MQP-JW1-0609

COMPETING MERCURY AND OZONE REACTIONS IN THE STRATOSPHERE

A MAJOR QUALIFYING PROJECT REPORT:
SUBMITTED TO THE FACULTY
OF
WORCESTER POLYTECHNIC INSTITUTE
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF BACHELOR OF SCIENCE

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DATE: FEBRUARY 29, 2008

TABLE OF CONTENTS

TABLE OF TABLES

TABLE OF FIGURES

ABSTRACT

The depletion of the ozone layer has been a topic of study and concern since the 1980's. Halogen free radicals caused by chlorofluorocarbons (CFC's) in the stratosphere are the main contributors to ozone depletion. It was recently discovered that mercury is stable enough and has a long enough residence time to accumulate in the lower stratosphere. It has also been found that mercury reacts with halogen free radicals in the atmosphere in much of the same manner as ozone, oxidizing in the presence of various species involved in cyclic chemistries that deplete ozone and create mercury salts that precipitate. The purpose of this study is to determine if it is possible for mercury to effect ozone depletion in the lower stratosphere. By comparing rate constants and thermochemical properties of several mercury-halogen, and ozone-halogen reactions it will be possible to establish if competition with the halogen free radicals is possible between the two species. In-depth studies of ozone chemistry and mercury reactions will be necessary to determine how mercury can effect ozone depletion.

CHAPTER 1: INTRODUCTION

The depletion of the ozone layer has been a topic of concern since the 1980's when a visible hole in the ozone layer was discovered above the arctic regions of the earth. The main cause of this depletion was determined to be due to the chlorofluorocarbon accumulation occurring in the stratosphere since the 1930's. It is well-accepted that catalytic reactions of species such as HFCs and CFCs with polar stratospheric clouds release reactive halogen radicals that then react with ozone. Through investigations of ozone depletion it has been discovered that at certain times of the year ozone diminishes, and at other times ozone regenerates. This process was originally explained by the fact that ozone and halogen free radical reactions are photochemically-activated; however, a recent study shows that the breakdown of chlorine radicals in the stratosphere is an order of magnitude lower than originally thought[23]. This means that some other type of mechanism must be occurring to affect the depletion and regeneration. This investigation proposes that mercury reactions with halogen free radicals may affect ozone depletion.

Understanding mercury's role in the atmosphere requires an understanding of its origin. Although elemental mercury can be released through natural sources such as forest fires, ocean vents and volcanoes, it can also be released from anthropogenic sources such as coal combustion, waste incineration, and crematoria. The combustion of coal generates flue gases and coal combustion residues (CCRs) such as fly ash, bottom ash, slag, and wet flue gas desulphurization (FGD) scrubber sludge. As combustion occurs, elemental mercury and a limited number of mercury compounds such as mercuric chloride are emitted into the atmosphere through these flue gases. Many mercury control devices have been established to reduce the amount of mercury that is able to enter the atmosphere and redirect the mercury deposits into the CCRs. In direct correlation to coal combustion, forest fires can be a large contributor of mercury emission into the atmosphere. When the elemental mercury is released into the atmosphere through coal combustion and is in the presence of vegetation it attaches to the foliage. When the foliage dies and decomposes the mercury creates a strong bond to the organic molecules within the soil preventing it from settling below the earth's surface. In a situation where a forest fire occurs, the mercury is vaporized into its elemental form and then reemitted into the atmosphere and through convection the mercury is able to enter the upper levels of the atmosphere.

Elemental mercury is a highly volatile and relatively inert gas with the potential for long range transport; however, it oxidizes into Hg^{2+} when exposed to radical species in the upper atmosphere. These radical species are produced both by natural and anthropogenic sources such as the release of aerosol salt particles in the Marine Boundary Layer (MBL), chlorofluorocarbons (CFCs), their successors hydrofluorocarbons (HFCs), and Halons. These sources provide relatively stable means of transport for the halogens into the upper atmosphere where several forms of heterogeneous chemistries release them as their radical species. Research suggests that stratospheric halogen oxidation is driven mostly by chlorine chemistry, and that tropospheric halogen oxidation is driven mostly by bromine chemistry[19]. These radical species are extremely short-lived due to their high reactivity, and there is thus the possibility of competition between reactions with elemental mercury and ozone in the stratosphere. While elemental mercury is highly volatile, its oxidized form Hg^{2+} precipitates rapidly by adsorbing on to nearby surfaces, thereby allowing it to reenter the biosphere.

It is known that mercury and ozone are both present in the stratosphere and both species react with halogen free radicals in much the same manner[12]. This investigation intends to use modeling data from the Wilcox research group, and other available data from the literature, to investigate the rate constants of mercury-halogen reactions, and compare them to ozone-halogen reactions. This will determine if it is possible for mercury and ozone to be in competition to consume halogen free radicals. A thermochemical analysis of these reactions will also be conducted to determine which reactions are thermodynamically stable enough to occur, and whether or not they are able to occur under atmospheric conditions.

CHAPTER 2: BACKGROUND

Understanding the causes of ozone depletion requires the knowledge of the origins of atmospheric mercury, halogen free radicals and the atmospheric chemistry that is occurring. Due mainly to coal combustion and various natural causes, such as forest fires and volcanoes, elemental mercury is released into the atmosphere. It was recently discovered that elemental mercury is stable and has a long enough residence time to accumulate in the lower stratosphere. Halogen radicals in the stratosphere originate from cycling in the marine boundary layer and from anthropogenic emissions. Sea-salt aerosols caused by breaking waves on the ocean surface can be rich in salts which can transform into gaseous diatomic halogens and further photolyze into radical form and can then be transported by wind-propagated advection. The elemental mercury reacts with halogen free radicals in the marine boundary layer in much of the same manner as ozone reacts with halogen free radicals in the stratosphere. By understanding these processes the comparison between these reactions and ozone depletion can be made. This section will investigate the sources of mercury in the atmosphere as well as the chemistry that is taking place in the stratosphere and troposphere.

2.1 Mercury in the Atmosphere, Anthropogenic Causes

Mercury is one of the most important contaminants emitted to the atmosphere due to its toxic effects on the environment and human health, persistence in the environment, and global atmospheric transport with air masses[31]. Coal combustion contributes a significant amount of the mercury emissions released into the atmosphere. Approximately 75 tons of mercury is used in power plants in the United States per year. Currently the U.S. emits 50 tons of mercury into the atmosphere annually through coal combustion while 25 tons of mercury is captured through emission controls such as wet scrubbers[27]. As the United States is trying to reduce the quantity of mercury emitted, countries such as China still use coal to heat their homes.

2.1.1 Mercury in Coal Combustion

The mercury in coal is a significant source of the world's mercury emissions. The U.S. has made continuous efforts to limit mercury emissions from the coal-fired utilities through the use of selective chemical leaching, laser-absorption ICP-MS, and other approaches. The U.S. Geological Survey (USGS) investigated the primary host of mercury in different sources of coal. Their results show that in bituminous coals, pyrite is the primary host of mercury whereas the proportion of mercury present in organic parts of coal is generally in lignite and sub-bituminous coal[13]. The bituminous coals are typically cleaned prior to use in the coal-fired utilities to reduce the sulfur contents and emissions. This process removes a portion of the pyrite thus removing about thirty-five percent of the mercury along with the other emission control devices[13]. These coals can have a large mercury concentration range; however, the world's average is 0.1 parts per million[34].

2.1.2 Mercury in High Emission Countries

It is evident that coal combustion releases massive quantities of mercury into the atmosphere; however, all over the world people depend on coal differently. In the United States the primary use of coal is for energy generation for machinery[33]. In China, only one third of the coal burned is used for electric power generation while the rest is used for household energy. In fact, it has recently been cited that more than 400 million people rely on coal for their domestic energy needs such as heating and daily cooking[33]. By relying on coal as a major source of energy, the total amount of mercury emitted into the atmosphere is not likely to decrease in the near future.

CHINA

The largest consumer and producer of coal in the world is the Peoples' Republic of China and 67% of the primary energy source is from coal combustion[33]. In 2003 about 1.7 billion tons of coal was produced and in 2006 that figure increased to 2.3 billion tons. The USGS estimates the coal consumption for China in year 2020 will be around 3.3 billion tons per year. As the leader in coal consumption and production, China is presumed to be the world's leader in mercury emissions. A study performed by the USGS of China estimated that 536 tons of mercury in the year 1999 was released through coal combustion which accounts for thirty-eight percent of the world's mercury emissions, compared to the U.S.'s 158 tons of mercury[1]. Although estimates of mercury emissions vary, China produces three times more mercury per ton of coal than the U.S. due to the lack of emission controls[20].

A possible reason for China's high emission of mercury is the elevated mercury content of the coal it consumes. Most Chinese coals have mercury content between 0.1 and 0.3 ppm but can be as high as 45 ppm, which is significantly higher than the world average content of 0.1 ppm. A possible explanation for the elevated content is that the coal formation might have been affected by low-temperature hydrothermal fluids preventing the release of elemental mercury due to its low solubility in the liquid phase[33]. The rapid increase in combustion of coal for industry applications around the world has caused the mercury deposition rate to increase to approximately 3 times higher than in pre-industrial times[33].

INDIA

India, a quickly industrializing country, is another large-scale consumer of coal for power. In 1998 India was the world's third largest producer of coal, with 292 million tons of coal produced, and rising. This number is expected to increase since approximately 75-80% of India's thermal energy is being generated from coal-fired utility and power plants. India is experiencing a rapid increase in coal production and a rapid decrease in coal quality (mainly due to increased ash content). Indian coal contains 0.26-0.49 mgHg/kg (dry) compared to a world average of 0.12 mgHg/kg (dry), which is a cause for concern for a country whose coal production is rising at a rate of 4.8% per year. Another serious cause for concern is that approximately 40% of the mercury contained in Indian coal is released in the flue gasses due to a lack of wet scrubbers in energy production processes[33].

