

Gaining Perspective with Environmental Chemistry

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ABSTRACT

The Environmental Chemistry course that was recently developed at the University of Kentucky is a very popular elective with “pre-service” students pursuing a bachelor’s degree in chemistry and a Masters degree in education. The goals of the course are: (1) to instruct students in the fundamental principles of the chemistry of the environment; (2) to increase students working knowledge of key chemical principles (equilibrium, kinetics, acid-base and oxidation-reduction reactions, gas phase reactions, etc.) by applying these principles to “complex” environmental systems and; (3) to have the students critically evaluate, what is often, conflicting information about environmental chemistry. The third objective, which is approached by having students write a position paper about a “controversial” environmental issue, is a practical exercise in risk assessment that these individuals are encouraged to pass on to their middle and high school students.

One major objective of nearly all science courses is instructing students in the fundamental principles and theories associated with the subject material. Instruction in the sciences is, however, an ideal setting to accomplish a second and, in my opinion, more important educational task: teaching students how to critically evaluate ideas and problems and formulate plausible solutions. Unfortunately, many courses, especially at the undergraduate level, are structured to emphasize the first objective - passing on a working knowledge of a set of "basic facts" - at the expense of the second - educating individuals who can think independently.

Both of the educational objectives described above can be achieved, in part, by teaching science in the same way that it is practiced - as a discovery process. Our roles as science educators should be to (1) motivate students to participate in the discovery process, (2) provide them with the basic information needed to begin exploring the subject matter at hand and, (3) guide them through the process. Allowing, or forcing, the students to participate in the learning discovery process will provide them with practical experience in the type of critical thinking that the process requires.

In the ideal situation, every science course would provide students with the opportunity to participate in the discovery process in both laboratory and classroom experiences. Unfortunately, many science courses at large undergraduate institutions now only include a classroom component because of time and monetary constraints. This does not mean, however, that we should abandon the key objective of educating students in the discovery process. In the classroom setting, one can encourage, cajole, and force students to participate in discovery by asking them to deduce, either from their own observations or from a series of data, the principle or idea that is to be discussed. In this way, the students, whether they arrive at a plausible conclusion on their own, or require a series of "leading" questions, gain experience in the critical thinking process.

The topic of environmental chemistry provides many opportunities to engage students in critical thinking. For example, a discussion of increased levels of greenhouse gases in the atmosphere and their potential impact on climate can begin with a plot of the change in concentration of CO_2 in troposphere over the last 40 years. These data can lead to a discussion of the absorption of electromagnetic radiation by greenhouse gases, global carbon balances, the atmospheric window, and radiative forcing of other, much lower concentration, greenhouse gases. From here, students can be lead through a discussion of climate modeling and predictions of the impact of increased concentrations of greenhouse gases. Many students will, undoubtedly, conclude at this point that we are already seeing an increase in average temperature because of greenhouse gases. While this may be the case, I challenge students to consider their conclusion in light of (1) the magnitude of temperature changes over the last 100,000 years (10^0C) and the last 1,000 years ($\sim 1.5^0\text{C}$); (2) the difference between correlation and causation in the temperature and greenhouse gas ice core measurements; and (3) the uncertainties associated with climate modeling. This discussion is then capped off by considering how science is currently being used to set national and international policy. The same questioning, discovery approach is used throughout the course as we consider the chemistry of acid rain, stratospheric ozone, air particulate pollution, drinking water standards, agricultural runoff pollution, and pesticide use.

Students in the Environmental Chemistry course are also challenged to critically evaluate, what is often,

conflicting information by requiring that they develop a position paper. In this paper, the student is asked to review public perception and/or popular press coverage of an environmental issue or related topic and then present a reasoned, scientific discussion of the issue. While their response is to be based upon “good scientific evidence” and sound reasoning, they are asked to gear the paper toward a general audience. Examples of topics that students have selected include:

disposal of radioactive waste
 greenhouse gases and global warming
 risk of asbestos
 aspartame and brain cancer
 hazards of EMF
 reformulated gasoline’s
 agriculture’s impact on water quality
 veterans and agent orange
 Gulf-war syndrome
 “Future Without Risk”
 CFCs and global warming
 CFCs and ozone loss
 risk of indoor radon
 new motor vehicle emission requirements
 the disposal of nerve gas by incineration
 power production and greenhouse gases
 EPA’s new standards for ozone
 EPA’s new standards for particulate matter
 deforestation and global warming

While not anticipated, the most beneficial aspect of this exercise in an upper-level chemistry course has been to challenge students to critically evaluate information. The majority of students in the course will locate information, primarily on the Internet, that appears to be from a credible source but is clearly incorrect. Through a pre-grade of their position paper, I identify “potential” factual errors and ask the student to re-think the information in light of what they already know about the chemistry of the subject matter.

