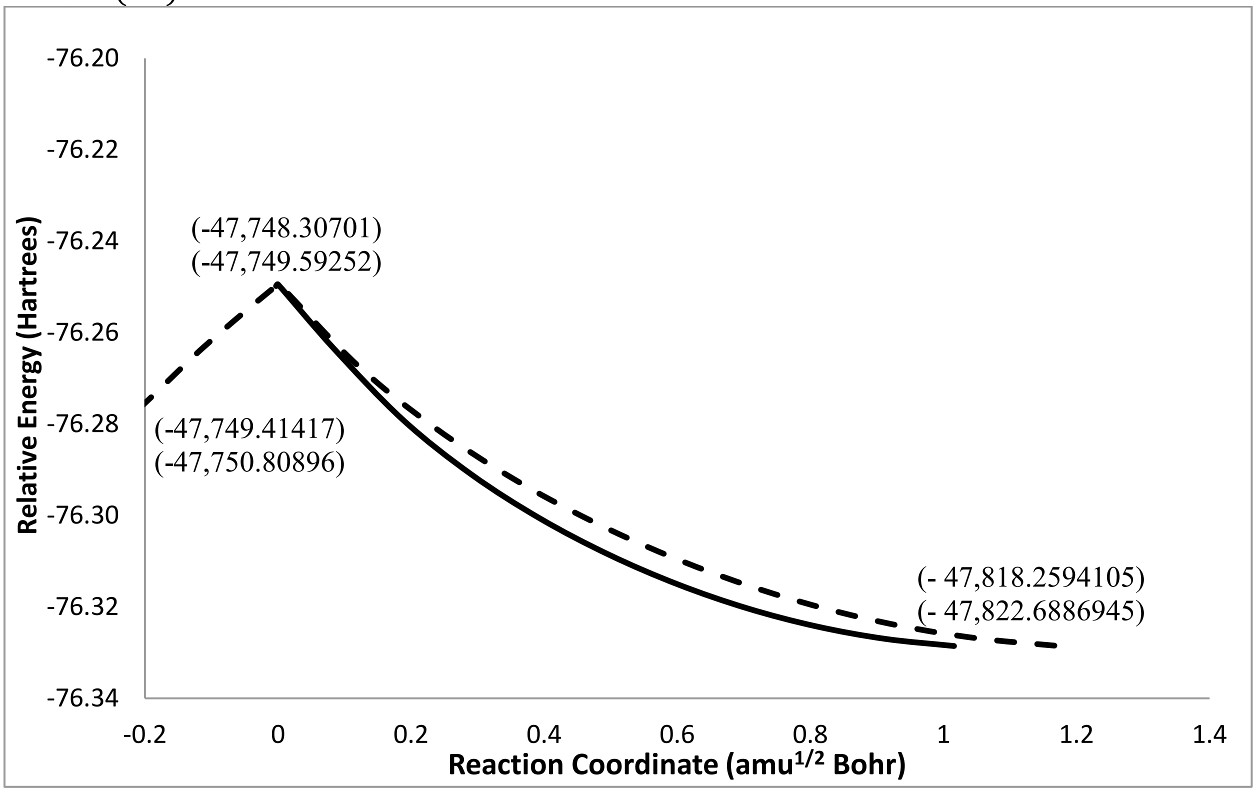
The results suggest that deuterium enrichment will have a small effect on the reaction rates of molecular hydrogen with the oxygen radical (Reaction 2) at either surface temperatures or stratospheric temperatures. KIEs calculated using kinetic constant ratio via changes in free energy show small isotope effects (KIE = 1.21). There is only a small difference in computed activation energies between Reaction 2a and 2b. Experimentally, this reaction reports an activation energy of approximately zero, implying a temperature-independent reaction. Our reaction profile for Reaction 2 also indicates a very small activation energy (1.1 kcal/mol) and a reaction profile that illustrates a relative fast reaction with lower energy products than reactants (Figure 6.5).

[74] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) profile.

[75] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

Figure 6.5: Reaction Profile for Reactions 2a and 2b[76,77]

$H_2 + O(1D) \rightarrow OH + H\bullet$
$HD + O(1D) \rightarrow OD + H\bullet$



Given the small KIE for Reaction 2 (H-abstraction), the D-abstraction KIE is, not unexpectedly, also small. This reaction coupled with Reaction 1, represents the main stratospheric hydrogen sink. The computed KIE value is in agreement with experimental rates reported for 230 K. The literature does not report KIEs for this reaction at 298 K. However, although Röckmann *et al.*, (2003) report no KIEs for monodeuterated hydrogen at 230 K, Presser and Gordon (1984) find KIEs of 1.6 and 1.7 for the reaction of hydrogen and O(^3P) at higher temperatures of 422.3 K – 471.7 K. Reaction 3 was found to exhibit increasing KIEs with decreasing temperature. As reported in Table 6.2, primary KIE ratio is 7.59 at 298 K. These results seem to be in agreement with theory. That is, in the absence of tunneling, isotope effects are mostly a result of zero-point

[76] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) reaction.
[77] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

energy differences, which vary approximately with the square roots of the reduced masses, depending on the size of the atoms to which H or D is being transferred. However, one refrains from drawing conclusions from rate constant results that show a 3-fold (200%) difference from experimental values. For this reason, the reaction profile for Reaction 3 is not reported. Computational methods can reproduce the experimental geometries with good accuracy; however, for some smaller polar systems, the computed values do not approach the experiment values as accurately as one would expect (Jursic, 2000). The computed rate constants for Reaction 3 are likely too small.

In sum, there are two major and one minor sinks for H_2, Reactions 1 and 2, that show KIEs for the first reaction and no or small KIEs for the second and third reactions. The available experimental results for the KIEs and kinetic rate constants for Reactions 1-3 are generally in good agreement with the various computational approaches used in our experiment. An increase in deuterated molecular hydrogen in the stratospheric may result in a marked change in the rate at which chlorine radical acts as a sink for H_2 producing the reservoir, HCl. However, the chlorine radical is minor H_2 sink. For the major H_2 sink reactions, a lack of a KIE for Reaction 2 with a small KIE for Reaction 1 may indicate that there would be some, albeit minor, effects from the deuterated products produced by Reaction 1b whereby a small increase in the concentration of hydroxyl radical and small decreases in $O(^1D)$may be possible. An increase in stratospheric hydroxyl radical can contribute to decreasing ozone concentrations and the removal of $O(^1D)$from the atmosphere slows the formation of ozone. In the tethered economy, hydrogen is produced in great quantities using steam reforming of methane and partial oxidation of hydrocarbon fuels. Thus, fossil fuel use and methane emissions from non-biogenic and biogenic sources would increase. An increase in methane would lead to a decrease in hydroxyl radical concentration, negating the effect of monodeuterated hydrogen discussed above. In fact, the United Nations Intergovernmental Panel on Climate Change (IPCC)/Montreal Protocol's Technology and Economic Assessment Panel (TEAP) (2005) concluded that the •OH concentration might change in the 21st century by –18 to +5% depending on GHG emission scenarios, and Revell *et al.* (2012) show that although increasing CH_4 concentrations increase the rate of reactive hydrogen-mediated ozone loss in the upper stratosphere, overall, increasing CH_4 concentrations leads to an increase in global-mean total column ozone.

The effect of deuterated methane is examined and discussed in the following section.

6.3.2 Reactions 4-6: Stratospheric Methane Oxidation

An increase in methane would negate the effect of monodeuterated hydrogen on ozone concentration. This is achieved through methane's reaction with the hydroxyl radical (Reaction 5). Methane, however, also reacts with atomic oxygen (Reaction 4) and the chlorine radical (Reaction 6). The latter reaction is an important radical reaction because it is the principal source of solid stratospheric HCl, which is absorbed on polar stratospheric cloud particles eventually releasing, through a series of other reactions, the chlorine radical which itself reacts with ozone leading to ozone's depletion[78]. Thus, the activation energies and examine the KIE effect of each methane reaction are determined, in turn. Note that the major source of ground state oxygen atoms in the stratosphere is photodissociation in the visible region of the electromagnetic spectrum. However, the photolysis of ozone results in excited atomic oxygen that is quenched to ground state O• upon collision with an air molecule such as N_2 or O_2. The quenching occurs very quickly, but there is enough O• to react with CH_4 (i.e. Reaction 4).

The geometry optimizations for the transition state structures were determined for Reactions 4, 5 and 6. The computational results for Reactions 4 and 5 are compared with those of Jursic (2000) who uses quadratic complete basis set (CBSQ) *ab initio* approach and where the geometry is optimized with MP2/6-31G(d'). The geometries are nearly identical to those presented in Jursic (2000). Comparing the rates of reactions with Sander *et al.* (2011) in Table 6.3 it is found that the rates for Reactions 4 and 5 are within reasonable limits to the experimentally reported rates.

---

[78] Solar absorption by ozone is a significant source of stratospheric warming. Depleted ozone levels thus delay the usual warmup of polar stratospheric clouds and leads to a prolonged ozone hole duration. Portmann and Solomon (2007) and Fleming *et al*. (2011) have shown that the predominant effect of increasing CH_4 is to increase total column ozone by way of H_2O induced stratospheric cooling in the middle stratosphere, which slows the temperature dependent gas-phase ozone loss cycles.