KOREA

Korea is one of the leading countries in mercury emissions from coal combustion. Until a study was carried out by S. Jun Lee et al. in 2004, there were no accurate measurements of mercury emissions recorded for Korea. The Korean Ministry of the Environment is in the process of modifying the existing Korean standard method for mercury speciation in the combustion flue gas[18]. S. Jun Lee et al. carried out a study on the mercury emissions using the U.S. EPA method 101A to obtain accurate data.

The study performed by Lee et al., was carried out at 12 different facilities measuring the mercury emissions from the stacks being observed. The industrial oil-fired boilers averaged 0.18 $\mu g/m^3$ of mercury and the oil-fired power plants averaged 0.21 $\mu g/m^3$ of mercury. Coal-fired power plants, on the other hand, had a much higher level of mercury per unit area than both the industrial oil-fired boilers and the oil-fired power plants combined. Coal-fired power plants averaged 6.373 $\mu g/m^3$ of mercury which is 16 times the amount of mercury released per unit area into the atmosphere as the oil-fired utilities combined.

2.2 Mercury in the Atmosphere, Natural Causes

The natural sources of mercury are a critical part of the total mercury emissions that are released into the atmosphere. The origin of most natural emitted mercury comes from volcanoes and forest fires. Since natural occurrences can not be controlled in the same manner as industrial sources, it is much harder to quantify the actual mercury that is emitted into the atmosphere. Despite this challenge, scientists have found ways to accurately measure the amount of mercury released from volcanoes and forest fires with minimal sources of error.

2.2.1 Forest Fires

As gaseous elemental mercury (GEM) is released from coal combustion it travels significantly through the troposphere until it settles in the biogeosphere on vegetation, and litterfall[15]. The mercury becomes intertwined with sulfur-reduced compounds that are on the earth's surface where carbonaceous materials are decomposed. The most common vegetations for mercury to interact with are needles, broadleaves, small branches, grasses, bark and mosses. All these materials are susceptible to combustion during intense heating[30].

Even though these materials are readily combustible they do not exist in all areas of the United States. Mercury emissions from forest fires are highly dependent upon location and seasonal conditions due to temporal variations and vegetation growth. The eastern states for example have relatively low emissions of mercury from forest fires due to the frequent occurrence of rain in the spring and summer months and the snow which almost prevents the occurrence forest fires in the winter months. The southeastern part of the United States on the other hand has a high potential for forest fires during the spring and fall months due to the dry weather and drought conditions.

2.2.2 Volcanoes

Most volcanoes go through several stages, such as pre-eruptive degassing and post-eruption. The pre-eruptive degassing, which can last anywhere from a day to weeks, is associated with the intensification of the explosive eruption. The post-eruption is characterized by fuming and increased fumarolic activity. After the post-eruption phase the extra eruption activity with fumarolic and solfataric activity can go on for hundreds of years. The emission of mercury is categorized through these different phases into two groups. The first group is the quiescent phase which involves pre and post explosive eruptions whereas the explosive phase deals with the main eruption.

Research carried out by Nriagu and Becker, has produced data for nearly 100 volcanoes with significant activity. The data is compiled from results gathered from 1980 through 2000. Over this twenty-year span some of the volcanoes have had multiple eruptions contributing to the approximately 1140 metric tons of mercury released overall with an annual flux of 57 tons.

Non-eruptive volcanoes also emit significant amounts of mercury due to the quiescent phase of mercury emission. The volcanoes are constantly emitting sulfur oxide and mercury through the degassing plumes until the volcano becomes inactive. During the twenty-year period 752 tons of mercury was released, which includes 66% of the active volcanoes[21].

Combining the data from both the eruptive volcanoes and the non-eruptive volcanoes estimates the worldwide emission of mercury from volcanoes to be approximately 94.6 tons per year[21] which only includes volcanoes measured for economic and political reasoning.

2.3 Cycling in the Marine Boundary Layer

The marine boundary layer (MBL) plays a large role in influencing the atmospheric chemistry of the entire planet. This portion of the ocean, located along the world's shorelines and on the ocean surface, is a major source of both mercury and sea-salt aerosol particles[10]. Crashing waves coupled with photolytic interactions provide sufficient energy to release salt particles which can react with nearby aerosols and form both Hg^0 and diatomic halogen species (via heterogeneous chemistry)[8].

For the purposes of this paper the most important section of the MBL involved in stratospheric chemistry is the area directly surrounding the polar regions. Since tropospheric scavenging phenomena largely prevents aerosols released from reaching the higher altitudes of the stratosphere, the large ice leads (long wide crevasses in the snowpack) that provide advection from the polar MBL are critical components in the chemistry of the polar vortices. The Polar MBL is a critical source of acid aerosols that contribute to the radical reaction cycles. As sulfates and nitrates are released they oxidize and become sulfuric and nitric acid, which precipitate as the water droplets containing them freeze and sublimate, later becoming aerosol particles at the low temperatures present in the polar atmosphere, providing surfaces for the production of radical species[2]. Concurrently mercury salts are liberated from the MBL and via heterogeneous chemical interactions are converted into elemental mercury (Hg^0) which contributes to the overall flux of mercury locally present in the atmosphere[10]. Sea-ice and surface interactions in the polar regions coupled with the formation of new ice and frost flowers are major contributors to Ozone Depletion Events (ODE's).

2.4 Arctic Snow and Frost Flowers

Arctic snow plays an important role in the autocatalytic release of bromine oxide and elemental halogen sources. The large surface area of the snow pack provides a location for brine to photolytically release diatomacious halogen species as well as provides a catalytic surface for the recycling of radical species. Arctic snow causes polar atmospheric transport that allows for the long-range transfer of reactive species. Arctic ice Leads provide a means for convective atmospheric transport large enough for reactive particles to reach high altitudes where they can react during polar sunrise.[8]

At the base of most Leads there exists a boundary layer between the Lead and the open ocean where new ice is formed[3]. Frost flowers are surface ice formations that form from water vapor deposition onto frozen surfaces which adsorb concentrated brines of young sea ice[28]. Ongoing research indicates that sulfate-depleted brine, "probably derived from frost flowers is the most common source of sea-salt in the polar atmosphere during winter/springtime"[6]. As new ice is formed some of the concentrated brine is pushed towards the surface where it experiences colder temperatures and wind-propagated advection. Water vapor and sea-salt then sublimate from the surface of frost flowers in the presence of cold air, to become sea-salt aerosols[23]. The increased surface area, greater potential for exposure to sunlight, and decreased temperature provides conditions favorable for sea-salt aerosols to photolyze and form gaseous halogen sources, such as BrO, and BrCl, that are subject to polar atmospheric transport phenomena and various heterogeneous chemistries.

2.5 Aerosol Chemistry

Aerosols are a particulate form of matter that float in the air, similar to a colloidal suspension in a liquid. Aerosols play an important role in the heterogeneous chemistry of the atmosphere. They can absorb and reflect various wavelengths of light, act as both reactants and catalytic surfaces in the atmosphere, partake in interfacial mass transport occurring on the surfaces of liquid and solid water and can be factors in the interactions between gaseous and particulate species.

Halogen radicals in the stratosphere originate by cycling in the marine boundary layer and through anthropogenic emissions. Sea-salt aerosols caused by breaking waves on the ocean surface can be rich in salts which, if not scavenged by tropospheric transport phenomena, can transform into gaseous diatomic halogens and further photolyze into radical form[23]. These radical species can be recycled on the surfaces of Polar Ice Clouds that consist mostly of cold particulate acid species such as nitric and sulfuric acids and through reactions with other radical generating aerosols[7]. Fluorine is relatively scarce in the atmosphere due to the relatively large stability of fluoric acid and the fast reaction rate of fluorine radicals. Most of the bromine in the stratosphere is produced from Halons used for fire extinguishing, interactions on polar ice surfaces, and from photolysis of methyl bromide which is an agricultural fumigant[19]. It has been known since as early as the 1980's that chlorofluorocarbons (CFC's) actively photolyze during the day thereby releasing chlorine radicals into the atmosphere, and have subsequently been phased out over time by EPA and the IPPC (the European Union's Integrated Pollution Prevention and Control bureau). The long life-spans of these chemicals (30-50 years) allow them to be transported into the stratosphere where they can photolyze and/or react on polar stratospheric clouds and release their radicals[19].

Research indicates that tropospheric chemistry is dominated by bromine chemistry, which is reliant upon sea-salt aerosols released from the MBL and from snow and ice formations. The sea-salt particles adhere to airborne surfaces such as ice and through heterogeneous chemistry, these aerosol particles release radical species such as BrO*, Br*, Cl*, ClO*, etc. and diatomic halogens. The radicals then react with ozone and mercury in the atmosphere through heterogeneous reaction cycles which can reduce O_3 to O_2 and can recycle radicals until local reactant species are exhausted sufficiently. This occurs primarily during the polar springtime during the first few days of sunlight, where light-induced interactions with molecules start what is known as an Ozone Depletion Event (O.D.E.). During these periods ozone and mercury levels are known to drop beneath measurable values due to their oxidation (and for mercury, subsequent precipitation), Figure 8[19,28]. These events occur over a period ranging from 7 hours to 9 days and frequently involve chemical pathways for other reactive species, such as mercury, to terminate radical chain reactions[28].