In addition to challenging students (and teachers) to abandon the “talking head” approach to the classroom, I find that, even in an upper level **elective** course, there is a need to motivate students to engage in a study of the subject matter. In environmental chemistry, it is quite easy to encourage students to study the subject material and participate in the discovery process by demonstrating to them the relevance of chemistry, and science in general, in our technological society. As noted above, this is accomplished by using “real world” and current topic examples, whenever possible, to illustrate fundamental principles in the course. It should be emphasized that the chemistry is not “glossed over” with this approach. (A problem set for “Atmospheric Chemistry” is provided at the end of this paper as an example of the depth and breadth of chemical concepts that the students are challenged with in Environmental Chemistry.) Rather, the course uses relevant, current, and controversial topics to reinforce and bring together many of the chemical principles that the student should have learned during their undergraduate career.

The course outline and an example problem set follow.

Course Outline

1. The Atmosphere
 - 1.1. Function and composition
 - 1.2. Mass transfer and residence times
 - 1.3. Major constituents
 - 1.4. Climate
 - 1.5. Greenhouse effect and greenhouse gases
 - 1.6. Chemistry of oxygen and the hydroxyl radical

- 1.7. Chemistry of the stratosphere – the ozone layer
- 1.8. Chemistry of the troposphere – photochemical smog
- 1.9. Indoor air pollution
2. The Hydrosphere
 - 2.1. The hydrologic cycle
 - 2.2. Unique physical and chemical properties of water
 - 2.3. Acids, bases and salts
 - 2.4. Acid rain
 - 2.5. Redox chemistry in aquatic systems
 - 2.6. Microorganisms and aquatic chemistry
 - 2.7. Water pollution
 - 2.8. Water treatment
3. The Geosphere
 - 3.1. Major minerals in the earth's crust
 - 3.2. Soil chemistry
 - 3.3. Fertilizers
 - 3.4. Management and treatment of hazardous wastes
4. Environmental toxicology
 - 4.1. Dose-response relationships
 - 4.2. Entry routes
 - 4.3. Metabolism of xenobiotics
 - 4.4. Pesticides
 - 4.5. Dioxins
 - 4.6. Metals

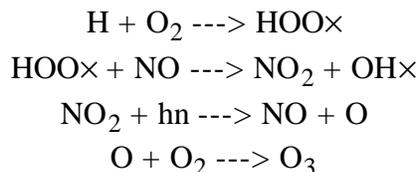
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Problem Set 1

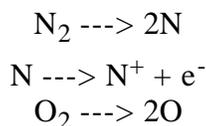
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1. Give the concentrations/pressures of each of the following at sea level in units of atm, mol L⁻¹, molecules cm⁻³ and ppmv.
 - a) oxygen (p = 0.21 atm)
 - b) methane (c = 1700 ppbv)
 - c) hydroxyl radical (c = 5 x 10⁵ molec cm⁻³)
2. Calculate the approximate masses of the three most abundant components of the atmosphere, assuming negligible masses of the minor components.
3. The heat capacity of an ideal gas at constant pressure is approximately 7R/2, where R is the ideal gas constant. It has been suggested that the Earth's atmosphere might increase in temperature by 2.5 °C over the next century. Estimate the average amount of heat that would need to be added to the atmosphere per year to achieve this heating effect. Assume no compensating heat losses.
4. Calculate the mean free path of molecules in air at 20 °C and 1.00 atm. Assume an average molecular diameter of 0.17 nm. Repeat the calculation for the outer atmosphere where the temperature is 1500 °C and the pressure is 10⁻¹⁰ atm. In this case, assume that most of the gas species are atomic and an average atomic diameter of 75 pm.
5. The oxidation of tropospheric trace gases is often described in terms of cycles in which the formation and destruction of all free radical species are made to cancel out. One such cycle for the oxidation of CO is:

