



Sample: Chemistry - Final Exam

Correctly use significant figures in any question where this applies. Show your work for calculation problems.

Essay Questions

1. (2 points) Describe where ozone (O_3) is found in the stratosphere. When anthropogenic ozone depletion is not a factor, what is the typical steady state (equilibrium) concentration there, and why is it found at that particular location at that concentration in spite of its continual creation and destruction?

Ninety percent of ozone is in the stratosphere, from the upper troposphere and up to an altitude of 50 kilometers. Stratospheric ozone - what scientists call the ozone layer - has uneven thickness above the Earth. The ozone layer over Antarctica is thinnest because of the unique atmospheric conditions that contribute to the concentration of chemicals that destroy ozone. If we take all of the ozone in the atmosphere to lower them to the earth surface and distribute it on the ozone layer will have a thickness of less than half a centimeter.

However, scientists believe that life on Earth probably could not arise and exist if not for the protective ozone layer in the stratosphere. Its depletion of human-made gases particularly alarming among scientists, taking into account the critical importance of ozone for life on Earth. The greatest damage to the stratospheric ozone is applied chlorine and bromine-containing gases.

In 1974, Mario Molina and Sherwood Rowland discovered that one of the most destructive chlorine gases are chlorofluorocarbons (CFCs) - Synthetic substances that are used as propellants in aerosols and refrigerants in refrigerators and air conditioners. In 1985, Joseph Farman and his colleagues found a dramatic depletion of the ozone layer over the Antarctic - the ozone hole created by the reaction of ozone with chlorine and bromine from CFCs and other anthropogenic gases.

CFCs were developed in the 1930s and have been used in industrial, commercial and residential purposes because they are non-toxic, non-flammable and does not react with other chemical compounds near the surface. "Thanks to the properties re-open connections enjoyed widespread popularity," - said with America.gov Anne Douglass, deputy project scientist for NASA satellite "Aura", which oversees the chemical composition of the upper and lower layers of the Earth's atmosphere. Before the invention of CFCs in refrigerators used dangerous gases such as ammonia, Douglass said. CFCs on the other hand, relatively inert and nonreactive near the Earth's surface. "These compounds are dangerous to about? ,,It is because they do not



break down below the height of 30 kilometers, that is, for the same reason that they are safe for people," - said Douglass.

Once in the atmosphere, CFCs slowly float up: gases released at the surface of the Earth, it takes five to six years to reach the stratosphere. Under the influence of UV-B radiation in the stratosphere of CFC molecules released chlorine. Reacting a molecule of ozone O_3 , chlorine and cleaves it forms an ordinary oxygen molecule O_2 plus chlorine monoxide molecule $Cl + O$, none of which absorb UV-B radiation.

Isolated O oxygen atom may react with the chlorine monoxide, releasing chlorine atom and forming an ordinary oxygen molecule O_2 . The released chlorine can now split even one molecule of ozone O_3 . One chlorine atom can repeat this cycle many thousands of times, destroying many thousands of molecules of ozone.

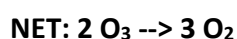
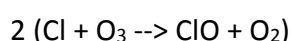
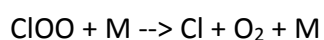
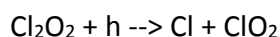
2. (2 points) Describe X catalyst degradation of ozone. Is the presence of chlorine and bromine radicals in the atmosphere solely due to human (anthropogenic) activities?

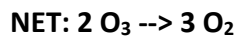
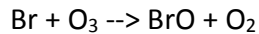
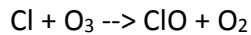
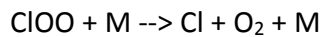
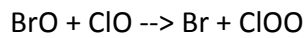
Some of the pollutants in the atmosphere such as nitrogen oxide and chlorofluorocarbons (CFCs) function as catalysts of depletion of the ozone.