2.6 The Ozone Hole

In 1974 Mario Molina and Frank Rowland published a paper in *Nature* describing the interactions of CFC's with the ozone layer predicting its eventual depletion due to a combination of natural and anthropogenic pollutants, and since then the scientific community has taken a much greater interest in the global impacts of atmospheric chemistry. International interest in preserving the protective layer between the surface of the earth and the suns radiation as well as concern over global warming has spurred several treaties setting standards for emissions, such as the 1989 Montreal Protocol on Substances That Deplete the Ozone Layer.

The heterogeneous chemistry of the polar atmosphere take part in annual cycles that are dependant upon the rarer conditions such as long periods of light and dark as well as low temperatures. During the polar winter, a vortex forms that is isolated from the rest of the atmosphere which acts like a chemical reactor[7]. Recent studies have detected rapid ozone depletion events (O.D.E) following polar sunrise, which may be due to the photo-catalytic production of radical species over polar snow and ice[28]. During O.D.E.'s ozone (and mercury) levels have been noted to drop beneath measureable levels, and upon completion slowly return to normal levels during the summer and springtime. These O.D.E.'s coincide with the period of time when the ozone hole is at its largest, i.e., during late winter and austral springtime. Figure 7[7] shows the concentration of ozone in the stratosphere as a function of time.

The National Oceanic and Atmospheric Association Ozone and Water Vapor Group compiles historical data on ozone for monitoring the ozone hole and “conducts research on the nature and causes of depletion of the stratospheric ozone layer and water vapor in forcing climate change…” and provides a veritable chronology of these events.

As industrialization activities continue to produce more long-range pollutants, the ozone hole will continue to grow unless steps are taken to reduce the emissions associated with these activities. With the cooperation of the governments of rapidly-industrializing nations, emissions could be cut and overall pollution and release of ozone and mercury-oxidizing chemicals can be reduced to pre-industrial levels.

CHAPTER 3: COMPUTATIONAL METHODOLOGY

3.1 Basis Set Justification

Calculations were carried out using the Gaussian 03 suite of programs[10]. Several different basis sets were used for the calculations. An extended Pople basis set, 6-311G*, including both diffuse and polarization functions was used for all atoms other than mercury. Two pseudopotentials were considered for mercury. The first basis set employs the ECP28MWB pseudopotential of the Stuttgart group[5]. For mercury, energy-optimized (4s,2p)/[3s,2p] Gaussian-type orbital (GTO) valence bases optimized using multiconfiguration Dirac-Fock (MCDF) calculations were used. The second mercury pseudopotential employs a relativistic compact effective potential, RCEP28VDZ of the Stevens et al. group[25], which replaces 60 of mercury's atomic core electrons, derived from numerical Dirac-Fock wave functions using an optimizing process based upon the energy-overlap functional. Density-functional calculations were carried out with the exchange energy functional described by Becke in part three of his series of papers[6] and the correlation functional produced by Lee, Yang, and Parr[17].

3.2 Kinetic Assessment

It is known that reactions between halogens and ozone in the stratosphere are one of the main causes of ozone depletion. It is also know that in the MBL, mercury reacts with halogen radicals in much the same way as ozone. The objective of this project is to determine whether or not it is possible for mercury to affect ozone depletion. By comparing the chemical kinetics of mercury-halogen reactions with ozone-halogen reactions reveals if this is possible. The rate constants of these reactions will describe the time scales on which these reactions occur. In order for competition to take place the rate constants for mercury-halogen and ozone-halogen reactions must be similar. If the ozone reactions have a significantly higher rate constant than the mercury reactions, then it is possible that they will consume all halogen radicals before mercury can react with the halogens. However, even if the rates are similar or if mercury's reactions are faster, there is a relatively low concentration of mercury in the atmosphere compared to ozone.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Rate Constant Comparison

After conducting an in-depth literature review, we were able to acquire kinetic data for several different ozone depletion reactions. Kinetic data was found for paralleled reactions with mercury replacing ozone. Using the pre-exponential factors and activation energies rate constants were calculated for each reaction using the Arrhenius expression:

$$K = Ae^{-\frac{Ea}{RT}} \tag{1}$$

The results of our kinetic assessment show that it is possible for competition to exist between mercury and ozone via reactions with halogen species in the presence of sufficient mercury concentrations. From Figure 1 it can be seen that the ozone and mercury reaction rate constants are cluttered in close proximity to one another. This implies that many of the ozone reactions occur at the same rate as the paralleled mercury reactions. The results were then grouped into three categories, i.e., fast, medium, and slow reactions. The fast reactions, as shown in Figure 2, are most likely to occur since they will consume all reactants before the slower reactions. The medium reactions in Figure 3 are probable; however, the slow reactions in Figure 4 may not be highly viable because the rate constants are so low in comparison to the faster reactions. The lifetimes of the reactants may not be long enough for the slow reactions to occur, allowing the quicker reactions to consume all of the halogens, assuming the presence of faster reacting species.

4.2 Thermodynamic Stability

Table 5 and 6 show the reaction enthalpies, entropies, Gibb's free energies, and equilibrium constants for all reactions that mirror existing experimental data. The Gibb's free energies were calculated according to the equation

$$\Delta G = \Delta H - T \cdot \frac{\Delta S}{1000} \tag{2}$$

All values with negative Gibb's free energies are not spontaneous and were not considered in our final results. Equilibrium constants were calculated according to the equation

$$K_{eq} = \exp \frac{-1000 / \Delta G}{RT} \tag{3}$$

The following reactions were found to be thermodynamically stable due to their large equilibrium constants:

$Br_2 + OH \rightarrow HOBr + Br$ (4)

$Cl_2 + OH \rightarrow HOCl + Cl$ (5)

$Hg + Cl \rightarrow HgCl$ (6)

$O + HOBr \rightarrow HO + BrO$ (7)

$HgBr + Br_2 \rightarrow HgBr_2 + Br$ (8)

$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$ (9)

$Hg + O_3 \rightarrow HgO + O_2$ (10)

$Hg + OH \rightarrow HgOH$ (11)

$O + HOCl \rightarrow HO + ClO$ (12)

Figures 5 and 6 show the trends in relative stability for fast and medium reactions respectively with respect to change in temperature. It should be noted that for reaction 1 the plot is discontinuous because the reaction became non-spontaneous above approximately 425K. The fast reactions generally tended to have parabolic equilibrium constants as plotted against temperature, which may be due to approaching non-spontaneity above certain temperatures not considered since they are outside the range of atmospheric conditions. Figure 6 indicates that the medium reactions tended to become less stable with an increase in temperature. All of the reactions with calculated equilibrium constants greater than one are expected to continue until exhaustion of the reactant species, indicating relatively stable thermodynamic product species. However, the reactions with calculated equilibrium constants between zero and one would not be as thermodynamically stable and may have a maximum concentration of the product amongst the reactants.

CHAPTER 5: CONCLUSION

The kinetics of the reactions examined in this investigation shows that mercury reacts with halogen species at approximately the same rate as ozone. The thermodynamic investigation proved that the calculations for the mercury reactions match experimental data by providing comparable heats of reaction for equations 4 through 12 as shown in the results and discussion. These reactions are thermodynamically favored by their equilibrium constants. This indicates that it would be possible for mercury to affect ozone depletion. However due to the relatively low concentration of mercury present in respect to the amount of ozone, the local mercury reserves would run out before the ozone depletion event was finished. Future work could include performing calculations at various higher levels of theory to acquire more accurate and reliable results. Also this investigation focuses entirely on gas phase homogeneous reactions and does not take into account heterogeneous, aqueous, or surface chemistries and further work could be done to expand upon our results.

APPENDIX A: TABLES

Enthalpy			Level of Theory	
Species	Multiplicity	Enthalpy (Hartrees)	B3LYP 6-311G*	PW91 6-311G*
Br	2		-2574.103	---
Br$_2$	1		-5148.280	---
BrO	2		-2649.270	---
Cl	2		-460.164	---
Cl$_2$	1		-920.401	---
ClO	2		-535.334	---
Hg	1		-153.083	-153.141
HgBr	2		-2727.225	-2727.440
HgBr$_2$	1		-5301.441	---
HgCl	2		-613.293	-613.3506
HgCl$_2$	1		-1073.578	-1073.634
HgO	1		-228.169	---
HgOH	2		-228.793	---
HOBr	1		-2649.914	---
HOCl	1		-535.976	---
O	3		-75.083	---
O2	3		-150.358	---
O3	3		-225.389	---
OBrO	4		-2724.359	---
OClO	2		-610.383	---
OH	2		-75.736	---

Table 1: Calculated Enthalpy Data

Entropy			Level of Theory	
Species	Multiplicity	Entropy (cal/mol)	B3LYP 6-311G*	PW91 6-311G*
Br	2		40.390	---
Br$_2$	1		58.706	---
BrO	2		55.644	---
Cl	2		37.964	---
Cl2	1		53.438	---
ClO	2		52.965	---
Hg	1		41.813	41.813
HgBr	2		65.467	65.435
HgBr$_2$	1		75.395	---
HgCl	2		62.696	62.684
HgCl$_2$	1		70.227	70.276
HgO	1		57.633	---
HgOH	2		60.599	---
HOBr	1		59.267	---
HOCl	1		56.612	---
O	3		36.438	---
O$_2$	3		48.981	---
O$_3$	3		58.513	---
OBrO	4		60.951	---
OClO	2		57.598	---
OH	2		42.588	---