$$\text{CO} + \text{OH}\cdot \rightarrow \text{CO}_2 + \text{H}\cdot$$



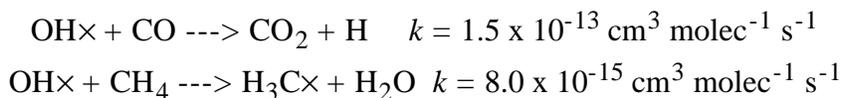
- What is the overall reaction for this cycle?
 - According to this mechanism, what is the net effect of oxidizing CO in the troposphere?
 - Which substances act as catalysts in the above cycle?
 - Quantitatively, what is the effect on the atmosphere in a large city of oxidizing 100 ppbv of CO?
- Calculate the residence time of ozone in the atmosphere if the total mass of ozone is 3×10^{12} kg and 3.5×10^8 kg are made and destroyed each day.
 - Estimate the wavelength of maximum intensity of radiation emission for the sun ($T = 6000$ K) and the earth ($T = 288$ K). Given that the approximate heat capacity for an ideal gas is $7R/2$, how much energy must be absorbed by the earth's atmosphere per unit volume to raise the temperature by 1°C ? Assume a pressure of 1 atm and a temperature of 288 K. Convert your answer to number of photons absorbed per liter both for maximum intensity solar photons and for the earth's maximum intensity IR emission.
 - Calculate the longest wavelength at which each of the following reactions will occur:



Calculate the energy, in kJ/mol, associated with the absorption of infrared radiation by greenhouse gases CO_2 at 2250 cm^{-1} and H_2O at 1800 cm^{-1} . Describe the physical process which occurs when this radiation is absorbed.

- At an altitude of 170 km ($T = 1100$ K), 80% of all oxygen molecules are dissociated into atoms. Assume that $p(\text{total}) = 3 \times 10^{-10}$ atm and that O_2 and N_2 dissociate in equal proportions.
 - Estimate DG for the reaction $2\text{O}(\text{g}) \text{---> O}_2(\text{g})$ at these conditions.
 - Why does the concentration for O (g) remain so high when DG is so highly negative?
- Model, for a period of 20 years, the predicted effect of a sudden, **one-time** injection of 100 ppmv of CO_2 into the atmosphere. Use the following data:
 - CO_2 in the atmosphere = 1.4×10^{16} mol
 - CO_2 in ocean surface waters = 6.1×10^{16} mol
 - CO_2 in deep ocean waters = 7.5×10^{17} mol
 - rate constant for transfer of CO_2 from atmosphere to surface water = 0.54 y^{-1}
 - rate constant for transfer of CO_2 from surface waters to deep waters = 0.02 y^{-1}
 - rate constant for transfer of CO_2 from surface waters to atmosphere = 0.10 y^{-1}

- The diurnally and seasonally averaged concentration of $\text{OH}\times$ in the troposphere is 5×10^5 molec cm^{-3} . The two major sinks for $\text{OH}\times$ are the following two reactions which consume 70% and 30%, respectively, of all hydroxyl radicals:



Both rate constants are given at 300 K. The concentration of CH_4 in the atmosphere is approximately 1700 ppbv. Estimate the diurnally and seasonally averaged concentration of CO. Estimate the reduction in the average $\text{OH}\times$ concentration at the new steady state if the concentration of CO were doubled.

12. Emissions of methane to the atmosphere are given below. Calculate the residence time of methane in the atmosphere if its current concentration in the atmosphere is 1.7 ppmv.

Sources of atmospheric methane (10^9 kg/year)	
Rice paddies	95
Wetlands	150
Oceans & Lakes	35
Cattle	120
Other sources	150

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Estimates of the total reserves of methane hydrate in the permafrost and below the ocean floors range up to 10^{17} kg. Suppose that 1% of this material were to melt per year. What would be the increase in the amount of methane in the atmosphere per year (ppmv y^{-1}), assuming no additional sinks for methane?