For example, in the stratosphere, chlorofluorocarbons (CFCs), which is used for refrigeration, propellants, UV light is capable of breaking weaker C-Cl bonds by homolysis to produce chlorine free radicals. CFCs usually remain in the troposphere but the CFCs molecules eventually diffuse into the upper atmosphere, stratosphere where they gain higher energy from UV light. When the CFCs is exposed to high energy UV radiation, photochemical decomposition occurs producing reactive chlorine gas atoms. Instead of C-F bond, which is more electronegative, thus stronger than C-Cl, the weaker C-Cl bond is broken down first.

The chlorine free radical produced from the photochemical decomposition of the CFCs functions as a catalyst in the decomposition of ozone.

As a result overall, an ozone molecule reacts with an oxygen free radical to form 2 oxygen molecules.





Human activities cause the emission of *halogen source gases* that contain chlorine and bromine atoms. These emissions into the atmosphere ultimately lead to stratospheric ozone depletion. The source gases that contain only carbon, chlorine, and fluorine are called “chlorofluorocarbons,” usually abbreviated as CFCs. CFCs, along with carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3), historically have been the most important chlorine-containing gases that are emitted by human activities and destroy stratospheric ozone

1). These and other chlorine-containing gases have been used in many applications, including refrigeration, air conditioning, foam blowing, aerosol propellants, and cleaning of metals and electronic components. These activities have typically caused the emission of halogen-containing gases to the atmosphere. Another category of halogen source gases contains bromine. The most important of these are the “halons” and methyl bromide (CH_3Br). Halons are halogenated hydrocarbon gases originally developed to extinguish fires. Halons are widely used to protect large computers, military hardware, and commercial aircraft engines.

Because of these uses, halons are often directly released into the atmosphere. Halon-1211 and halon-1301 are the most abundant halons emitted by human activities. Methyl bromide, used primarily as an agricultural fumigant, is also a significant source of bromine to the atmosphere.

Human emissions of the principal chlorine- and bromine-containing gases have increased substantially since the middle of the 20th century. The result has been global ozone depletion, with the greatest losses occurring in polar regions.

Other human sources of chlorine and bromine.

Other chlorine- and bromine-containing gases are released regularly in human activities. Common examples are the use of chlorine gases to disinfect swimming pools and wastewater, fossil fuel burning, and various industrial processes. These activities do not contribute significantly to stratospheric amounts of chlorine and bromine because either the global source is small or the emitted gases are short-lived (very reactive or highly soluble) and, therefore, are removed from the atmosphere before they reach the stratosphere.

Natural sources of chlorine and bromine. There are a few halogen source gases present in the stratosphere that have large natural sources. These include methyl chloride (CH_3Cl) and methyl bromide (CH_3Br), both of which are emitted by oceanic and terrestrial ecosystems. Natural sources of these two gases contribute about 17% of the chlorine currently in the stratosphere and about 30% of the bromine. Very short-lived source gases containing bromine, such as bromoform (CHBr_3), are also released to the atmosphere primarily from the oceans.



Only a small fraction of these emissions reaches the stratosphere, because these gases are rapidly removed in the lower atmosphere. The contribution of these very short-lived gases to stratospheric bromine is estimated to be about 24%, but this has a large uncertainty. Changes in the natural sources of chlorine and bromine since the middle of the 20th century are not the cause of observed ozone depletion.

Lifetimes and emissions. After emission, halogen source gases are either naturally removed from the atmosphere or undergo chemical conversion. The time to remove or convert about 60% of a gas is often called its atmospheric "lifetime." Lifetimes vary from less than 1 year to 100 years for the principal chlorine- and bromine-containing gases. Gases with the shortest lifetimes (e.g., the HCFCs, methyl bromide, methyl chloride, and the very short-lived gases) are substantially destroyed in the troposphere, and therefore only a fraction of each emitted gas contributes to ozone depletion in the stratosphere. The amount of a halogen source gas present in the atmosphere depends on the lifetime of the gas and the

3.(7 points)The airborne concentration of sulfur dioxide in the immediate vicinity of a steel mill was measured to be 100 ppm on a volumetric basis. Use dimensional analysis to calculate the corresponding concentration in terms of mass per volume (mg/m³). There are 64.1 g SO₂/mol SO₂, 10³ L/m³, 10³ mg/g, and the ideal gas law constant is 0.0821 L atm/mol K; assume 25.0 °C, and 1.00 atm pressure.