Table 2: Calculated Entropy Data

	Reaction	Calculated				Experimental			
		ΔH kcal/mol	ΔS cal/mol	ΔG kcal/mol	Keq	ΔH kcal/mol	ΔS cal/mol	ΔG kcal/mol	Keq
Slow Reactions	$Hg + Br_2 \rightarrow HgBr + Br$	21.377	5.338	19.785	0.918	29.577	6.265	27.709	0.940
	$Hg + Cl_2 \rightarrow HgCl + Cl$	16.516	5.409	14.904	0.892	33.071	6.486	31.137	0.947
	$Hg + HOCl \rightarrow HgCl + OH$	18.266	6.859	16.221	0.901	31.199	7.705	28.901	0.943
	$HgBr_2 \rightarrow HgBr + Br$	70.717	30.462	61.635	0.972	72.055	30.197	63.051	0.973
	$HgCl_2 \rightarrow HgCl + Cl$	75.663	30.433	66.589	0.974	82.705	31.168	73.412	0.977
Medium Reactions	$Cl_2 + OH \rightarrow HOCl + Cl$	-1.749	-1.45	-1.316	3.602	1.872	-1.219	2.235	0.469
	$HgBr + Br_2 \rightarrow HgBr_2 + Br$	-24.574	-8.388	-22.073	1.079	-25.973	-5.182	-24.427	1.071
	$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$	-29.607	-7.943	-27.239	1.063	-24.723	-5.523	-23.076	1.075
	$Hg + O_3 \rightarrow HgO + O_2$	-34.650	6.288	-36.525	1.047	-38.769	7.244	-40.928	1.042
	$Hg + OH \rightarrow HgOH$	15.789	-23.802	22.885	0.928	---	---	---	---
	$O + HOCl \rightarrow HO + ClO$	-7.019	2.503	-7.765	1.242	-7.434	3.062	-8.346	1.224
	$O_3 + OBr \rightarrow O_2 + O_2 + Br$	-100.137	24.195	-107.350	1.015	---	---	---	---
	$OBr + O_3 \rightarrow O_2 + OBrO$	-36.379	-4.225	-35.119	1.049	---	---	---	---
	$OCl + O_3 \rightarrow O_2 + OClO$	-10.947	-4.899	-9.486	1.194	-33.291	-0.784	-33.057	1.052
Fast Reactions	$Br_2 + OH \rightarrow HOBr + Br$	-0.819	-1.637	-0.331	162.5	-1.772		-1.772	2.592
	$Cl_2 + OH \rightarrow HOCl + Cl$	-1.749	-1.45	-1.316	3.602	1.872	-1.219	2.235	0.469
	$Hg + Br \rightarrow HgBr$	-24.765	-16.736	-19.775	1.089	-16.505	-18.75	-10.914	1.167
	$Hg + Cl \rightarrow HgCl$	-29.539	-17.081	-24.446	1.071	-24.911	-24.775	-17.524	1.101
	$O + HOBr \rightarrow HO + BrO$	-5.715	2.527	-6.468	1.298	-8.384	---	-8.384	1.223
	$O_3 + Br \rightarrow BrO + O_2$	-85.203	5.722	-86.909	1.019	-30.784	-1.288	-30.399	1.057
	$O_3 + Cl \rightarrow ClO + O_2$	-87.349	5.469	-88.980	1.019	-38.898	6.6	-40.865	1.042

Table 3: Calculated and Experimental Data[8]

Species	Bond Length	Bond Angle	Vibrational Frequencies
Br_2	2.333	180	310.34
BrO	1.763	180	677.36
Cl_2	2.056	180	508.10
ClO	1.626	180	792.97
HgBr	2.614	180	166.53
$HgBr_2$	2.464	180	59.94
	2.464	---	59.94
	---	---	201.58
HgCl	2.487	180	256.09
$HgCl_2$	2.338	180	81.90
	2.338	---	81.90
	---	---	312.98
HgO	1.964	180	534.11
HgOH	1.656	180	508.61
	2.058	---	509.35
	---	---	527.17
HOBr	0.968	103.7367	604.73
	1.872	---	1207.93
	---	---	3736.41
HOCl	0.969	103.6662	693.47
	1.736	---	1296.60
	---	---	3727.56
O_2	1.205	---	1641.19
O_3	1.341	167.9463	-390.72
	1.340	---	585.70
	---	---	763.71
OBrO	1.925	180	506.76
	1.925	180	---
OClO	1.817	180	491.38
	1.817	180	---
OH	0.976	180	3650.17

Table 4: Species Bond Length, Angle and Vibrational Frequencies

Reaction	Temp	ΔH kcal/mol	ΔS cal/mol	ΔG kcal/mol	Keq
$Br_2 + OH \rightarrow HOBr + Br$	223.15	-0.70	-1.17	-0.44	1.73E+02
	253.15	-0.75	-1.39	-0.40	1.44E+02
	298.15	-0.82	-1.63	-0.33	1.60E+02
	400	-0.94	-1.99	-0.14	6.05E+03
	500	-1.01	-2.15	0.06	1.21E-07
	600	-1.04	-2.21	0.28	5.06E-02
$Cl_2 + OH \rightarrow HOCl + Cl$	223.15	-1.65	-1.07	-1.41	4.94E+00
	253.15	-1.69	-1.24	-1.38	4.23E+00
	298.15	-1.75	-1.45	-1.32	3.60E+00
	400	-1.86	-1.77	-1.15	2.98E+00
	500	-1.93	-1.92	-0.97	2.84E+00
	600	-1.97	-1.99	-0.77	2.97E+00
$O + HOBr \rightarrow HO + BrO$	223.15	-5.77	2.32	-6.29	1.43E+00
	253.15	-5.75	2.41	-6.36	1.37E+00
	298.15	-5.72	2.53	-6.47	1.30E+00
	400	-5.66	2.68	-6.74	1.21E+00
	500	-5.64	2.73	-7.01	1.15E+00
	600	-5.64	2.74	-7.28	1.12E+00
$Hg + Cl \rightarrow HgCl$	223.15	-29.44	-16.70	-25.72	1.09E+00
	253.15	-29.48	-16.87	-25.21	1.08E+00
	298.15	-29.54	-17.08	-24.45	1.07E+00
	400	-29.66	-17.43	-22.69	1.06E+00
	500	-29.77	-17.67	-20.93	1.05E+00
	600	-29.88	-17.87	-19.16	1.04E+00
$HgBr + Br_2 \rightarrow HgBr_2 + Br$	223.15	-24.69	-12.81	-21.83	1.11E+00
	253.15	-24.63	-12.58	-21.45	1.10E+00
	298.15	-24.55	-12.26	-20.89	1.08E+00
	400	-24.35	-11.70	-19.67	1.07E+00
	500	-24.16	-11.27	-18.52	1.06E+00
	600	-23.96	-10.91	-17.41	1.05E+00

Table 5: Thermodynamic Data

Reaction	Temp	ΔH kcal/mol	ΔS cal/mol	ΔG kcal/mol	Keq
$HgCl + Cl_2 \rightarrow HgCl_2 + Cl$	223.15	-29.77	-8.56	-27.86	1.08E+00
	253.15	-29.70	-8.29	-27.60	1.07E+00
	298.15	-29.61	-7.94	-27.24	1.06E+00
	400	-29.39	-7.32	-26.46	1.05E+00
	500	-29.18	-6.86	-25.75	1.04E+00
	600	-28.98	-6.48	-25.09	1.03E+00
$Hg + O_3 \rightarrow HgO + O_2$	223.15	-34.70	6.11	-36.06	1.06E+00
	253.15	-34.68	6.20	-36.24	1.06E+00
	298.15	-34.65	6.29	-36.53	1.05E+00
	400	-34.62	6.37	-37.17	1.03E+00
	500	-34.61	6.40	-37.81	1.03E+00
	600	-34.60	6.42	-38.45	1.02E+00
$Hg + OH \rightarrow HgOH$	223.15	15.92	-23.27	21.12	8.99E-01
	253.15	15.86	-23.54	21.82	9.13E-01
	298.15	15.79	-23.80	22.89	9.29E-01
	400	15.71	-24.04	25.32	9.52E-01
	500	15.70	-24.06	27.73	9.64E-01
	600	15.74	-23.98	30.13	9.73E-01
$O + HOCl \rightarrow HO + ClO$	223.15	-7.07	2.29	-7.59	1.35E+00
	253.15	-7.05	2.39	-7.66	1.30E+00
	298.15	-7.02	2.50	-7.77	1.24E+00
	400	-6.96	2.66	-8.03	1.17E+00
	500	-6.94	2.73	-8.30	1.13E+00
	600	-6.93	2.74	-8.57	1.10E+00
$HgBr_2 \rightarrow HgBr + Br$	223.15	70.73	34.47	63.03	9.65E-01
	253.15	70.71	34.42	62.00	9.68E-01
	298.15	70.69	34.34	60.45	9.72E-01
	400	70.62	34.14	56.97	9.78E-01
	500	70.54	33.97	53.56	9.81E-01
	600	70.46	33.81	50.17	9.83E-01

Table 6: Thermodynamic Data Cont.