Table 6.3: Reaction rate Constants and KIEs Computed from Free Energy Differences for Reactions 4-6 at 298K

Reaction		Ea (experimental) kcal/mol	Ea (other computational studies[79])	Ea (computed) kcal/mol	k (experimental) $cm^3 molecule^{-1} s^{-1}$	k (computed) $cm^3 molecule^{-1} s^{-1}$	% difference[80] from experimental	KIE (experimental)	KIE (computed)
4a	$CH_4 + O(1D) \rightarrow \bullet CH_3 + \bullet OH$	0	7.3	7.87	1.31 x 10^{-10}	1.72 x 10^{-11}	153%		
4b (H-abstraction)	$CH_3D + O(1D) \rightarrow \bullet CH_2D + \bullet OH$	n/a		7.89	n/a	1.65 x 10^{-11}		n/a	1.04
4b (D-abstraction)	$CH_3D + O(1D) \rightarrow \bullet CH_3 + \bullet OD$			8.07	n/a	1.22 x 10^{-11}		n/a	1.41
5a	$CH_4 + \bullet OH \rightarrow \bullet CH_3 + H_2O$	3.55	2.1	11.51	6.3 x 10^{-15}	2.94 x 10^{-14}	-129%		
5b (H-abstraction)	$CH_3D + \bullet OH \rightarrow \bullet CH_2D + H_2O$	3.9 (includes both types of abstractions)	n/a	11.52	n/a	2.90 x 10^{-14}		n/a	1.01
5b (D-abstraction)	$CH_3D + \bullet OH \rightarrow \bullet CH_3 + HOD$		n/a	12.62	5.0 x 10^{-15}	4.19 x 10^{-15}	18%	1.26[81]	7.02
6a	$CH_4 + Cl \bullet \rightarrow \bullet CH_3 + HCl$	2.56		3.1	8.2 x 10^{-8}	*[82]	>200%		
6b (H-abstraction)	$CH_3D + Cl \bullet \rightarrow \bullet CH_2D + HCl$	2.76 (includes both types of abstractions)		28.0	8.8 x 10^{-27}	*	>200%		>>1
6b (D-abstraction)	$CH_3D + Cl \bullet \rightarrow \bullet CH_3 + DCl$			28.0		*	>200%		>>1

The percentage difference between the computed rate for Reaction 4a and the experimentally determined rate is 153%. There is no experimentally determined rate for Reaction 4b. Also, activation energies for Reaction 4a (7.87 kcal/mol) are comparable to those computed by Jursic (2000) (7.3 kcal/mol). The reaction profile, Figure 6.6, for Reactions 4a and Reaction 4b (D-abstraction) indicates a small, but notable primary isotope effect on the activation energy.

---

[79] Jursic (2000).

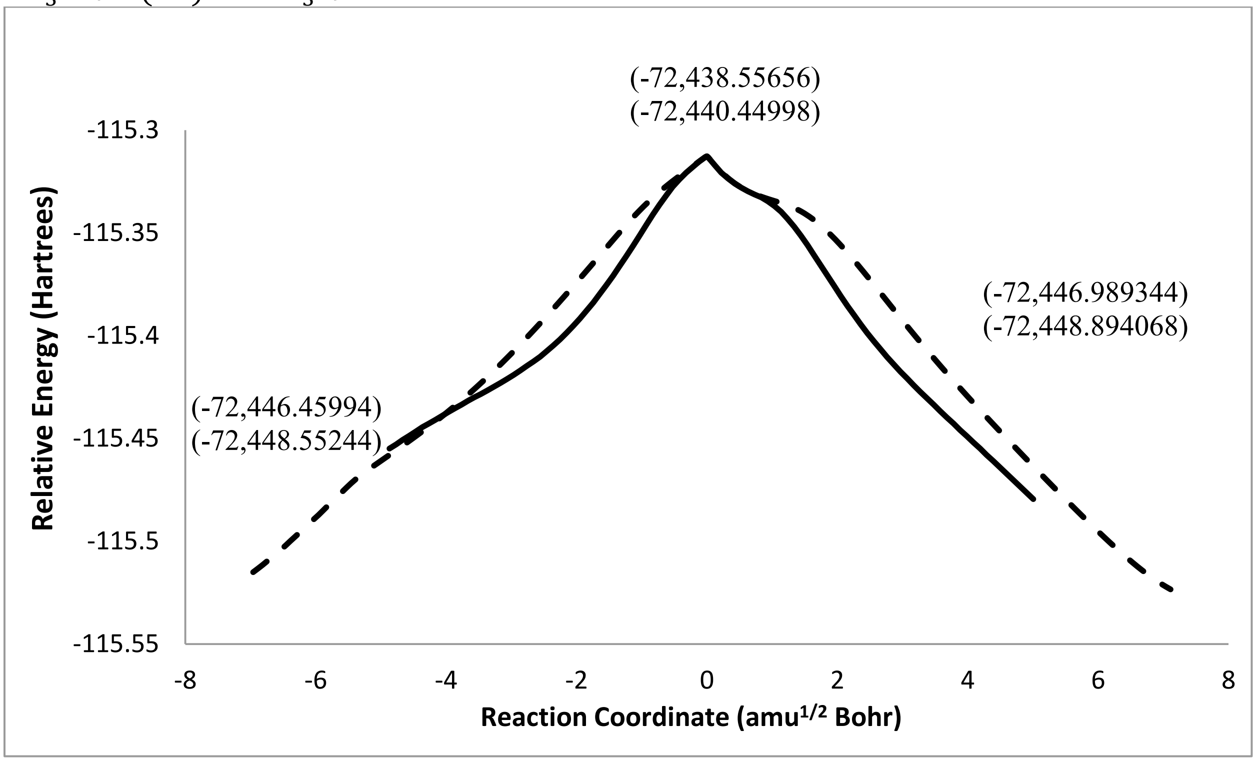
[80] The difference between two values divided by the average of the two values. Shown as a percentage.

[81] This KIE reported in Sander *et al.* (2011) does not specifically refer to primary isotope effects. Their reaction is more generally that that indicated in this study: $CH_3D + OH \rightarrow$ products.

[82] Computed activation is not reported. Values are too large to reflect accuracy in computational method used.

Figure 6.6: Reaction Profile for Reactions 4a and 4b [83,84]

$CH_4 + O(1D) \rightarrow \bullet\, CH_3 + \bullet\, OH$
$CH_3D + O(1D) \rightarrow \bullet\, CH_3 + \bullet\, OD$



The computed rate for Reaction 5a is less than that determined experimentally, but is within 129% of the experimental value. In contrast, the rate for the deuterated Reaction 5b (primary isotope effect) is within 18% of the experimental value. It is noted that for the reactions of methane with atomic oxygen and the hydroxyl radical, respectively, are hydrogen abstraction reactions in which the experimental errors are very high (Jursic, 2000) and the use of MP2 perturbation theory within the finite aug-cc-pVTZ produces results that reasonable approach the experimental values for Reactions 4 and 5.

Jursic and the literature[85] do not examine primary or secondary KIEs of monodeuterated methane at any temperature. Primary KIEs for Reaction 5 can be calculated using rate constants

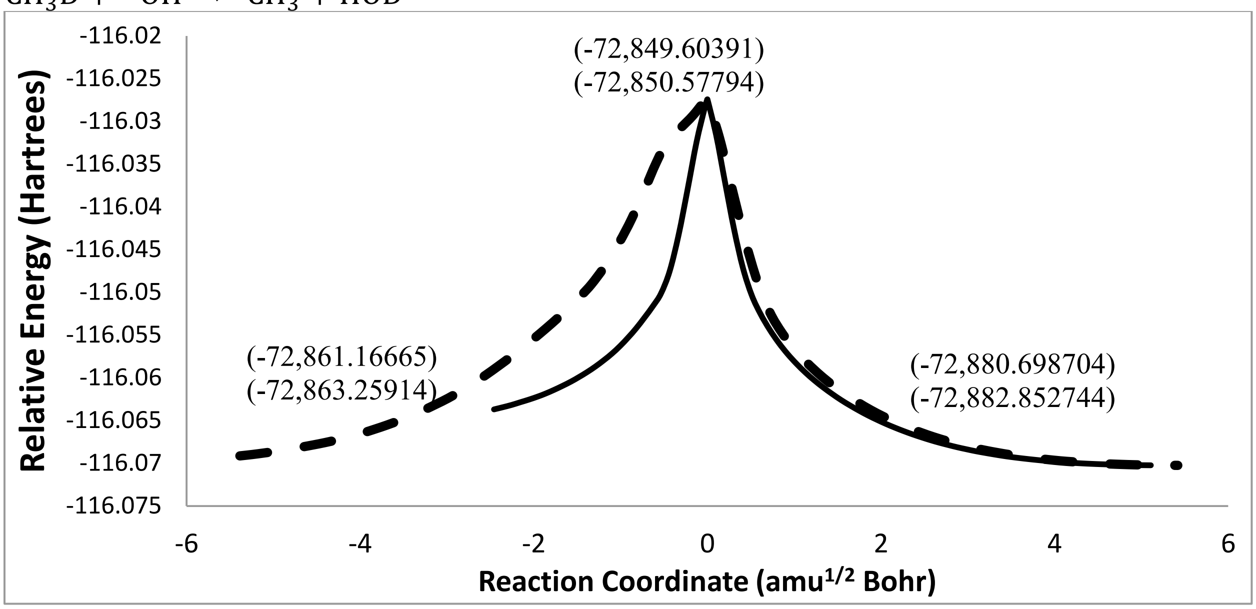
[83] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) reaction profile.

[84] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

from Sander *et al.* (2011). The computed primary KIE for Reaction 5 is 7.02, while that from *Sander et al.* (2011) is 1.26. This large difference can be explained by noting two issues: first, the computation rate of reaction for the non-deuterated reaction (i.e. Reaction 5a) is moderately slower than that reported experimentally, and second, the kinetic rate constant from Sander *et al.* (2011) is from a more general deuterated reaction; namely, $CH_3D + \bullet OH \rightarrow$ products, which includes both the faster H-abstraction (i.e. secondary KIE) and the slower D-abstraction (primary KIE). This is also illustrated in Figure 6.7 where the reaction profile profile for D-abstraction shows a slower rise to the activated complex than the non-deuterated reactants.

Figure 6.7 Reaction Profile for Reactions 5a and 5b [86,87]

$CH_4 + \bullet OH \rightarrow \bullet CH_3 + H_2O$
$CH_3D + \bullet OH \rightarrow \bullet CH_3 + HOD$



This study computes the primary KIE separately from the secondary KIE. It is found that H-abstraction by the hydroxyl radical from monodeuterated methane has little effect on the kinetics of the reaction (secondary KIE = 1.01). However, D-abstraction by the hydroxyl radical from

---

[85] To the extent of our knowledge, our literature review did not produce any studies that examine the KIE as described by Reaction 4b.

[86] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) reaction profile.