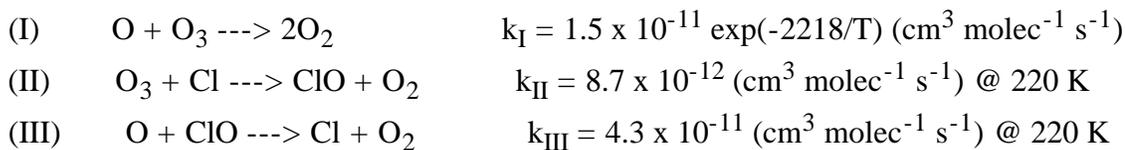
13. The following reaction has a rate constant $k = 1.1 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at 220 K.



- a) What is the rate of reaction in $\text{mol L}^{-1} \text{ s}^{-1}$ if $p(\text{total}) = 0.10 \text{ atm}$ and $c(\text{O}) = 2.1 \times 10^{-4} \text{ ppmv}$?
- b) Calculate the pseudo-first order rate constant for this reaction (Which concentrations do you assume to be constant?). Calculate the half-life of $\text{O}(\text{g})$ under these conditions. What does your result tell you about the concentration of $\text{O}(\text{g})$ in the atmosphere once the sun sets?
14. Suppose that a city is 25 km across. What is the number of moles of NO_x in the atmosphere above the city if the average NO_x concentration is 0.04 ppmv and this is uniformly mixed to an altitude of 1.0 km?
15. The numerical value of the rate constant for the reaction below is $2.6 \times 10^{12} \exp(-3200/T)$ in $\text{L mol}^{-1} \text{ s}^{-1}$.



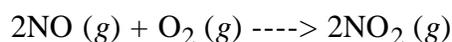
- a) Calculate the activation energy for this reaction.
- b) Calculate the rate constant for the reaction at 800 K and 288 K.
- c) Calculate the half-life for the reaction at 800 K and 288 K when $p(\text{NO})$ is initially 45 ppbv.
16. Consider the oversimplified scheme for the destruction of ozone in the atmosphere:



and the steady state concentrations (molec cm^{-3}) of $[O] = 5.0 \times 10^7$; $[Cl] = 1.0 \times 10^5$; $[ClO] = 6.4 \times 10^7$; and $[O_3] = 3.2 \times 10^{12}$ to calculate the following:

- The activation energy of reaction I.
- The rates of reactions I, II, and III.
- The overall rate of the cycle Reaction II + Reaction III.
- What fraction of the ozone is destroyed by the direct reaction (I) as opposed to the cycle in part (c).

17. Assume that the following is the slow elementary step in a reaction:



- Write the rate law for this reaction
- A sample of air at 290 K is contaminated with 1.0 ppmv of NO. Under these conditions can the rate law be simplified? If so, write the simplified rate law.
- Under the conditions described in part (b), the half-life of NO has been estimated as 100 h. What would the half-life be if the initial NO concentration were 12 ppmv?
- Suppose that in the laboratory 0.1 L of pure NO were mixed with 5.0 L of air, both at 1.00 atm and 290 K, what would be the half-life of NO under these conditions?

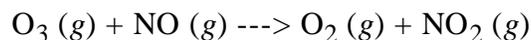
18. Peroxyacetyl nitrate (PAN) decomposes thermally with a rate constant of:

$$1.95 \times 10^{16} \exp(-13540/T) \text{ s}^{-1}$$

Calculate the half-life of PAN in the atmosphere at 25 °C and at -10 °C. Warm air containing 20 ppbv of PAN rises and cools to -10 °C. What assumptions would you have to make if this air mass was thought to be the origin of a concentration of 1.5 ppbv of PAN measured at a rural location 2000 km away two weeks later?

19. An oil-fired power station consumes 10^6 L of oil daily. Assume the oil has an average composition of $C_{15}H_{32}$ and a density of 0.80 g cm^{-3} . The gas emitted from the stack contains 75 ppmv of nitric oxide. Calculate the mass of NO emitted per day. Assuming that the stack gases become uniformly mixed to an altitude of 2 km over a city 20 km across, what concentration of NO (in ppmv) would be added to this air?

20. The rate of the reaction listed below has been measured at several temperatures. Calculate the activation energy for the reaction from the data listed below. Also, calculate the rate of the reaction at -20 °C.



t, °C	-30	-10	+10	+30
k, $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	5.9×10^{-15}	9.3×10^{-15}	1.4×10^{-14}	1.9×10^{-14}