APPENDIX B: FIGURES

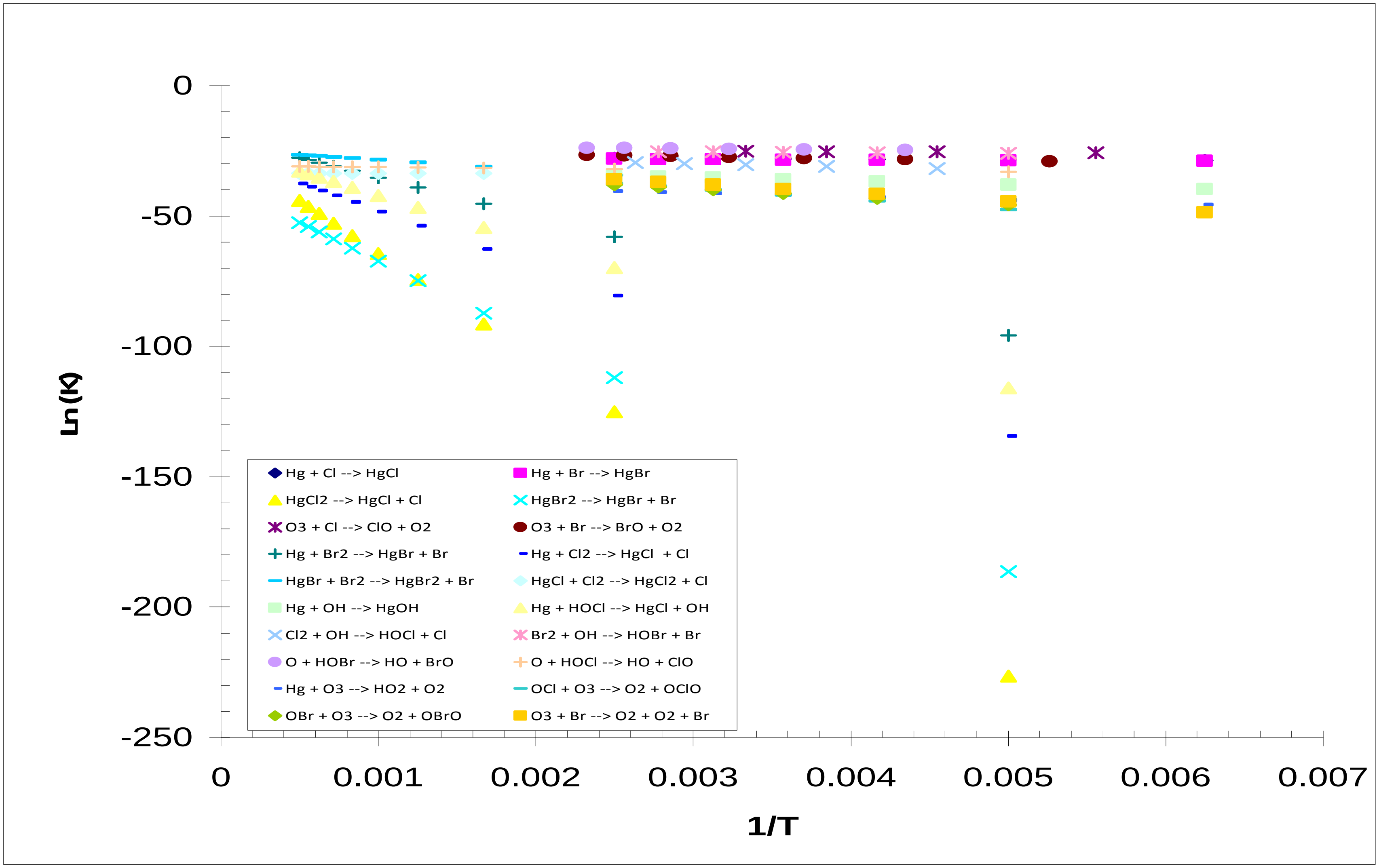

Figure 1: All Reaction Rate Constants

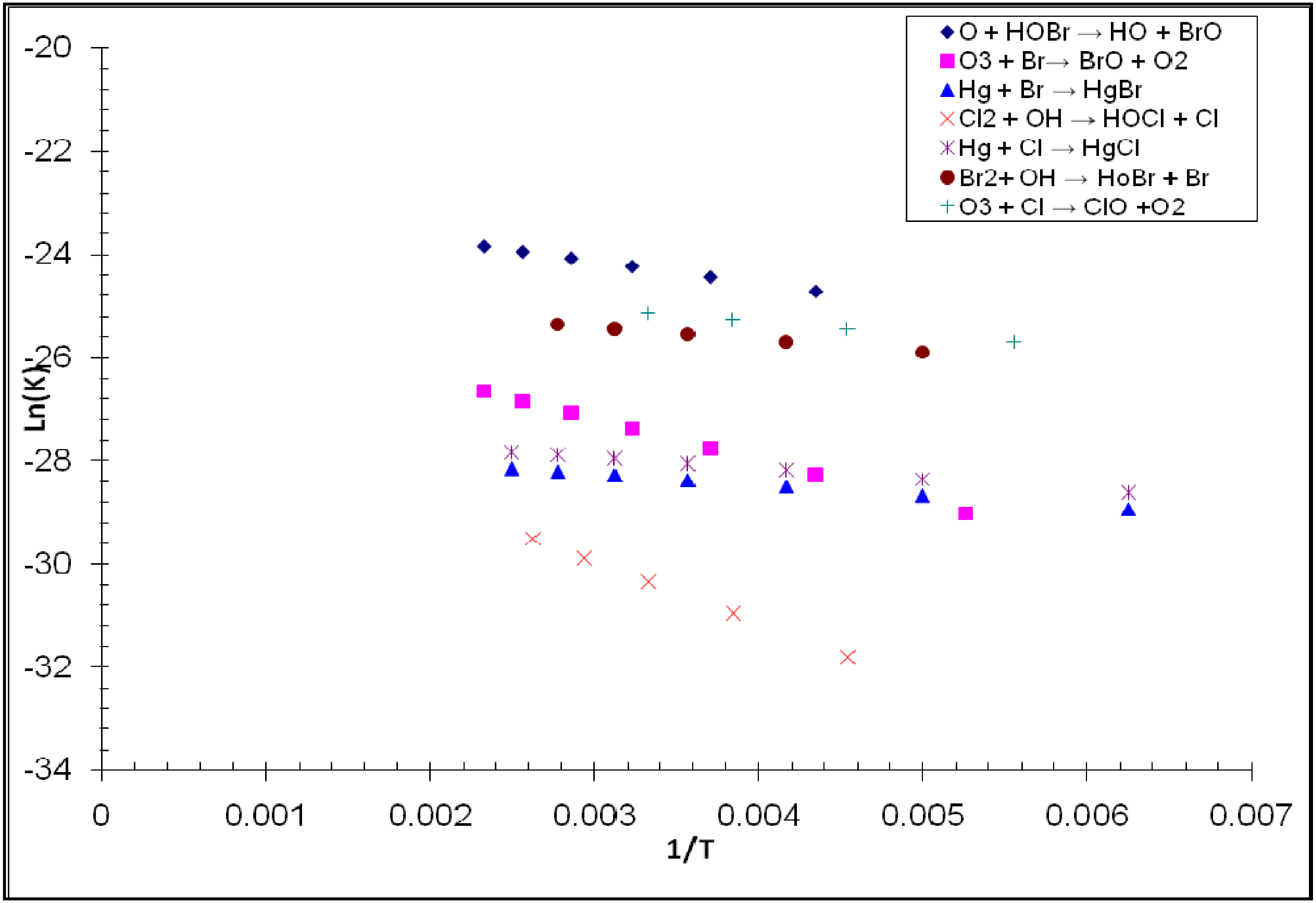

Figure 2: Fast Reaction Rate Constants

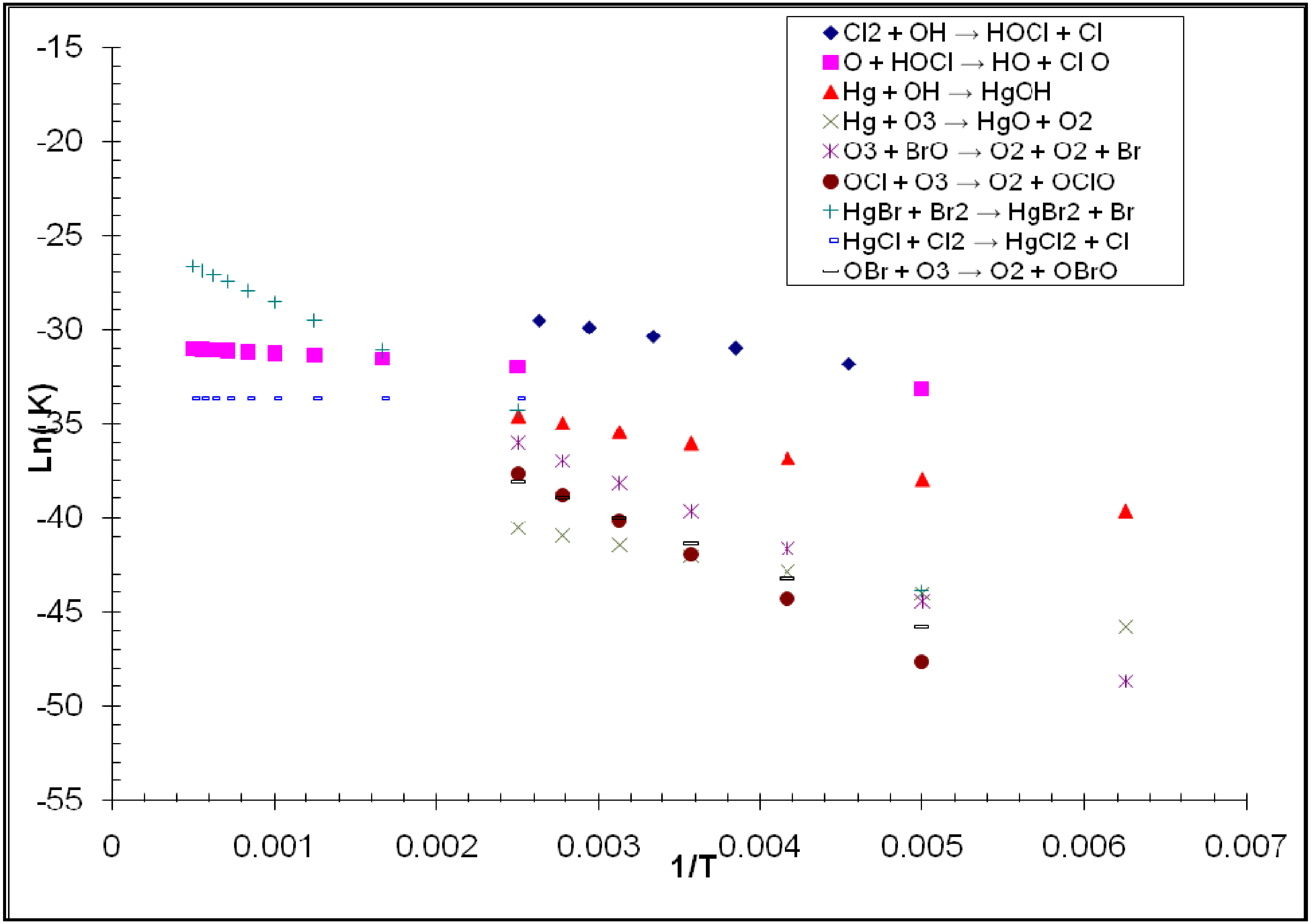