[87] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

monodeuterated methane has a relatively large effect on the kinetics of the reaction (primary KIE = 7.02). This implies that there would be a substantial decrease in the rate at which stratospheric methane would be consumed by the hydroxyl radical if the concentration of deuterated methane is largely increased due to a tethered hydrogen economy. Given that a large portion of stratospheric water vapour results from the oxidation of methane by the hydroxyl radical after methane has been transported from the troposphere to the stratosphere[88], one can theoretically have a decrease in water's mixing ratio in the stratosphere from the computed primary KIE. This primary KIE could positively affect the ozone concentration via decreased polar stratospheric cloud formation[89], albeit it would be a minor factor in ozone depletion relative to stratospheric chlorine loading.

This study is the first to report the computational determined primary and secondary KIEs for Reaction 4. Similar to the oxidation of methane by the hydroxyl radical in Reaction 5, primary and secondary isotope effects for the oxidation of methane by singlet oxygen are found. The effect is, however, less pronounced with Reaction 4 than it is with Reaction 5. The primary KIE (D-abstraction by singlet oxygen) is computed to be 1.41, while the secondary KIE (H-abstraction by radical oxygen) is computed to be 1.04. Hence, one would expect a small decrease in the rate at which stratospheric methane would be consumed by singlet oxygen if the concentration of deuterated methane is largely increased due to a tethered hydrogen economy. Consequently, there would also be a decrease in the concentration of •OH, a product of Reaction 4. Given that the product of Reaction 4 is the hydroxyl radical and that •OH is the oxidizing agent for methane in Reaction 5, one should expect a compounding effect in the reduction of H_2O production. This would cause a further decrease in water's mixing ratio in the stratosphere, thus conceivably reducing the formation of Type II polar stratospheric clouds. A reduction in Type II polar stratospheric clouds would lead to a less ozone destruction. All things equal, the

[88] The stratosphere, unlike the troposphere is quite dry. Tropospheric water vapour is caught in a 'cold trap', that is, tropospheric water would have to pass through very cold temperatures to reach the stratosphere and is thus mostly frozen out before reaching the stratosphere.

[89] There are two types of polar stratospheric cloud (PSC) particles. Type I PSCs are small HNO_3-rich particles and Type II PSCs particles, which are bigger and are composed mainly of H_2O-ice together with minor amounts of HNO_3 as hydrates, such as nitric acid dihydrate (HNO_3•H_2O) and nitric acid trihydrate (HNO3•3H2O). According to Holloway and Wayne (2010), it is generally established that all chlorine-activation reactions proceed more rapidly on Type II PSCs than they do on Type I PSCs.

net effect from this primary KIE (and that of Reaction 5) could lead to an increase in stratospheric ozone concentration.

It should be remarked, however, that Allen *et al.* (2013) note that TST-based computational methods give contradictory estimates of the KIE. According to Allen *et al.* (2013), the CVT/SCT and QI methods[90] overpredict the KIE, and the VTST-ISPE/SCT and CUS/μOMT methods[91] underpredict the KIE. The KIE of the seven-atom reactions •OH + CH_4 → •CH_3 + H_2O and •OH + CD_4 → •CD_3 + HDO over the temperature range 200 - 1000 K is investigated using ring polymer molecular dynamics (RPMD) by Allen *et al.* (2013) and they show that RPMD is a more reliable theoretical approach for systems with more than 6 atoms, which provides a predictable level of accuracy.[92]

This study's transition state geometry for Reaction 6 (i.e. $\mathrm{CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl}$) was found to be nearly identical to the optimized geometry present in Truong *et al.* (1989). However, our computed rates are slower in the absence of deuterated methane and faster in the presence of deuterated methane when compared to the experimental rates at low temperature. This is not altogether surprising using MP2 where our basis set places one *s,* one *d*, and one *p* diffuse functions on hydrogen atoms, and one *d*, one *p*, one *d*, and one *f* diffuse functions on Cl. In fact, Dobbs and Dixon (1994) find that the reaction rate for Reaction 6 calculated at the QCISD(T) and CCSD(T) levels with a modified correlation consistent basis set is low and the activation energy is too high compared to experimental values at low temperature, but reasonable agreement is found for T > 300 K. A comparison of our method with those used Dobbs and Dixon (1994) show similar computation results (i.e. a higher computed activation energy than that found experimentally). Truong *et al.* (1989) also conclude that it is necessary to use two *d* sets on Cl to achieve a fully polarized, correlation-balanced basis set for Reaction 6. Moreover,

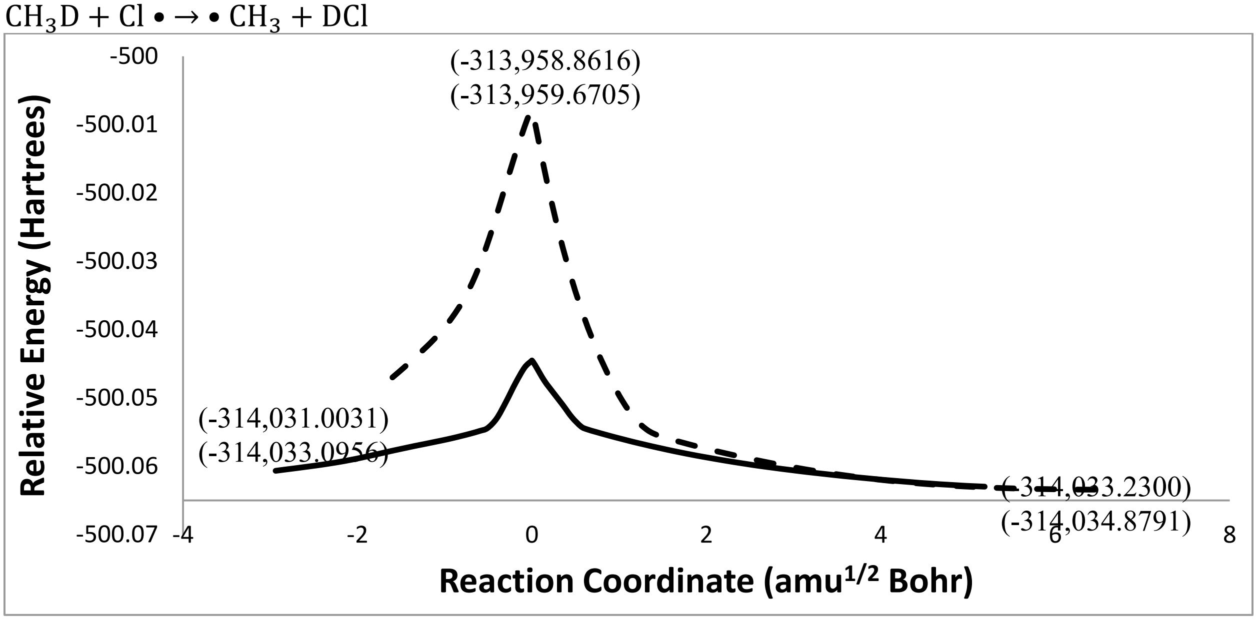
[90] CVT/SCT: The canonical variational transition (CVT) state theory method with small-curvature tunneling (SCT). QI methods: Quantum instanton methods.
[91] The treatment of loose transition states is based on variable-reaction-coordinate or variational transition state theory (VTST) with interpolated single-point energies (ISPE). CUS/μOMT: Coordinatively unsaturated sites (CUS) with microcanonical optimized multidimensional tunneling (μOMT).
[92] According to Allen et al. (2013), "… the success of RPMD is a direct result of its independence of the choice of transition state dividing surface, a feature that is not shared by any of the transition state theory-based methods. Our results demonstrate that RPMD is a prospective method for studies of KIEs for polyatomic reactions for which rigorous quantum mechanical calculations are currently impossible."

Chan and Radom (2012) find that the VTST+E approach yields the closest agreement with experimental rate constants for Reaction 6 and similar systems.

The reaction profile for this reaction (Figure 6.8) illustrates that the reaction is exothermic. The reaction proceeds with a higher activation energy when deuterium is present[93], as expected. A relatively high isotope effect for Reaction 6 implies that the rate of formation of the principal source solid stratospheric HCl would be reduced. A decrease in solid stratospheric HCl, which is absorbed on polar stratospheric cloud particles, would release smaller amounts of Cl_2 (upon reaction with another reservoir molecule present on PSCs, $ClONO_2$). Cl_2 photodissociates to form two chlorine radicals which, in turn, react with ozone. Thus, smaller amounts of stratospheric HCl may have a positive effect on stratospheric ozone concentrations.

Figure 6.8: Reaction Profile for Reactions 6a and 6b[94,95]

$CH_4 + Cl \bullet \rightarrow \bullet CH_3 + HCl$
$CH_3D + Cl \bullet \rightarrow \bullet CH_3 + DCl$



---

[93] Note that the reaction profile figure seems to imply a higher Ea for the non-deuterated reaction. However, the reaction coordinate is plotted against negative Ha energies. Therefore, it is the deuterated reaction that exhibits a larger activation energy.

[94] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) reaction profile.

[95] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

6.3.3 Reaction 7: Source of Stratospheric Chlorine Radical

The optimized transition state structure for Reaction 7 was determined using *Gaussian 09*. Computed measurements are found in Table 6.5. The key trait of the perturbed chemistry of the polar stratosphere is the conversion of reservoir compounds such as HCl, to catalytically active species such as Cl radical. In Reaction 7, hydrochloric acid reacts with the hydroxyl radical to form water and radical chlorine, for which HCl is the main reservoir for the Cl radical. Most of the chlorine in the stratosphere is held in the reservoir compounds hydrogen chloride and chlorine nitrate (Holloway and Wayne (2010)). Although Sander *et al.* (2011) report a rate constant of 7.8 x 10^{-13} $cm^3molecule^{-1}s^{-1}$ for Reaction 7, none is reported for the more stratospherically relevant temperature of 220 K. As well, the literature review did not produce any studies that examine the KIE of replacing H with D in the chlorine reservoir, hydrochloric acid. Furthermore, the optimized transition state using MP2 perturbation theory within the finite aug-cc-pVTZ is the first to be described computationally.[96]

The computational results for Reaction 7 shows a small decrease in the KIE with decreasing temperature. The KIE ratio is 4.3 at 298 K and 3.8 at 230 K. The kinetic rate constant results obtained from free energy changes show a 167% difference from experimental values. Thus, the computational method used is not inconsistent with established theory and is within reasonable limits if the one experimental value for which we have for comparison. However, the activation energies show a larger discrepancy than the rates constants (1 kcal/mol experimentally versus 10 kcal/mol computationally at 298 K). Once again, we note that for some smaller polar systems, the computed values do not approach the experiment values as accurately as one would expect (Jursic, 2000).