Solution:

100 ppm means 100 parts per million.. ie..100 L SO₂ / 1x10⁶ L of air

64.1g = 1 mol SO₂

10³ L = 1m³

10³mg = 1g

PV = nRT

V = nRT / P

and at 25.0°C and 1.00 atm for 1 mole of gas.

V = (1 mol) x (0.08206 Latm/molK) x (298.15K) / (1.00 atm) = 24.47L

1 mole (of an ideal gas) = 24.47L @25°C and 1.00 atm

(100 L SO₂ / 10⁶ L air) x (1 mol SO₂ / 24.47L SO₂) x (64.1g SO₂ / mol SO₂) x (10³mg SO₂ / g SO₂) x (10³L air / m³ air) = 262 mg/m³

(L SO₂ / L air) x (mol SO₂ / L SO₂) x (g SO₂ / mol SO₂) x (mg SO₂ / g SO₂)

x (10³L air / m³ air)



4. (2 points) The destruction of ozone (O_3) in the stratosphere is a problem. Explain why increased concentrations of O_3 at ground level is a problem for human health

Ground-level ozone - this term to denote ozone, which is in near-earth air masses. This gas is extremely toxic and in high concentrations it can not tolerate a single living organism. The toxicity of ozone is due to its high oxidizing properties, giving rise to free radicals of oxygen. Pulmonary disease, low immunity and other symptoms caused by ozone in animals and humans, were the reason that this gas was referred to the Russian Federation to the class extremely hazardous substances - the maximum on the scale of the danger. It should be noted that there are no sources directly producing and emitting ozone atmosphere. Ground-level ozone - a secondary gas, ie it arises in the course of a complex interaction of sunlight and volatile compounds - oxides of nitrogen and carbon, which, in turn, produced cars, factories, boilers with fossil fuels. Ozone has a general toxic, irritant, carcinogenic, mutagenic, genotoxic effect, can cause fatigue, headache, nausea, vomiting, and respiratory tract irritation, cough, respiratory distress, chronic bronchitis, emphysema, asthma, pulmonary edema, hemolytic anemia. Ozone reduces lung function; Ozone contributes to the development of asthma and increases the number of attacks of the disease, (15 bn / year of childhood asthma)Ozone is the most common allergic substances - dust, cockroaches, pollen, pet Ozone aggravates bronchitis and emphysema; Ozone significantly lowers immunity to infection. Especially dangerous is the impact of ozone on children, their lungs are severely affected by exposure to ozone and this has a negative impact on their development; ([www.epa.gov / air now](http://www.epa.gov/airnow))Ozone acts on the respiratory enzymes, like ionizing radiation: a 30-minute inhalation of Ozone concentration of 0.8 mg / l is equivalent to 100 X-rays irradiation. Physical activity during exposure to ozone worsens its portability. Toxicity OZONE very increased in the presence of nitrogen oxides in the air: they act jointly to 20 times stronger than apart. "

5. (2 points) Testing of the contents found in an unlabeled container showed that it was mostly water, with a pH value of 4.3. What are the corresponding $[H_3O]^+$ and $[OH]^-$ values in this aqueous solution?

Solution:

$$pH = -\log[H_3O^+]$$

$$[H_3O^+] = 10^{-pH}$$

$$\text{when } pH = 4.3, [H_3O^+] = 10^{-4.3} = 5,01 \times 10^{-5}$$

$$K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$$

$$[OH^-] = 1 \times 10^{-14} / 5,01 \times 10^{-5} = 1,99 \times 10^{-10}$$



6. (2 points) If the contents of the container described in question 5 had been a non-aqueous liquid would a pH value obtained be meaningful? Why or why not?

Solution:

It is acidic.

The $\text{pH} = -\text{LOG}(\text{H}_3\text{O}^+)$, so you can figure that.

The pOH is $14 - \text{pH}$. $\text{pOH} = -\text{LOG}(\text{OH}^-)$

And no, pH is not a meaningful measurement for nonaqueous phase liquids.

Because acidity and alkalinity are all about water and how it loses or gains a proton in solution.