Figure 3: Medium Reaction Rate Constants

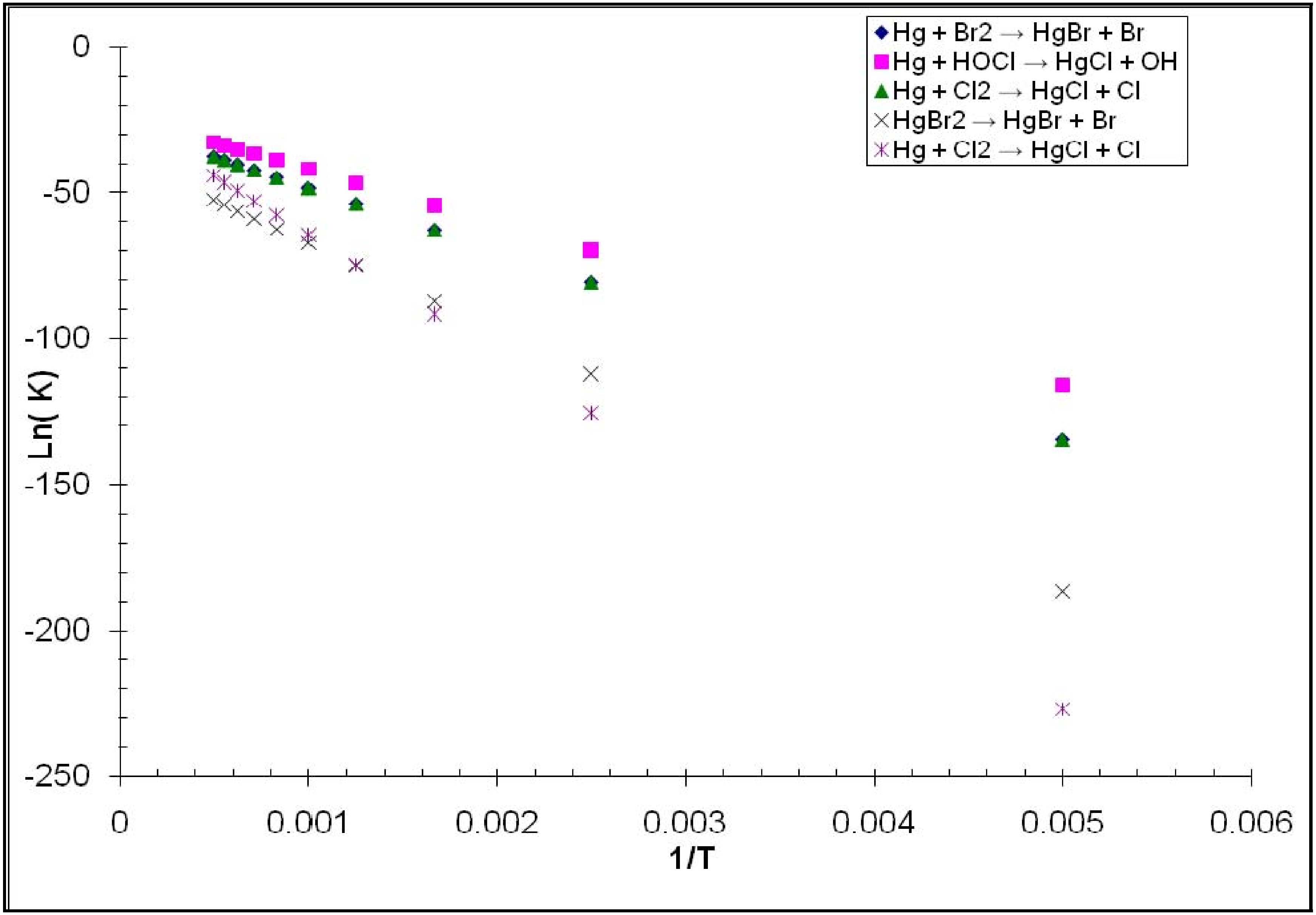

Figure 4: Slow Reaction Rate Constants

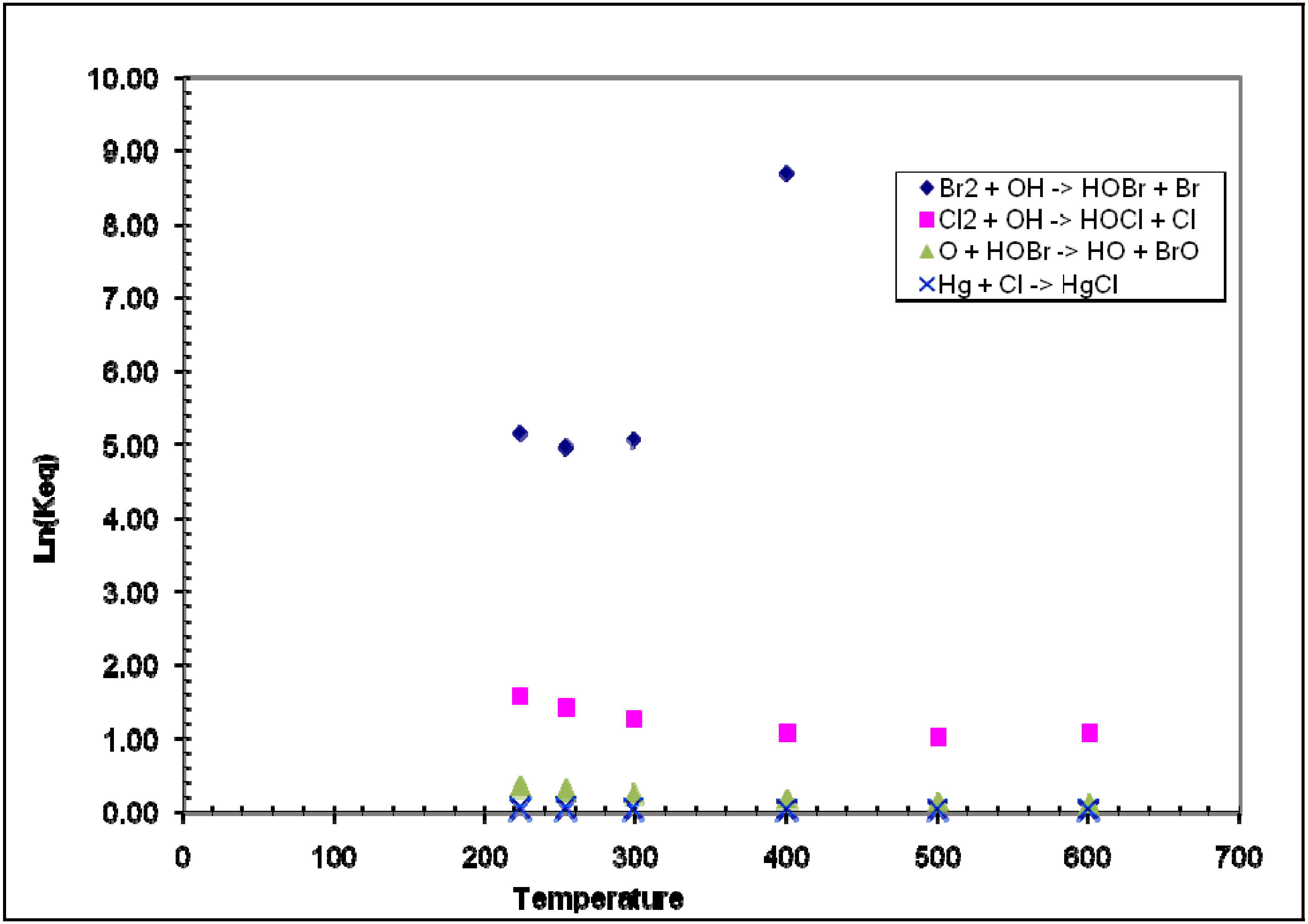