[96] To the extent of our knowledge, our literature review did not produce any studies that describe the transition state for Reaction 7 using MP2 perturbation theory within the finite aug-cc-pVTZ.

Table 6.4: Activation Energies, Reaction Rate Constants and KIEs for Reaction 7 at 298 K and 220 K

Reaction		Ea (experimental) kcal/mol	Ea (computed) kcal/mol	k (experimental)	k (computed)	% difference[97] from experimental	KIE (experimental)	KIE (computed)
298K								
7	$HCl + \bullet OH \rightarrow H_2O + Cl\bullet$	1.0	11.0	7.8 x 10^{-13}	6.9 x 10^{-14}	167%	n/a	
7 (with deuterium)	$DCl + \bullet OH \rightarrow HOD + Cl\bullet$	n/a	11.8	n/a	1.6 x 10^{-14}			4.3
220K								
7	$HCl + \bullet OH \rightarrow H_2O + Cl\bullet$	n/a	9.1	n/a	1.8x 10^{-12}		n/a	
7 (with deuterium)	$DCl + \bullet OH \rightarrow HOD + Cl\bullet$	n/a	9.9	n/a	4.8x 10^{-13}			3.8

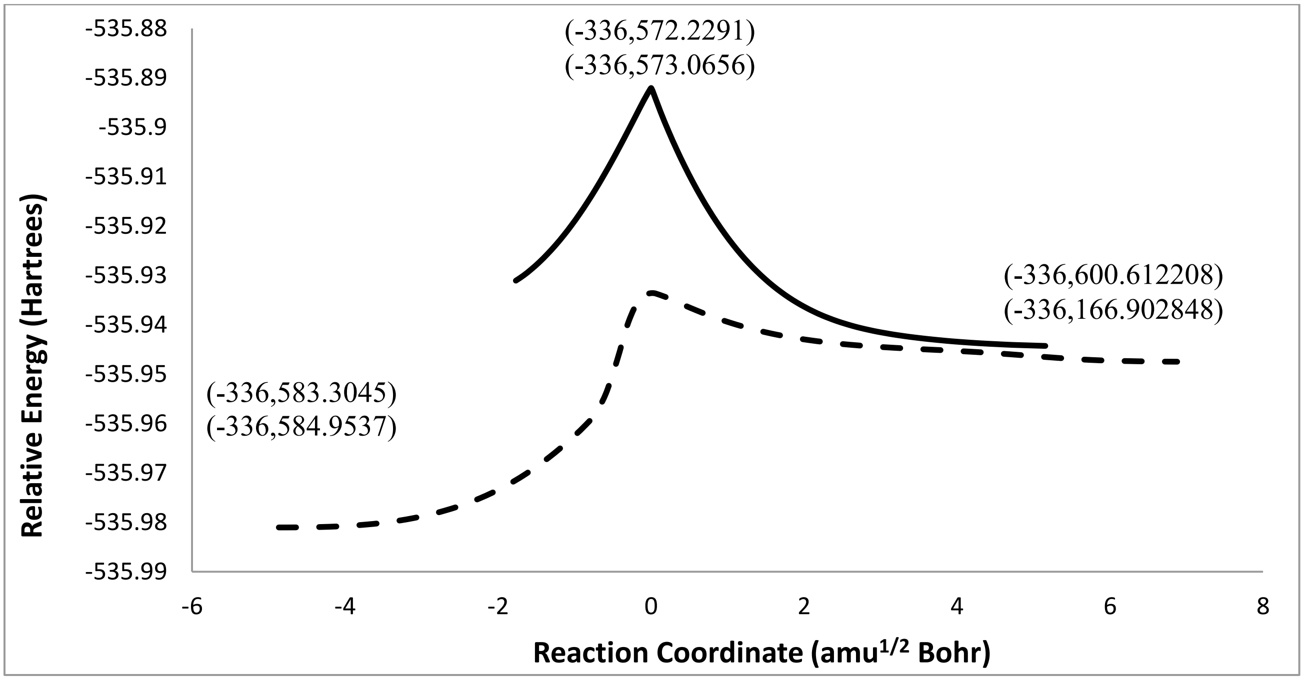
The reaction profile illustrates that the reaction is endothermic. The reaction proceeds with a higher activation energy when deuterium is present[98], as expected. The relatively large KIE for Reaction 7 at both temperatures investigated implies that increased deuterium content in the stratosphere from the transitory phase of a tethered hydrogen economy will, in theory, slow the rate at which HCl reacts with the hydroxyl radical by, approximately, a factor of four.

[97] The difference between two values divided by the average of the two values. Shown as a percentage.

[98] Note that the reaction profile figure seems to imply a higher Ea for the non-deuterated reaction. However, the reaction coordinate is plotted against negative Ha energies. Therefore, it is the deuterated reaction that exhibits a larger activation energy.

Figure 6.9: Reaction Profile for Reaction 7 at 298K[99,100]

$HCl + \bullet OH \rightarrow H_2O + Cl \bullet$
$DCl + \bullet OH \rightarrow DOH + Cl \bullet$



Given that the release of active chlorine from its reservoirs, HCl and $ClONO_2$ (chlorine nitrate) is generally slow (Holloway and Wayne, 2010), a slower rate of reaction with DCl in Reaction 7 increases the availability of hydrochloric acid and thus may increase the rate of reaction of the two reservoir molecules, which can react together on polar stratospheric cloud particles to produce chlorine gas and nitric acid: $HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$. As discussed in Section 6.3.2, the chemistry that occurs on polar stratospheric cloud particles contributes to ozone's depletion. Alteration of the kinetics of Reaction 7 may affect the manner in which this depletion occurs. That is, the increased presence of hydrochloric acid as a result of increased deuterium content increases the release molecular chlorine gas from the polar stratospheric cloud particles, which then photodissociates to two chlorine atoms (radicals) that react with ozone to form ClO and O_2.

[99] The solid line representing the reaction profile is in reference to the non-deuterated reaction. The broken line represents the deuterated reaction (D-abstraction) reaction profile.

[100] Numbers in parentheses along the reaction profile represent the free energies in kcal/mol for the reactants (the sum of both reactants), the activated complex, and the products (the sum of both products), respectively. The top number represents the energy for the non-deuterated reaction (i.e. the solid line), while the bottom number represents the energy for the deuterated reaction (i.e. the broken line).

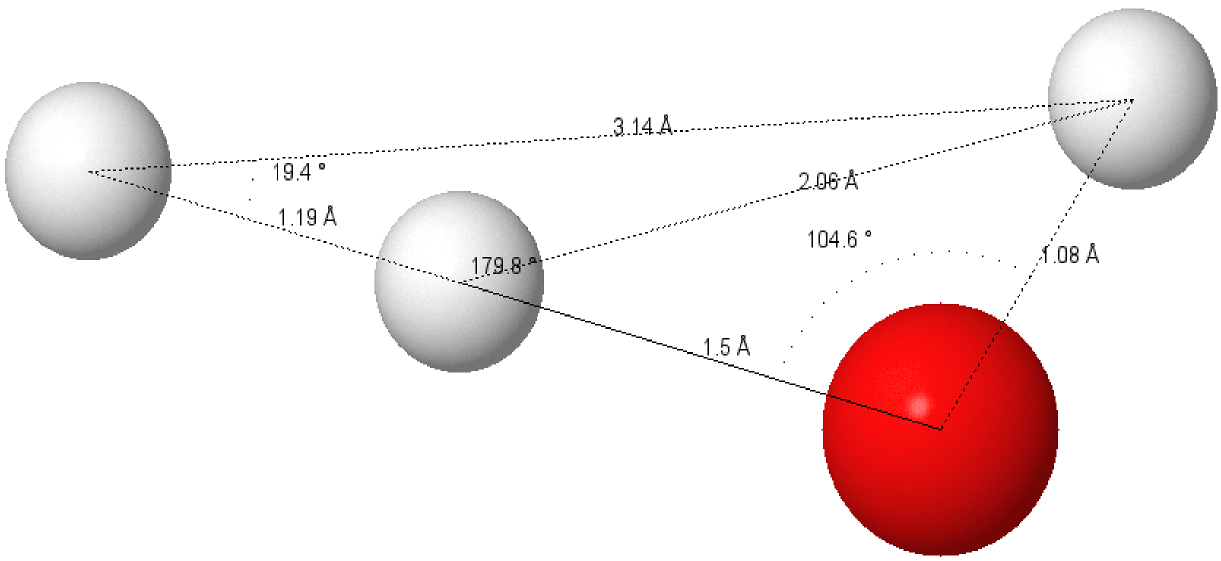
Although Reaction 7 has the chlorine radical as a reaction product and isotopic substitution of HCl by D slows the rate of reaction leading to less chlorine production over time, the ability of HCl/DCl and $ClONO_2$ reacting together on polar stratospheric cloud particles may actually increase the availability of chlorine radicals will lead to ozone depletion.