7. (2 points) Would you expect the relative proportion of ^{14}C in fossil fuels to be higher or lower than the relative proportion found in typical living biological organisms? Explain your answer.

Archaeologists use the exponential, radioactive decay of carbon 14 to estimate the death dates of organic material. The stable form of carbon is carbon 12 and the radioactive isotope carbon 14 decays over time into carbon 12 and other particles. Carbon is naturally in all living organisms and is replenished in the tissues by eating other organisms or by breathing air that contains carbon. At any particular time all living organisms have approximately the same ratio of carbon 12 to carbon 14 in their tissues. When an organism dies it ceases to replenish carbon in its tissues and the decay of carbon 14 to carbon 12 changes the ratio of carbon 12 to carbon 14. Experts can compare the ratio of carbon 12 to carbon 14 in dead material to the ratio when the organism was alive to estimate the date of its death. Radiocarbon dating can be used on samples of bone, cloth, wood and plant fibers.

The half-life of a radioactive isotope describes the amount of time that it takes half of the isotope in a sample to decay. In the case of radiocarbon dating, the half-life of carbon 14 is 5,730 years. This half life is a relatively small number, which means that carbon 14 dating is not particularly helpful for very recent deaths and deaths more than 50,000 years ago. After 5,730 years, the amount of carbon 14 left in the body is half of the original amount. If the amount of carbon 14 is halved every 5,730 years, it will not take very long to reach an amount that is too small to analyze. When finding the age of an organic organism we need to consider the half-life of carbon 14 as well as the rate of decay, which is -0.693 .

For example, say a fossil is found that has 35% carbon 14 compared to the living sample.



8. (3 points) Using a ruler and calculator, estimate from Figure 6-13 in your textbook (Baird and Cann, page 268) the fraction of CO₂ emissions in 2009 compared to 1990 (a) from the United States, and (b) collectively from China and India. What does the change in the fraction of total CO₂ emissions from the two large developing countries over that 19 year period imply for efforts in the U.S. or other developed countries to cap CO₂ emissions at current rates to slow the rate of increase of global atmospheric CO₂ concentration?

Solution;

The United States

the fraction of CO₂ emissions in 1990 is **19.1**

the fraction of CO₂ emissions in 2009 is **17.2**

China and India

the fraction of CO₂ emissions in 1990 is $2.2 + 0.8 = 3.0$

the fraction of CO₂ emissions in 2009 is $6.2 + 1.5 = 7.7$

From the calculations we see that the emissions in the U.S. in 2009 decreased, while in the China and India, on the contrary risen.

In 1997, the State of Illinois adopted a trading program for volatile organic compounds in most of the Chicago area, called the Emissions Reduction Market System. Beginning in 2000, over 100 major sources of pollution in eight Illinois counties began trading pollution credits.

In 2003, New York State proposed and attained commitments from nine Northeast states to form a cap-and-trade carbon dioxide emissions program for power generators, called the Regional Greenhouse Gas Initiative (RGGI). This program launched on January 1, 2009 with the aim to reduce the carbon "budget" of each state's electricity generation sector to 10% below their 2009 allowances by 2018.

Also in 2003, U.S. corporations were able to trade CO₂ emission allowances on the Chicago Climate Exchange under a voluntary scheme. In August 2007, the Exchange announced a mechanism to create emission offsets for projects within the United States that cleanly destroy ozone-depleting substances.

Also in 2003, the Environmental Protection Agency (EPA) began to administer the NO_x Budget Trading Program (NBP) under the NO_x State Implementation Plan (also known as the "NO_x SIP Call") The NO_x Budget Trading Program was a market-based cap and trade program created to reduce emissions of nitrogen oxides (NO_x) from power plants and other large



combustion sources in the eastern United States. NO_x is a prime ingredient in the formation of ground-level ozone (smog), a pervasive air pollution problem in many areas of the eastern United States. The NBP was designed to reduce NO_x emissions during the warm summer months, referred to as the ozone season, when ground-level ozone concentrations are highest. In March 2008, EPA again strengthened the 8-hour ozone standard to 0.075 parts per million (ppm) from its previous 0.008 ppm.