Figure 5: Equilibrium Constant Plot, Fast Reactions

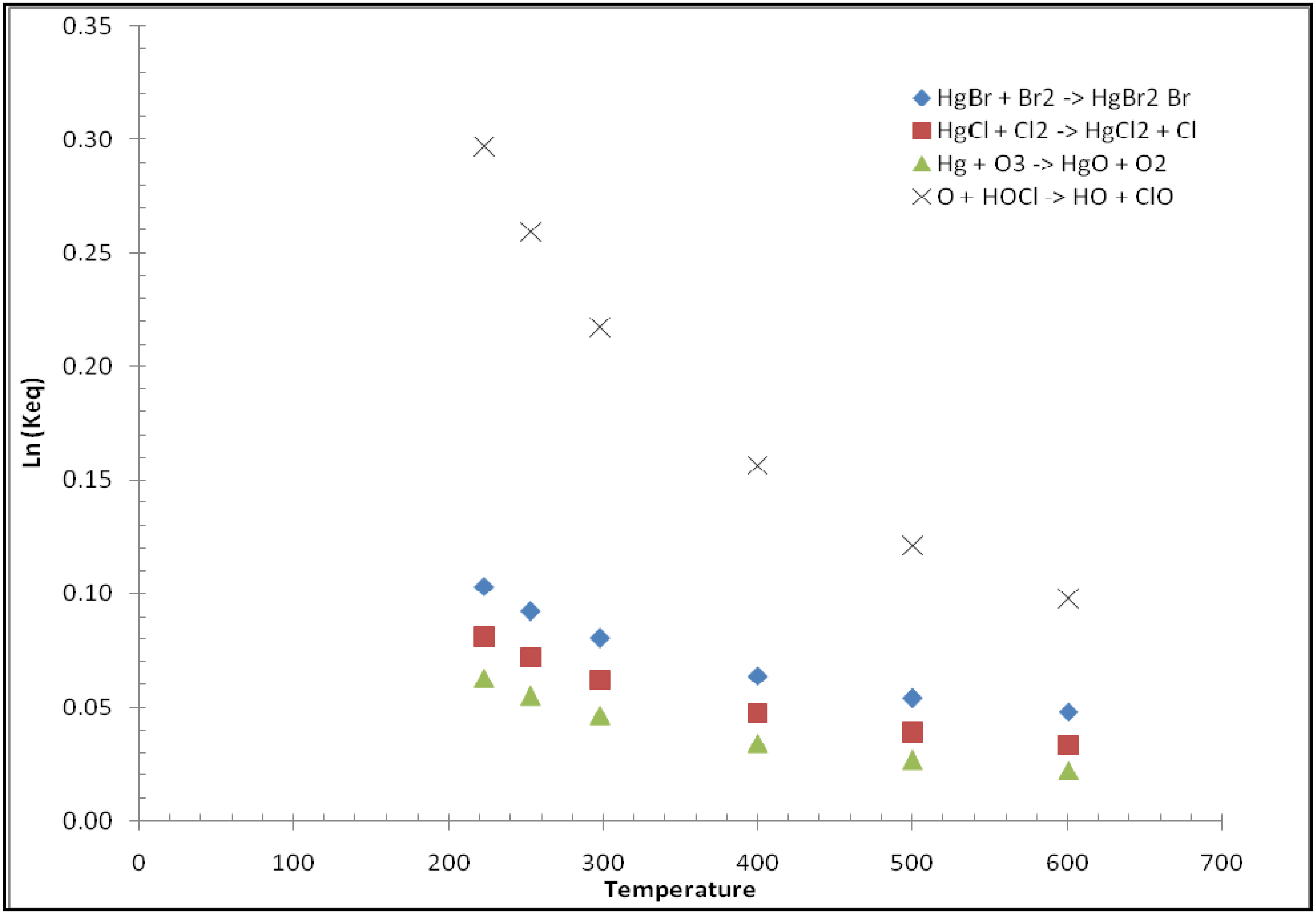

Figure 6: Equilibrium Constant Plot, Medium Reactions

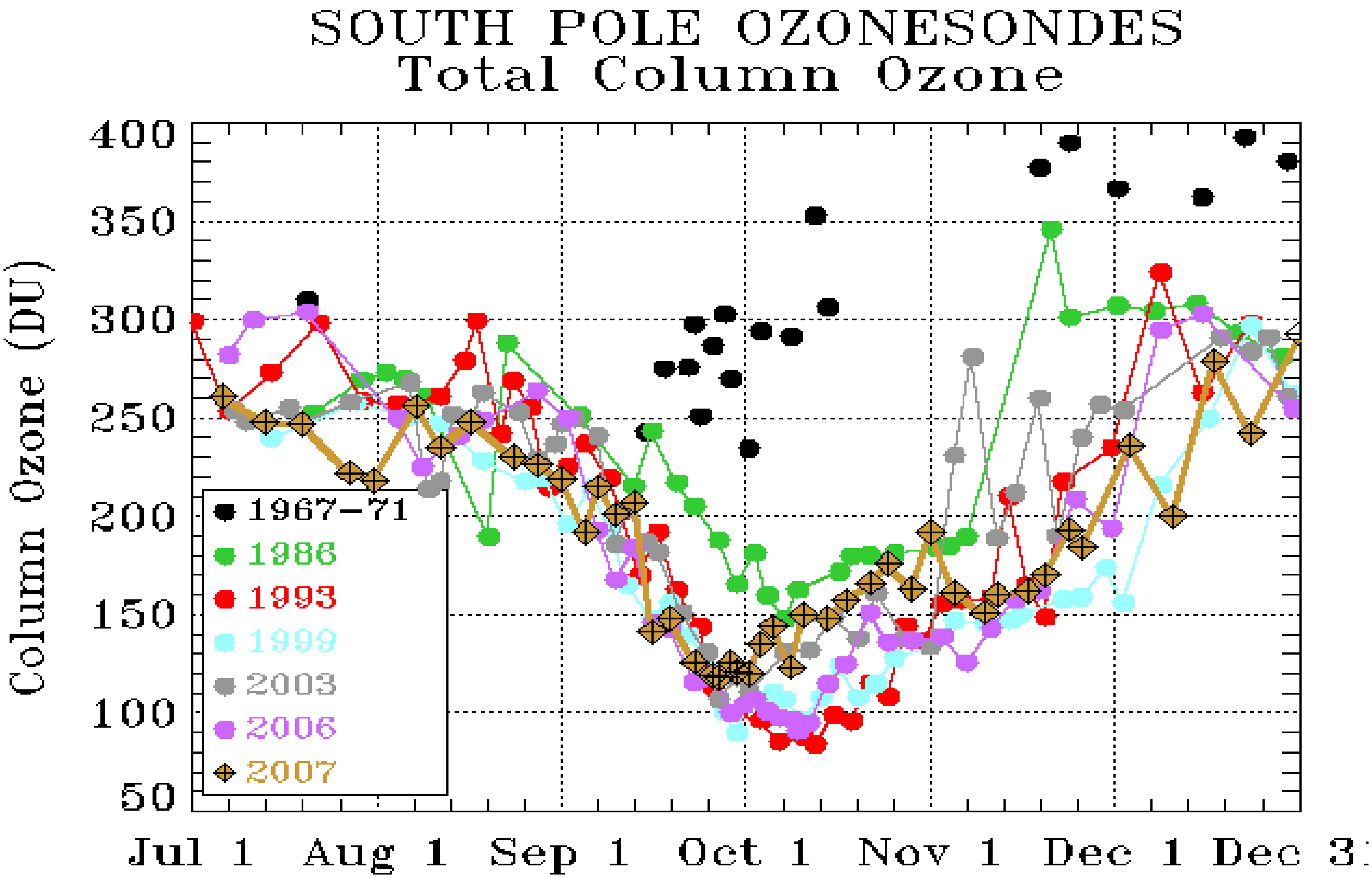

Figure 7: Total Column Ozone[26]