6.4 Conclusion

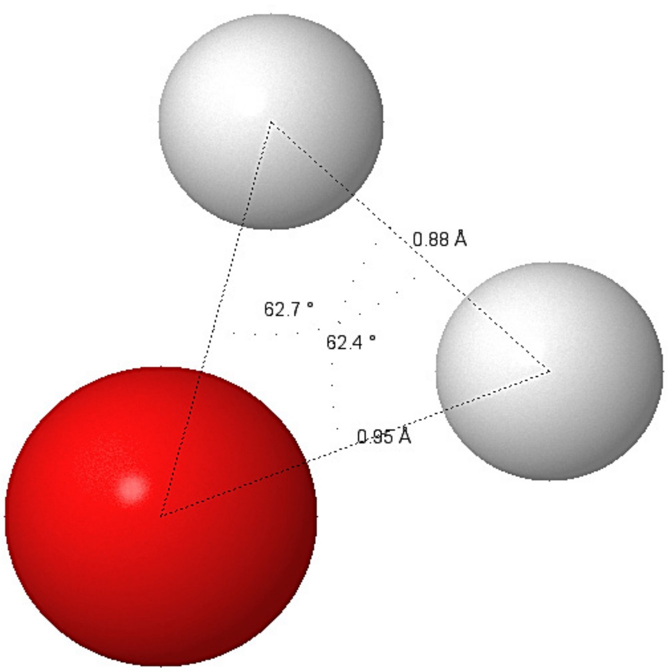
The KIEs for the various reactions examined indicate that stratospheric ozone concentration can be altered during the transitory phase to a hydrogen economy. In addition, this thesis is the first to report the computational determined primary and secondary KIEs for Reaction 4 and the first to examine the KIE of D in the chlorine reservoir: $\mathrm{DCl} + \bullet\mathrm{OH} \rightarrow \mathrm{DOH} + \mathrm{Cl}\bullet$. However, without further investigation, via kinetic Monte Carlo methods, the extent to which the concentration would be altered is uncertain. That is, (1) the small KIE for Reaction 2 may indicate a minor decrease in the concentration of ozone, (2) increased removal of $O(^1D)$ *can s*low the formation of ozone, and (3) an increase in stratospheric HD may slow the rate at which $\mathrm{Cl}\bullet$ acts as a sink (i.e. HCl) for H_2 (**more** O_3 destruction). Yet, results for CH_4 oxidation imply decreases in PSC formation and decreases in solid HCl , which would lead to **less** O_3 destruction.