In 2006, the California Legislature passed the California Global Warming Solutions Act, AB-32, which was signed into law by Governor Arnold Schwarzenegger. Thus far, flexible mechanisms in the form of project based offsets have been suggested for three main project types. The project types include: manure management, forestry, and destruction of ozone-depleted substances. However, a recent ruling from Judge Ernest H. Goldsmith of San Francisco's Superior Court states that the rules governing California's cap-and-trade system were adopted without a proper analysis of alternative methods to reduce greenhouse gas emissions. The tentative ruling, issued on January 24, 2011, argues that the California Air Resources Board violated state environmental law by failing to consider such alternatives. If the decision is made final, the state would not be allowed to implement its proposed cap-and-trade system until the California Air Resources Board fully complies with the California Environmental Quality Act.

Since February 2007, seven U.S. states and four Canadian provinces have joined together to create the Western Climate Initiative (WCI), a regional greenhouse gas emissions trading system. July 2010, a meeting took place to further outline the cap-and-trade system which if accepted would curb greenhouse gas emissions by January 2012.

On November 17, 2008 President-elect Barack Obama clarified, in a talk recorded for YouTube, his intentions for the US to enter a cap-and-trade system to limit global warming.

The 2010 United States federal budget proposes to support clean energy development with a 10-year investment of US \$15 billion per year, generated from the sale of greenhouse gas (GHG) emissions credits. Under the proposed cap-and-trade program, all GHG emissions credits would be auctioned off, generating an estimated \$78.7 billion in additional revenue in FY 2012, steadily increasing to \$83 billion by FY 2019.

The American Clean Energy and Security Act (H.R. 2454), a greenhouse gas cap-and-trade bill, was passed on June 26, 2009, in the House of Representatives by a vote of 219-212. The bill originated in the House Energy and Commerce Committee and was introduced by Representatives Henry A. Waxman and Edward J. Markey. Although cap and trade also gained a significant foothold in the Senate via the efforts of Republican Lindsey Graham, Independent



Democrat Joe Lieberman, and Democrat John Kerry, the legislation was ultimately abandoned due to a confluence of political factors.

9. (3 points) In “Toward a Liquid Hydrogen Fuel Economy” Jones describes a vision where vehicles and other energy-requiring systems use liquid H_2 . In order to avoid carbon emissions from the use of such a power source, what are the possibilities regarding how the H_2 would need to be obtained?

Hydrogen (H_2) is being aggressively explored as a fuel for passenger vehicles. It can be used in fuel cells to power electric motors or burned in internal combustion engines (ICEs).

It is an environmentally friendly fuel that has the potential to dramatically reduce our dependence on imported oil, but several significant challenges must be overcome before it can be widely used.

Hydrogen produces no air pollutants or greenhouse gases when used in fuel cells; it produces only nitrogen oxides (NO_x) when burned in ICEs.

Because pure hydrogen does not occur naturally, it takes energy to manufacture it. There are different ways to manufacture it, such as, electrolysis and steam-methane reforming process. In electrolysis, electricity is run through water to separate the hydrogen and oxygen atoms. This method can be used by using wind, solar, geothermal, hydro, fossil fuels, biomass, and many other resources. The non-polluting methods of making electricity (wind, solar, hydro, geothermal, biomass), rather than fossil fuels, would be better used as to continue the environment-friendly process of the fuel. Obtaining hydrogen from this process is being studied as a viable way to produce it domestically at a low cost. Steam-methane reforming process extracts the hydrogen from methane. However, this reaction causes a side production of carbon dioxide and carbon monoxide which are greenhouse gases and contribute to global warming. Even so, the current leading technology for producing hydrogen in large quantities is steam reforming of methane gas (CH_4).