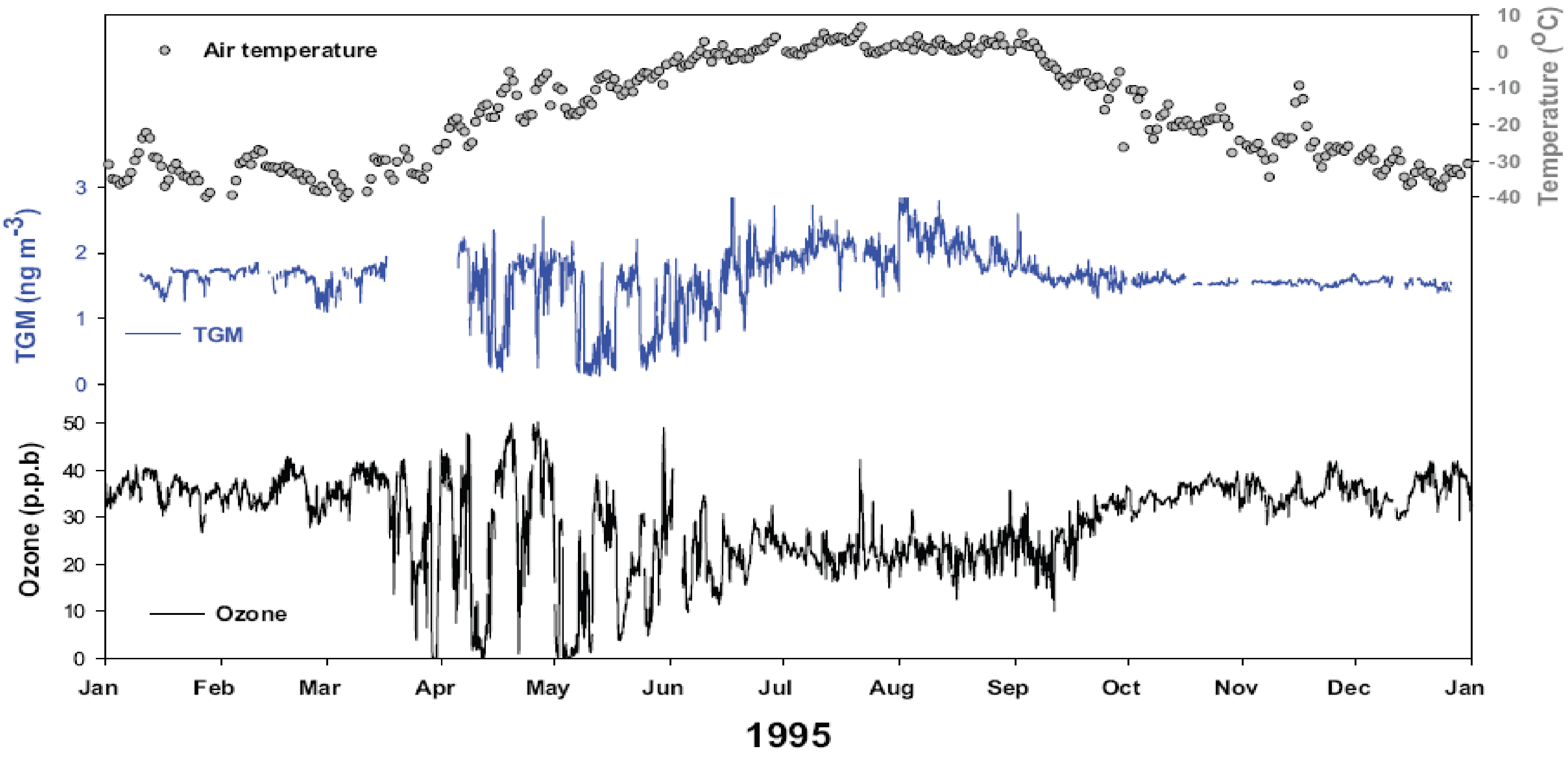

Figure 3 — Time series of air temperature, total gaseous mercury (TGM), and ozone concentrations at Alert, Canada, in 1995. Adapted by A. Steffen from Schroeder et al. *(1998) with permission from Macmillan Publishers Ltd.,* Nature, *394, 331-332, copyright 1998.*

Figure 8: Ozone Mercury Correlation[12]

REFERENCES

[1] Abbott, M. L. (2007). *Atmospheric and surface science research laboratory: Mercury in the environment.* Retrieved December 6, 2007, from http://www.inl.gov/appliedgeosciences/mercury.shtml

[2] Adams, J.W., Cox, R.A.. *Halogen chemistry of the marine boundary layer.* J. Phys. IV France. Volume: 12 Issue: Pr10 Pages PR10-105 – PR10-124. 2002.

[3] A.M. Rankin,V. Auld and E.W. Wolff.: *Frost Flowers as a Source of Fractionated Sea Salt Aerosol in the Polar Regions.*. Geophysical Research Letters. Volume 27, Number 21. Pages 3469-3472. 2000.

[4] Balabanov, N. B.; Peterson, K. A. *A Systematic Ab Initio Study of the Structure and Vibrational Spectroscopy of $HgCl_2$, $HgBr_2$, and HgBrCl.* J. Chem. Phys. **2003**, *119*, 12271-12278.

[5] Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem Phys.* 1993. *98*, 5648-5652

[6] Bernath, Peter F.. *Atmospheric Chemistry Experiment (ACE): Analytical Chemistry from Orbit*. Trends in Analytical Chemistry. Volume: 25, Number: 7. Pages 647-654. 2006.

[7] Chase, 1998Chase, M.W., Jr.,NIST-JANAF Themochemical Tables, Fourth Edition,J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.

[8] C.T. McElroy, C.A. McLinden, and J.C. McConnell.: *Evidence for bromine monoxide in the Free Troposphere during the Arctic polar sunrise.*. Nature, Volume 397, 1999.

[9] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[10] Hedgecock, Ian M., Pirrone, Nicola, and Gensini, Mario. *The Interaction Between Sea Salt Aerosol, Halogen Species in the MBL and Mercury.* CNR-Istituto sull'Inquinamento Atmosferico. http://ies.jrc.cec.eu.int/Units/cc/events/torino2001/torinocd/Documents/Marine/MP19.htm Accessed: January

[11] Hov, Oystein; Shepson, Paul; Wolff, Eric. *The Chemical Composition of the Polar Atmosphere-The IPY Contribution*. WMO Bulletin Volume: 56 Number: 4. Pages 263-269. October 2007.

[12]J. Sommar, I.Wangberg T. Berg, K. Gardfeldt, J. Munthe, A. Richter, A. Urba, F. Wittrock, and W. H. Schroeder. *Circumpolar transport and air-surface exchange of atmospheric mercury at Ny-A° lesund (79_ N), Svalbard, spring 2002.* Atmos. Chem. Phys. Volume: 7, Pages: 151-166. 2007.

[13]Kolker, A., & Engle, M. (2007). *Mercury in coal.* Retrieved December 6, 2007, from http://energy.er.usgs.gov/health_environment/mercury/mercury_coal.htm

[14]Kolker, A., & Engle, M. (2007). *Investigating atmospheric mercury with the U.S. geological survey mobile mercury laboratory*

[15]Kolker, A., & Engle, M. (2007). *Atmospheric Mercury Speciation,*Retrieved December 6, 2007, from http://energy.er.usgs.gov/health_environment/mercury/mercury_atmospheric.html

[16]Kolker, A., Engle, M. & Belkin, H. (2007). *Mercury emissions from china.* Retrieved December/06, 2006, from http://energy.er.usgs.gov/health_environment/mercury/mercury_china_emissions.html

[17]Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* **1998**, *37*, 785-789

[18]Lee, S. J., Seo, Y., Jurng, J., Hong, J., Park, J., Hyun, J. E., et al. (2004). *Mercury emissions from selected stationary combustion sources in Korea*. Science Direct, *325*, 155-161.

[19]Molina, M., Molina L., Kolb, C. E.. *Gas-Phase and Heterogeneous Chemical Kinetics of the Troposphere and Stratosphere*. Annu. Rev. Phys. Chem.. 1996. 47:327-67

[20]Mukherjee, A.B., Zevenhoven, R.. *Mercury in coal ash and its fate in the Indian subcontinent: A synoptic review.* Science of the Total Environment. Volume: 368, Pages: 384-392. 2006.

[21]Nriagu, J., & Becker, C. (2003). Volcanic emissions of mercury to the atmospher: Global and regional inventories. *The Science of the Total Environment, 304*, 3-12.

[22]Pirrone, N., Costa, P., Pacyna, J. M., & Ferrara, R. (2001). Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmospheric Environment, 35*, 2997-3006.

[23]Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M., Crutzen, P. J., Duce, R. A., Hönninger, G., Huebert, B. J., Maenhaut, W., Mihalopoulos, N., Turekian, V. C., and Van Dingenen, R.: *Inorganic bromine in the marine boundary layer: a critical review*, Atmos. Chem. Phys., 3, 1301-1336, 2003.

[24]Schiermeier, Q. (2007). *Chemists poke holes in ozone theory.* Retrieved December, 2007, from http://www.ncas.ac.uk/news/stories/chemists_poke_holes_in_ozone_hole.html

[25]Stevens, W. J.; Krauss, M. Relativistic Compact Effective Core Potentials and Efficient, Shared-Exponent Basis Sets for the Third-, Fourth-, and Fifth-Row Atoms. *Can. J. Chem.* **1992**, *70*, 612-630

[26] U.S. Department of Commerce-National Oceanic and Atmospheric Administration-Earth System Research Laboratory-Global Monitoring Division. (2007). *South pole total column ozone*. Retrieved January 05, 2008, from http://www.esrl.noaa.gov/gmd/dv/spo_oz/spototal.html

[27] U. S. EPA (2007). *Controlling Power Plant Emissions: Overview*. Retrieved February 25, 2008. from: http://www.epa.gov/hg/control_emissions/index.htm

[28] W. R. Simpson, R. von Glasow, K. Riedel, P. Anderson, P. Ariya, J. Bottenheim, J. Burrows, L. J. Carpenter, U. Frieß, M. E. Goodsite, D. Heard, M. Hutterli, H.-W. Jacobi, L. Kaleschke, B. Neff, J. Plane, U. Platt, A. Richter, H. Roscoe, R. Sander, P. Shepson, J. Sodeau, A. Steffen, T. Wagner, and E.Wolff.: *Halogens and their role in the polar boundary-layer ozone depletion*. Atmos. Chem. Phys., 7, 4375-4418, 2007.

[29] Wang, D., He, L., Wei, S., & Feng, X. (2006). Estimation of mercury emission from different sources to atmosphere in chongqing, china. *Science Direct,* (366), 722-728.

[30] Wiedinmyer, C., & Friedli, H. (2007). Mercury emissions estimates from fires: An initial inventory for the United States. *Environment Science Technology, 41*(23), 8092-8098.

[31] Yudovich, Y. E., & Ketris, M. P. (2005). *Mercury in coal: A review part 2*. coal use and environmental problems. *Science Direct, 62*, 135.

[32] Yung, Y. L., Pinto, J. P., Watson, R. T., and Sander, P.: *Atmospheric bromine and ozone perturbations in the lower stratosphere*. J. Atmos. Sci., 37, 339-353, 1980.

[33] Zheng, Liugen, Guijian, Liu, Chou, Chen-Lin. *The distribution, occurrence and environmental effect of mercury in Chinese coals*. Science of the Total Environment. Volume: 384, Pages 374-383. 2007.

[34] Zheng, L., Lui, G., & Chou, C. (2007). The distribution, occurrence and environmental effect of mercury in Chinese coals. *Science Direct, 384*, 374.