Appendix IV: Transition State Structures

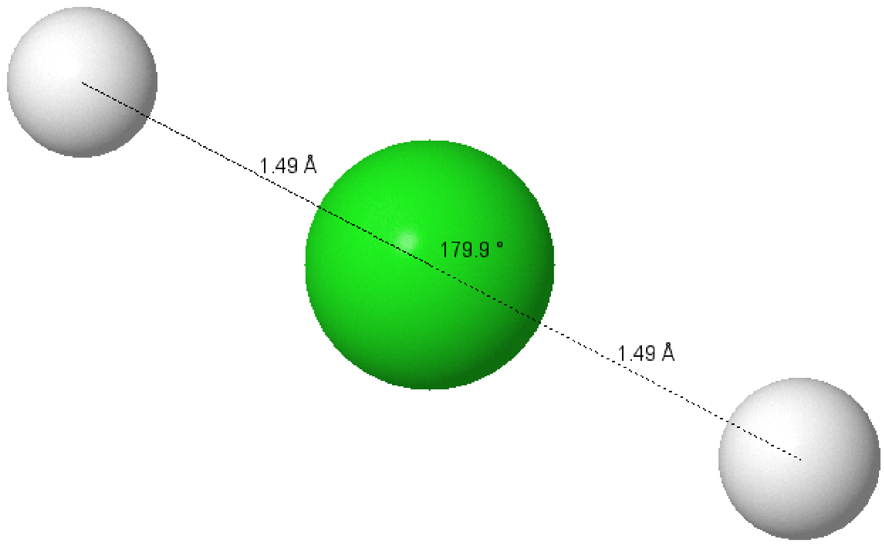
Reaction 1, TS Complex: DO-H



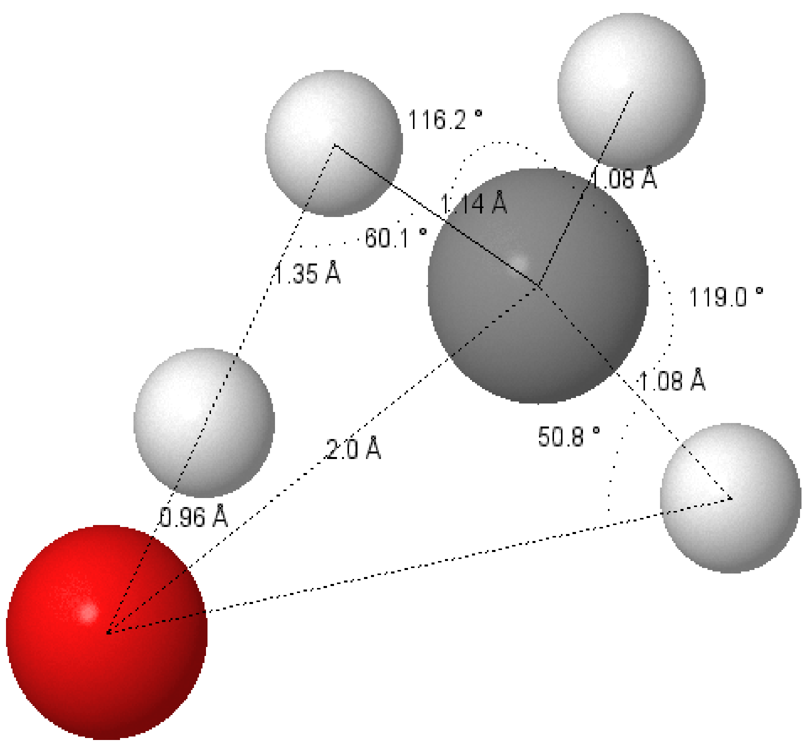
Reaction 2, TS Complex: DO-H



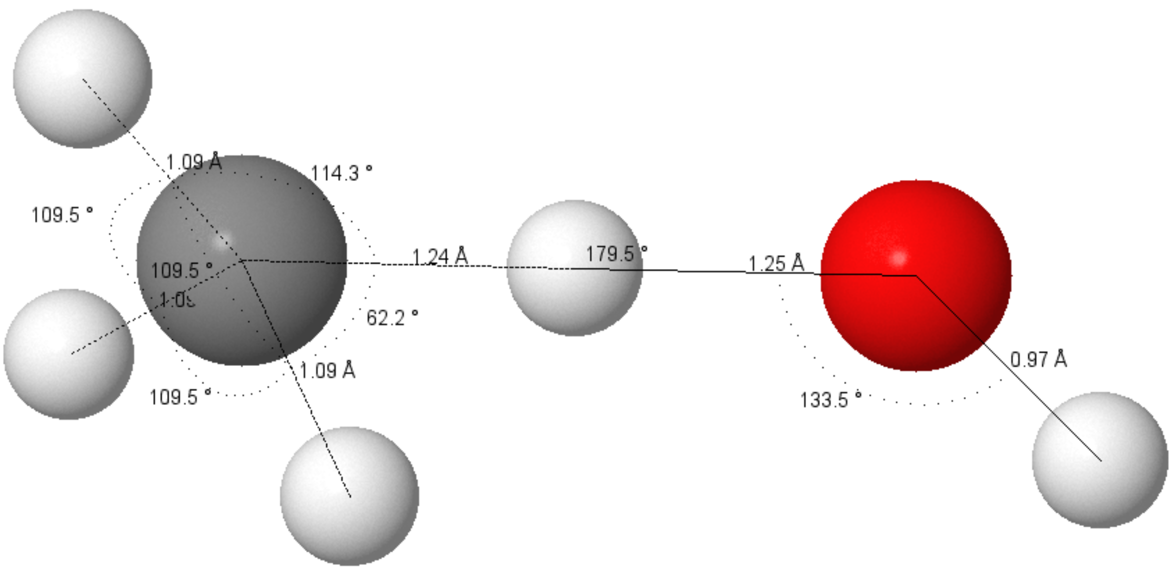
Reaction 3, TS Complex: HCl-H



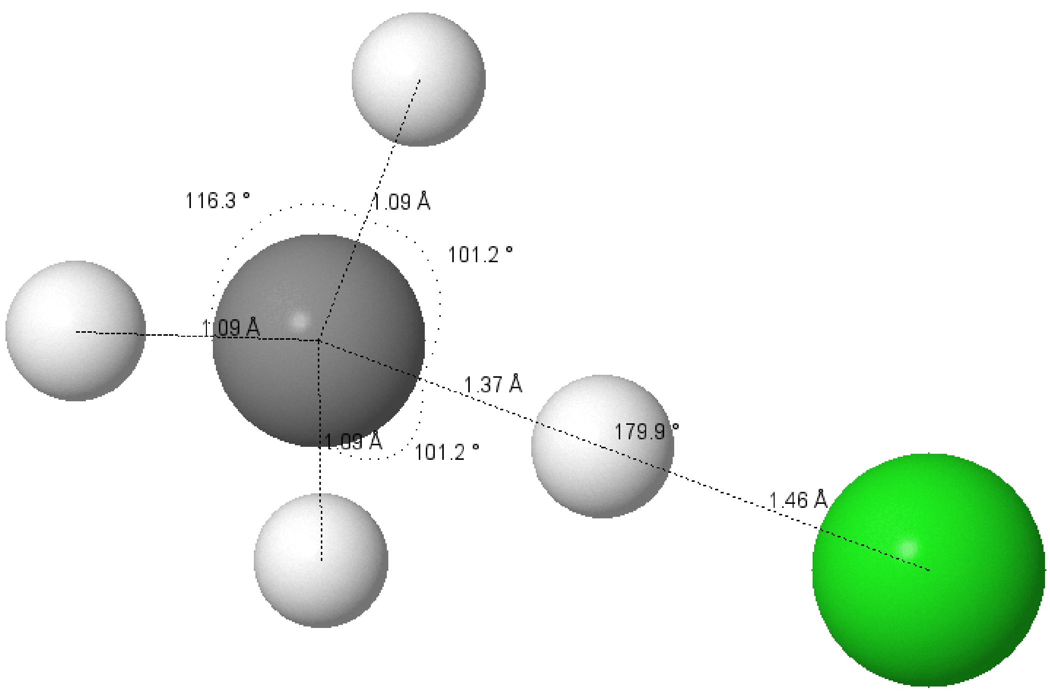
Reaction 4, TS Complex: H_3C-O-H



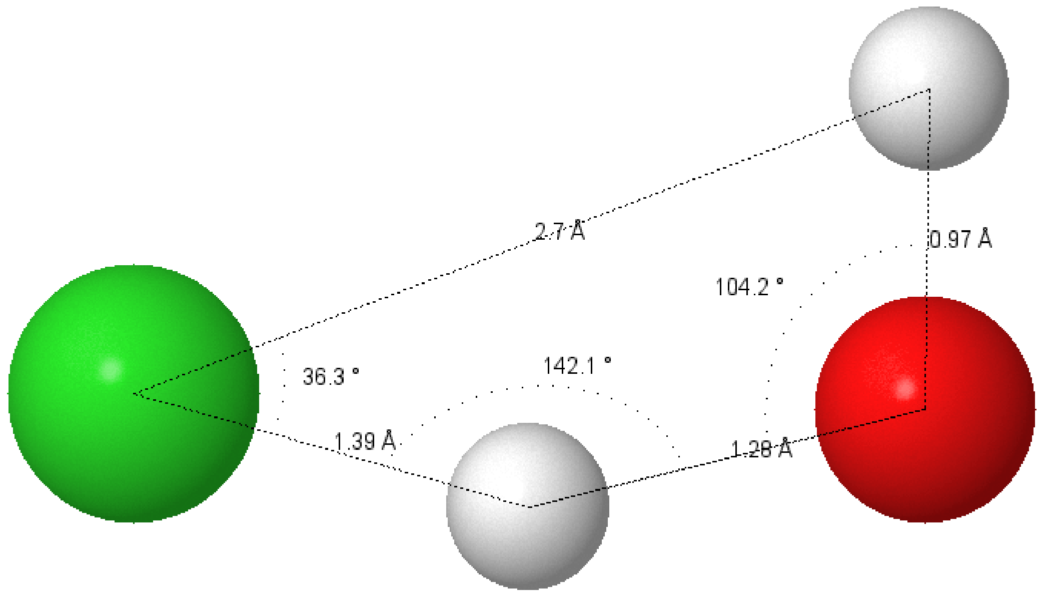
Reaction 5, TS Complex: H_2DC-H-OH



Reaction 6, TS Complex: H_3C-H-Cl



Reaction 7, TS Complex: Cl-D-OH



Chapter 7: Conclusion and Future Work

Many economic models on growth arrive at a similar conclusion that technology or innovations spur growth and sustain growth. In this respect, our model is no different. However, in other respects, this thesis' model predicts that once energy and technology are uniquely defined and thus separate factors, then both are required for sustained growth given some temporal relationship between them. The magnitude to which either energy or technology spur on economic growth, once we consider the biosphere, becomes important so as to determine whether the increase in growth can actually be sustained in the long-run. This economic growth modeling approach is distinctive because it puts strict conditions on the idea that no innovative society need accept Malthusian diminishing returns. At the other end of the spectrum, the BET model also makes it clear that it is not a foregone conclusion that current well-being is bought at the expense of future generations.

The model's main finding is that pervasive technology shocks lead to large increases in consumption, but in the absence of new GPESs or a late adoption of a new GPES, technology alone will not sustain economic growth because there may be an eventual collapse of the biosphere. Agents that are not fully myopic would avoid the collapse because they would trade current consumptions for future biosphere levels. This inter-temporal trade-off allows for greater time lags between GPT and GPES shocks. This additionally results in two different reallocations of labour resources. After a GPT shock, more labour resources move to the energy sector and away from consumption goods production and, after a GPES shock, labour resources move from the consumption sector to the energy knowledge sector. This result carries fundamental policy implications.

The BET model is unique in that it incorporates energy, technology and entropy as distinct factors that generate transitional competitive equilibria. It is also consistent with historical observations and it does not oppose the 'Stylised facts' introduced in Chapter 1. The model can benefit, however, from future work on endogenising both the technology and energy parameters. However, the nature of GPES diffusion in an economy needs to be explored, which could then be modeled in our framework to reduce improbable spikes in growth rates[101]. Full dynamic programming of our model is important tool for solving our model under uncertainty and can provide further policy insights.

The BET does not assume anything about technology or energy shocks. The numerical simulations show that there is only one GPT and GPES in existence at any one time. The same model can be used for any sequence of shocks. This approach is no different than what is presented by Lipsey *et al.*'s (2006) baseline model and by others in the GPT literature (e.g. Aghion and Howitt, 1992; Bresnahan and Trajtenberg, 1992; Helpman, 1998). Lipsey *et al.* (2005) present a full discussion of growth within a single GPT. It gives the growth process a homogeneous appearance, but it is somewhat removed from reality. Including arrival rates of GPTs and GPESs would introduce a source of randomness in our model and express a relationship between an incumbent GPT (or GPES) and a new GPT (or GPES) that challenges or replaces it. Lipsey *et al.* (2006) note that other authors have also introduced this randomness in their GPTs models; for example, "Helpman and Trajtenberg (1998) have GPTs arriving exogenously at predetermined intervals while Aghion and Howitt (1998) have GPTs arriving exogenously with a probability so small that they only consider the history of a single GPT. Aghion and Howitt (1998) have technologies arriving at a rate determined by a Poisson arrival process that is endogenously influenced by an instantaneous flow of labour services." Lipsey *et al.* (2006) themselves introduce a source of randomness where the amount of fundamental knowledge is generated by a given amount of resources, and they further introduce a random process to which the accumulation of applied knowledge is subjected. According to Lipsey *et al.* (2006), their GPT model, compared with most other types of endogenous growth models, has a balanced equilibrium growth path that is never reached and allows the recursive and imperfectly foresighted nature of the model makes it easier to allow for behavior that is more realistic but also more complex. Introducing randomness in this thesis' model and allowing GPT and GPES shocks to be endogenously determined is the scope of future work, which can make the model move closer to historically observed behaviours of GPT-GPES interactions. These are not

[101] Lipsey *et al.* (2005) suggest that GPT applications follow a logistic curve nature such that "each new GPT causes the productivity of applied R&D to rise slowly at first, then ever more rapidly, then finally slowing again as the GPT's possibilities are more or less fully exploited". The nature of GPES diffusion would add significantly to our model.

undertaken here because the main purpose of the thesis is to make the case for the simpler method of modelling GPT-GPES biosphere interactions over many centuries.

In addition, exogenous energy shocks in the BET model are a result of new energy sources that affect, in theory, all sectors of the economy. The BET model, for purposes of simplicity, does not simulate entropy reduction effects from small shocks that may arise from multiple, though non-GPES, energy adoptions that challenge the use of a current period's GPES. These small shocks may arise from adoption of various alternative energy sources (wind, geothermal, solar, etc.) that challenge the use of a current GPES (i.e. petroleum). However, these alternative energy sources are not themselves GPESs because they do not fit the definition provided herein and therefore the adoption and effect on consumption cannot be simulated using the current BET model. Future work on the incorporation of non-GPES energy shocks in the BET can provide further insight on resource allocation and whether the technology-energy race is at all altered.

Finally, although some of the parameters can be validated, notably those involving the biosphere, the BET model can benefit from measures of labour movement and distribution between energy-technology sectors and technology-only sectors. There are no statistics from national statistical agencies that make this distinction and, even if they did exist, there are no long-term historical series of such data. Analysis of labour mobility between these sectors during a GPT and/or GPES arrival can help determine the robustness of the energy-technology-biosphere model findings; otherwise, one needs to rely on comparisons to historical events. Furthermore, while the model predicts permanent movements of resources out of consumption goods sector to the technology and energy sectors after a GPES shock, empirical evidence is required to validate this prediction. Although the intention is to model both of these phenomena to add insight and form the work of future research, keeping the number of complications in the present model to a minimum allows us to make clear the basic behaviour of this unconventional model.

The historic interplay of GPT and GPES described in Chapter 2 implies that time spent on developing new ideas related to energy technologies, d_t^E, cannot be the sole contributor to the flow of knowledge in the energy sector and that time spent on developing new ideas related to non-energy technologies, d_t^G, plays a complementary and necessary role. In sum, non-energy knowledge (GPT sector) and energy knowledge (joint GPT-GPES sector) do not contribute equally in conveying technical progress. New energy knowledge needs to be embodied in new kinds of GPESs before it can be made effective.

This work clearly shows that the introduction of entropy in an economic growth model is best accomplished qualitatively and that new energy sources or carriers that promise reductions in entropy production need to be validated for their effect on the biosphere independently from their entropy reduction potential. Hydrogen, as a potential GPES, is evaluated under this notion; that is, in its potential effect on stratospheric ozone concentrations. This thesis is the first to report on KIEs for various stratospheric reactions at varying temperatures. In a scenario where our economy is a tethered hydrogen economy, it is found that an increase in deuterated molecular hydrogen in the stratospheric may result in a marked change in the rate at which chlorine radical acts as a sink for H_2 producing the reservoir, HCl, and that a small increase in the concentration of hydroxyl radical and can contribute to decreasing ozone concentrations. It is generally established that while mid- and lower-stratospheric ozone increases in response to increased CH_4, upper stratospheric ozone decreases due to an increase in the rate of the ozone-depleting hydrogen cycles (Revell, 2012). However, the KIE results for methane oxidation reactions imply that decreases in polar stratospheric clouds formation and decreased solid HCl are possible with a tethered hydrogen economy resulting in less ozone destruction.

While this theoretical study concludes that mono-deuterated molecular hydrogen and methane may not, in sum, contribute to appreciable stratospheric ozone loss and even have a net positive effect, future work on incorporating deuterium in more atmospheric ozone cycles is necessary. Verification of additional KIE on other ozone cycle reaction rates would permit the use of the kinetic Monte Carlo method to simulate the time evolution of the stratospheric reactions using the reaction rate constants derived at low temperature. Nevertheless, the study of the effects of increased (mono)deuterated molecular hydrogen and (mono)deuterated methane on the catalytic destruction of ozone by hydroxyl and chlorine radicals, and the predictions on the net effect on ozone are also complicated by the changes in •OH concentrations from rising GHGs.

REFERENCES

1. Aghion, P. and Howitt, P. (1992). A model of growth through creative destruction. *Econometrica,* 60, 323-351.

2. Allen, J. W., Green, W.H., Hua Guo, Y.L. and Suleimanov, Y.V. (2013). Communication: Full dimensional quantum rate coefficients and kinetic isotope effects from ring polymer molecular dynamics for a seven-atom reaction OH + $CH_4 \longrightarrow CH_3$ + H_2O. *Journal of Chemical Physics*, 138, dx.doi.org/10.1063/1.4811329.

3. Aoki, I. (1988). Entropy Flows and Entropy Productions in the Earth's Surface and in the Earth's Atmosphere. *Journal of the Physical Society of Japan*, 57, (9), 3262-3269.