Once manufactured, hydrogen is an energy carrier (i.e. a store for energy first generated by other means). The energy can be delivered to fuel cells and generate electricity and heat, or burned to run a combustion engine. In each case hydrogen is combined with oxygen to form water. The heat in a hydrogen flame is a radiant emission from the newly formed water molecules. The water molecules are in an excited state on initial formation and then transition to a ground state; the transition unleashing thermal radiation. When burning in air, the temperature is roughly $2000^\circ C$. Historically, carbon has literally been the carrier of hydrogen as more hydrogen is packed in fossil fuels than pure liquid hydrogen of the same amount. The carbon atoms have classic storage capabilities and also adds more energy output when burned with hydrogen. However, burning carbon base fuel and releasing its exhaust has produced too



much global warming due to the greenhouse effect of carbon gases. Pure hydrogen is the smallest element and some of it will inevitably escape from any known container or pipe in micro amounts, yet simple ventilation could prevent such leakage from ever reaching the volatile four percent hydrogen-air mixture.

So long as the product is in a gaseous or liquid state, pipes are a classic and very efficient form of transportation. Pure hydrogen, though, has a long term effect on metal pipes causing metal to become more brittle, thus this might require a little more maintenance in the long run. Potentially, there is plenty of wind power to supply all of the world's electrical supply many times over. Once the construction cost of a windmill is paid off, very little maintenance cost is required and the energy is practically free. Although electricity can be delivered long distances, large amounts of electricity cannot be stored and must be generated as needed, and this requires complicated distribution processes. This is where hydrogen can act as a good carrier. With electrolysis, electricity can affect the extraction of hydrogen and oxygen from water with a little lost of energy in process. Then the hydrogen can be piped long distances and reconverted into electricity. A greater quantity of hydrogen can be delivered while bonded to carbon and there won't be micro leakage nor will metal become brittle. The carbon based exhaust from burning coal could be combined, piped and stored with hydrogen and aid hydrogen as a carrier to combustion engines that generate electricity when needed. If hydrogen can be feasibly extracted from the gas before being burned, then pure water can be recycled and the carbon base exhaust could be further sequestered into algae. Algae farms can produce organic fertilizer, feed for animals, and algae oil from which numerous petroleum products can be made. In this way, carbon base exhaust from burning coal becomes a carrier for hydrogen fuel and becomes plants (algae) instead of global warming.

10. (7 points) The half-life for ^{239}Pu is 2.4×10^4 years. If ^{239}Pu is released to the atmosphere due to a nuclear accident, how long will it take for the initial activity from ^{239}Pu to decay to 10% of the original value (A_0)? The activity at time t (e.g., when t = the time at which the activity has decayed to 10% of the original value) may be calculated as follows: $A_t = A_0 e^{-kt}$ given that $k = 0.693/t_{1/2}$

Solution:

$$\tau_{1/2}(^{239}\text{Pu}) = 2,4 \cdot 10^4$$

$$k = 0,693 / \tau_{1/2}$$

$$A_t = A_0 \cdot e^{-kt}$$

$$k = 0,693 / 2,4 \cdot 10^4 = 0.000028875$$



$$A_0 = [\tau_{1/2} * 10\%]/100\% = 2400 \text{ years}$$

$$A_t = A_0 * e^{-kt}$$

$$A_t = 2400 * e^{-(0,0000288754 * 24000)}$$

$$A_t = 1200$$

11. (7 points total) A chemical substance has a K_{ow} value of 600,000.

A. (6 points) Assume that 1-octanol is a perfect surrogate for lipid tissues in aquatic organisms, and that the concentrations of this chemical in the water where these organisms live and in the lipid tissues of fish there are in equilibrium, and that the concentration of the chemical in the water is 3.0×10^{-5} ppm. What is the expected concentration of this chemical in the lipid tissues of the fish?

Solution

$$K_{ow} = C_o/C_w$$

$$K_{ow} \text{ (for substance)} = 600000$$

$$C_o = C_w * K_{ow}$$

$$C_o = 600000 * 3,0 * 10^{-5} \text{ ppm}$$

$$C_o = 18 \text{ – for water}$$

$$C_o \text{ (for substance)} = 18/1000000 = 0,000018 \text{ ppm.}$$

B. (1 point) What is the log K_{ow} value for the chemical in question?

$$\log[K_{ow}] = \log[C_o]/\log[C_w]$$

$$\log[K_{ow}] = -4,74/-4,52 = 1,048$$