4. Atkinson, R. (2003). Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes. *Atmos. Chem. Phys*., 3, 2233 –2307.

5. Balakrishnan, N. (2004). Quantum calculations of the $O(^3P) + H_2 \longrightarrow$ OH + H reaction. *Journal of Chemical Physics*, 212, (13), 6346-6351.

6. Balat, M. (2008). Potential importance of hydrogen as a future solution to environmental and transportation problems. *International Journal of Hydrogen Energy*, 33, 4013-4029.

7. Barnosky, A.D., Hadly, E.A., Bascompte, J., Berlow, E.L., Brown, J.H., Fortelius, M., Getz, W.M., Harte, J., Hastings, A., Marquet, P.A., Martinez, N.D., Mooers, A., Roopnarine, P., Vermeij, G., Williams, J.W., Gillespie, R., Kitzes, J., Marshall, C., Matzke1, N., Mindell, D.P., Revilla, E., Smith, A.B. (2012). Approaching a state shift in Earth's biosphere. *Nature*, 486, (7), 52-58.

8. Blanchard, O. (1981). Output, the stock market and interest rates. *American Economic Review*, 71, 132-143.

9. Blumenfeld, L.A. (1981). *Problems of Biological Physics*. Springer-Verlag: Berlin, Germany.

10. Bond, S.W., Gul, T., Reimann, S., Buchmann, B., and Wokaun, A. (2011). Emissions of anthropogenic hydrogen to the atmosphere during the potential transition to an increasingly H_2-intensive economy. *International Journal of Hydrogen Energy*, 36, 1122-1135.

11. Bond, S.W., Vollmer, M.K., Steinbacher, M., Henne, S., and Reiman, S. (2011). Atmospheric molecular hydrogen (H_2): observations at the high-altitude site Jungfraujoch, Switzerland. *Tellus*, 63B, 64-76.

12. Bresnahan, T., and Trajtenberg, M. (1995). General purpose technologies 'Engines of growth'? *Journal of Econometrics*, 65, 83-108.

13. Brock, W.A., and Taylor, M.S. (2010). The Green Solow Model. *Journal of Economic Growth*, 15, (2), 127-153.

14. Burnett, E.B., and Burnett, C.R. (1995). Enhanced Production of Stratospheric OH from Methane Oxidation at Elevated Reactive Chlorine Levels in Northern Midlatitudes. *Journal of Atmospheric Chemistry*, 21, 13-41.

15. Cantrell, C.A., Mauldin, L., Zondlo, M., Eisele, F., Kosciuch, E., Shetter, R., Lefer, B., Hall, S., Campos, T., Ridley, B., Walega, J., Fried, A., Wert, B., Flocke, F., Weinheimer, A., Hannigan, J., Coffey, M., Atlas, E., Stephens, S., Heikes, B., Snow, J., Blake, D., Blake, N., Katzenstein, A., Lopez, J., Browell, E.V., Dibb, J., Scheuer, E., Seid, G., and Talbot, R. (2003). Steady state free radical budgets and ozone photochemistry during TOPSE. *Journal of Geophysical Research*, 108, (D4), xxx-8361, doi:10.1029/2002JD002198.

16. Carlaw, K.I., Lipsey, R.G. (2006). GTP-Driven, Endogenous Growth. *The Economic Journal*, 116, 155-174.

17. Chan, B. and Radom, L. (2012). Approaches for Obtaining Accurate Rate Constants for Hydrogen Abstraction by a Chlorine Atom. *Journal of Physical Chemistry A*, 116, 3745−3752, dx.doi.org/10.1021/jp3007409.

18. Chen, M-D. Han, K-L. and Lou, N-Q. (2003). Theoretical study of stereodynamics for the reactions Cl + H_2/HD/D_2. *Journal of Chemical Physics*, 118, (10), 4463-4470.

19. Cleveland, C.J. and Ruth, M. (1997). When, where, and by how much do biophysical limits constrain the economic process? A survey of Nicholas Georgescu-Roegen's contribution to ecological economics. *Ecological Economics*, 22, 203–223.

20. Conrad, R. (1999). Soil Microorganisms Oxidizing Atmospheric Trace Gases (CH_4, CO, H_2, NO). *Ind. J. Microbiol.*, 39, 193-203.

21. Cottrell, F. (1955). *Energy and Society*. McGraw-Hill, New York.

22. Cox, R.A. (2011). Evaluation of laboratory kinetics and photochemical data for atmospheric chemistry applications. *Chemical Society Review*, DOI: 10.1039/c2cs35092k.

23. Denman, K.L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P.M., Dickinson, R.E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P.L., Wolfsy, S.C., and Zhang, X. (2007). Couplings Between Changes in the Climate System and Biogeochemistry. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Solomon, S.D., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

24. Derwent, R., Simmonds, P., O'Doherty, S., Manning, A., Collins, W., and Stevenson, D. (2006). Global environmental impacts of the hydrogen economy. *Int. J. Nuclear Hydrogen Production and Application*, 1, 57-67.

25. Diamond, J. (1999). *Guns, Germs, and Steel: The Fates of Human Societies*. W.W. Norton and Company, New York.

26. Diehl, R.A., and Mandeville, M.D. (1987). Tula and wheeled animal effigies in Mesoamerica. *Antiquity*, 61, (232), 239-46.

27. Dupuis, M., Fitzgerald, G., Hammond, B., Lester, W.A. Jr., and Schaefer, H.F. III. (1986). Theoretical study of the $H + O_3 \longleftrightarrow OH + O_2 \longleftrightarrow O + HO_2$ system. *Journal of Chemical Physics*, 84, (5), 2691-2697.

28. Easterly, W. and Levine, R. (2001). It's not factor accumulation: Stylized facts and growth models. *The World Bank Review*, 15, 177-219.

29. Eicher, T.S. and Turnovsky, S.J. (1998). Non-Scale Models of Economic Growth. *Mimeo* University of Washington.

30. Ehhalt, D.H., and Rohrer, F. (2009). The Tropospheric cycle of H_2: a critical review. *Tellus*, 61B, 500-535.

31. Ehrlich, P. (1968). *The Population Bomb*. Ballantine, New York.

32. Faber, M., Manstetten, R., Proops, J.L.R. (1996). *Ecological Economics: Concepts and Methods*. E. Elgar, Cheltenham, UK.

33. Fujii, N. (1982). An entropy model of environmental pollution economic growth. *Applied Mathematical Modelling*, 6, December, 431-435.

34. Galor, O., Weil, D. (2000). Population, technology, and growth. *American Economic Review*, 90, (4), 806– 828.

35. GaussView, **Version 5**, Roy Dennington, Todd Keith, and John Millam, Semichem Inc., Shawnee Mission, KS. (2009). Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven,

J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT.

36. Georgescu-Roegen, N. (1971). *The Entropy Law and the Economic Process*. Harvard University Press Cambridge, Massachusetts.

37. Georgescu-Roegen, N. (1976). *Energy and Economic Myths*. Pergamon, New York.

38. Georgescu-Roegen, N. (1977). The Steady-state and Ecological Salvation. *Bioscience*, 27, 266-270.

39. Georgescu-Roegen, N. (1986). The Entropy Law and the Economic Process in Retrospect. *Eastern Economic Journal*, 12, 3 - 23.

40. Gierczak, T., Talukdar, R.K., Herndon, S.C., Vaghjiani, G.L. and Ravishankara, A.R. (1997). Rate Coefficients for the Reactions of Hydroxyl Radicals with Methane and Deuterated Methanes. *Journal of Physical Chemistry A, 101,* 3125-3134.

41. Gößling, S. (2001). Entropy production as a measure for resource use: method development and application to metallurgical processes. *Ph.D. Dissertation*, zur Erlangung des Doktorgrades des Fachbereichs Physik der Universität Hamburg, Herford, Hamburg.

42. Ghosh, P., Hickey, K.J. and Jaffe, S.B. (2006). Development of a Detailed Gasoline Composition-Based Octane Model. *Ind. Eng. Chem. Res.* 45, 337 – 345.

43. Grossman, G.M. and Helpman, E. (1991). *Innovation and growth in the global economy*. MIT Press, Cambridge, MA.

44. Helpman, E., (1992). Endogenous macroeconomic growth theory. *European Economic Review*, 36, 237-267.

45. Holloway, A.M. and Wayne, R.P. (2010). *Atmospheric Chemistry*. The Royal Society of Chemistry Publishing, Cambridge, UK.

46. Hongyi, H., Dibble, T.S., Tyndall, G.S., and Orlando, J.J. (2012). Temperature-Dependent Branching Ratios of Deuterated Methoxy Radicals (CH_2DO•) Reacting With O_2. *Journal of Physical Chemistry A*, 116, 6295−6302, dx.doi.org/10.1021/jp211873w.

47. Hwang, D-Y. and Mebel, A.M. (1998). *Ab initio* study on the reaction mechanism of ozone with the chlorine atom. *Journal of Chemical Physics*, 109, (24).

48. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/

49. Johnson H., and Kinnison, D. (1998). Methane photooxidation in the atmosphere: Contrast between two methods of analysis. *Journal of Geophysical Research*, 103(D17), 21 967- 21 984.

50. Jones, C.I. (1995). R & D-Based Models of Economic Growth. *Journal of Political Economy*, 103, (4), 759-784.

51. Jones, C. I. (1998). *Introduction to Economic Growth*. W.W. Norton and Company, New York.

52. Jones, L.E. and Manuelli, R.E. (1997). The Sources of Growth. *Journal of Economic Dynamics and Control,* 21, 75-114.

53. Jursic, B.S. (2000). Computing transition state structure and estimating reaction barriers with complete basis set *ab initio* method. *Journal of Molecular Structure (Theochem*), 499, 223–231.

54. Kümmel, R. (1989). Energy as a factor of production and entropy as a pollution indicator in macroeconomic modelling. *Ecological Economics*, 1, (2), 161-180.

55. Lahankar, S.A., Zhang, J., McKendrick, K.G., and Minton, T.K. (2013). Product-state-resolved dynamics of the elementary reaction of atomic oxygen with molecular hydrogen, $O(^3P) + D_2 \longrightarrow OD(X^2\Pi) + D$. *Nature Chemistry*, 5, 315-319.

56. Laidler, K.J. (1987). *Chemical Kinetics, Third Edition*. HarperCollinsPublishers, Inc., New York.

57. Lipsey, R.G., Carlaw, K.I., Bekar, C.T., (2005). *Economic Transformations: General Purpose Technologies and Long-term Economic Growth*. Oxford University Press, Oxford.

58. Lipsey, R.G., Carlaw, K.I. (2006). GTP-Driven, Endogenous Growth. *The Economic Journal*, 116, 155–174.

59. Lucas, R.E., (1988). On the mechanics of economic development. *Journal of Monetary Economics*, 22, (1), 3-42.

60. Maddison, A. (2006). *The World Economy (Volume 2): Historical Statistics*. OECD, Paris.

61. Martyushev, L.M. (2013). Entropy and Entropy Production: Old Misconceptions and New Breakthroughs. *Entropy*, 15, 1152-1170.

62. Maugeri, L. (2006). *The Age of Oil: The Mythology, History, and Future of the World's Most Controversial Resource*. Praeger Publishers, Westpoint.

63. Meadows, D.H., Meadows, D.L., Randers, J., Behrens, W.W. (1972). *The Limits to Growth*. Universe Books, New York.

64. Melissas, V.S. and Truhlar, D.G. (1993). Deuterium and carbon-13 kinetic isotope effects for the reaction of OH with CH_4. *Journal of Chemical Physics*, 5, 3542-3552.

65. Mokyr, J. (1998). *The political economy of technological change: Resistance and innovation in economic history,* In: *Technological Revolutions in Europe: Historical Perspectives* (eds. Berg, M., and Bruland, K.). Edward Elgar, Cheltenham.

66. Mokyr, J. (2005). *Chapter 17: Long-Term Economic Growth and the History of Technology*, In: *Handbook of Economic Growth, Volume 1B,* (eds. Aghion, P. and Durlauf, S.N.). North-Holland, Amsterdam.

67. Mokyr, J. (2005). The intellectual origins of modern economic growth. *Journal of Economic History*, 65, (2), 285-351.

68. Moser, P., and Tom, N. (2004). Was Electricity a General Purpose Technology? Evidence from Historical Patent Citations. *American Economic Review, Papers and Proceedings*, 94, (2), 388-394.

69. Mrotzek, M. (2011). Approaching the tipping point: critical transitions in systems. Mimeo University of Graz.

70. Muhyedeen, B.R.J. (2007). DFT and *Ab Initio* Study of the Mechanism of Ozone Reaction with Light Hydrocarbons in the Troposphere. *European Journal of Scientific Research*, 16, (4), 490-505.

71. Müller, I. (2007). *A History of Thermodynamics: The Doctrine of Energy and Entropy*. Springer-Verlag Berlin, Heidelberg.

72. Ockwell, D.G. (2008). Energy and economic growth: Grounding our understanding in physical reality. *Energy Policy*, 36, 4600-4604.

73. Peixoto, J.P., Oort, A.H., De Almeida, M., Tome, A. (1991). Entropy Budget of the Atmosphere. *Journal of Geophysical Research*, 96, (D6), 10981-10988.

74. Peter, M and van den Bergh, J.C.J.M. (2001). Evolutionary Economic Theories of Sustainable Development. *Growth and Change*, 32,110-134.

75. Phillips, P.C.B. (2003). Challenges of trending time series econometrics. *Conference paper,* MODSIM, Townsville.

76. Pomeranz, K. (2000). *The Great Divergence: China, Europe, and the Making of the Modern World Economy*. Princeton University Press, Princeton, NJ.

77. Porter, M.E., and van der Linde, C. (1995). Toward a new conception of the environment-competitiveness relationship. *Journal of Economic Perspectives*, 9, 97–118.

78. Presser, N. and Gordon, R.J. (1985). The kinetic isotope effect in the reaction of O(^3P) with H_2, D_2, and HD. Journal of Chemical Physics, 82, (3), 1291-1297.

79. Proops, J. and Arons, J.D.S. (2006). *Chapter 3: Thermodynamics of Joint Production Joint Production and Responsibility*, In: *Ecological Economics on the Foundations of Environmental Policy* (eds. Baumgärtner, S., Faber, M., Schiller, J.). Edward Elgar Publishing Limited, Cheltenham, UK.

80. Revell, L.E., Bodeker, G.E., Huck, P.E., Williamson, B.E., and Rozanov, E. (2012). The sensitivity of stratospheric ozone changes through the 21st century to N_2O and CH_4. *Atmospheric Chemistry and Physics Discussions*, 12, 17583–17605, doi:10.5194/acpd-12-17583-2012.

81. Reynolds, D. (1994). Energy Grades and Economic Growth. *Journal of Energy and Development*, 19, (2), 245-264.

82. Richard, M. (2012). *SuperFuel: Thorium, the Green Energy Source for the Future*. Palgrave Macmillan, New York.

83. Röckmann, T., Walter, S., Bohn, B., Wegener, R., Spahn, H., Brauers, T., Tillmann, R., Schlosser, E., Koppmann, R., Rohrer, F. (2009). Isotope effect in the formation of H_2 from H_2CO studied at the atmospheric simulation chamber SAPHIR. *Atmospheric Chemistry and Physics Discussions*, 9, 25187-25212.

84. Rogers, S., Wang, D. and Kuppermann, A. (2000). Chemically Accurate *ab Initio* Potential Energy Surfaces for the Lowest 3A' and 3A'' Electronically Adiabatic States of $O(^3P) + H_2$. *Journal of Physical Chemistry A*, 104*,* 2308-2325.

85. Romer, P.M. (1986). Increasing returns and long run growth. *Journal of Political Economy*, 944, 1002-1037.

86. Romer, P. (1990). Endogenous technological change. *Journal of Political Economy*, 98, 71-102.

87. Romm, J.J. (2015). *The Hype About Hydrogen: Fact and Fiction in the Race to Save the Climate*, Island Press, 2015.

88. Rondo, C. (1989). *A Concise Economic History of the World*, Cambridge: Cambridge University Press, 1989.

89. Rosen, M.A. and Scott, D.S. (2003). Entropy production and exergy destruction: Part II—illustrative technologies. *International Journal of Hydrogen Energy*, 28, 1315-1323.

90. Ruth, M. (2007). Entropy, Economics, and Policy. *Forschungszentrum Nachhaltigkeit Nr.*, 140.

91. Sachs, J.D. (2005). *The End of Poverty*. The Penguin Press, 2005.

92. Sala-i-Martin, X. (1990). Lecture notes on economic growth (I) and (II): Five prototype models of endogenous growth. *NBER working paper*, 3563-3564.

93. Sander, S. P., J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin and P. H. Wine (2011). Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17. *JPL Publication* 10-6, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov.

94. Schultz, M.G., Diehl, T., Brasseur, G.P., and Zittel, W.N. (2003). Air Pollution and climate forcing impacts of a global hydrogen economy. *Science*, 302, 624-627.

95. Schumpeter, J. (1942). *Capitalism, Socialism, and Democracy*. Harper & Bros., New York.

96. Schwartzman, D. (1996). Solar Communism. *Science & Society*, 60, (3), 307-331.

97. Schwartzman, D. (2008). The Limits to Entropy: the Continuing Misuse of Thermodynamics in Environmental and Marxist Theory. *Science & Society*, 72, (1), 43-62.

98. Scott, D.S. (2007). *Smelling Land: The Hydrogen Defence Against Climate Catastrophe*. Canadian Hydrogen Association.

99. Seinfeld, J.H. and Pandis, S.N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Second Edition*. John Wiley & Sons, Hoboken, New Jersey.

100. Scheiner, S. (2000). Review: Calculation of isotope effects from first principles. *Biochimica et Biophysica Acta,* 1458, 28-42.

101. Shinnar, R. (2004). The mirage of the H2 economy. *Clean Technologies and Environmental Policy*, 6, 223–226.

102. Smil, V. (1994). *Energy in World History*. Westview Press, Boulder, CO.

103. Solow, R. (1956). A contribution to the theory of economic growth. *Quarterly Journal of Economics*, 70, 65-94.

104. Sovacool, B.K., and Brossmann, B. (2010). Symbolic convergence and the hydrogen economy. *Energy Policy*, 38, 1999-2012.

105. Tainter, J.A. (1988). *The Collapse of Complex Societies*. Cambridge University Press, Cambridge.

106. Tromp, T., Shia, R.L., Allen, M., Eiler, J.M., Yung, Y.L. (2003). Potential environmental impact of a hydrogen economy on the stratosphere. *Science,* 300, 1740-1742.

107. Truong, T.N. and Truhlar, D.G. (1989). Transition state structure, barrier height, and vibrational frequencies for the reaction $Cl + CH_4 \rightarrow CH_3 + HCl$. Journal of Chemical Physics, 90, (12), 7137-7142.

108. Truong, T.N. and Truhlar, D.G. (1990). *Ab initio* transition state theory calculations of the reaction rate for $OH + CH_4 \rightarrow H_2O + CH_3$. *Journal of Chemical Physics*, 93, (3), 1761-1769.

109. Tsai, W.C. and Hu, W-P. (2013). Theoretical Analysis on the Kinetic Isotope Effects of Bimolecular Nucleophilic Substitution (SN2) Reactions and Their Temperature Dependence. *Molecules*, 18, 4816-4843, doi:10.3390/molecules18044816

110. Van Nes, E.H. and Scheffer, M. (2007). Slow Recovery from Perturbations as a Generic Indicator of a Nearby Catastrophic Shift. *The American Naturalist*, 169, (6), 738-747.

111. Warwick, N.J., Bekki, S., Nisbet, E.G., and Pyle, J.A. (2004). Impact of a hydrogen economy on the stratosphere and troposphere studied in a 2-D model. *Geophysical Research Letters*, 31, L05107.

112. Weiss, W. (1996). The Balance of entropy on earth. *Continuum Mechanics and Thermodynamics*, 8, 37-51.

113. Weil, D.N. (2013). *Introduction to Economic Growth, Third Edition*. Prentice Hall.

114. Yu, H-G. and Nyman, G. (1999). Reaction dynamics of chlorine atom with methane: Dual-level ab initio analytic potential energy surface and isotope effects. *Journal of Chemical Physics*, 111, (15), 6693-6704.

115. Van den Berg, H. (2000). *Economic Growth and Development*. McGraw Hill Irvin.