

Chemistry 471/671  
Introduction to Green Chemistry

Problem Set #4: Climate Change (12 points)  
Due Tuesday, October 4, 2011

- 1) A gas has an atmospheric concentration of 37 ppm and a residence time of nine years.  
a) Calculate the net release of this gas to the atmosphere (in ppm/y).  
b) Given the molar mass of this substance is 43 g/mol, convert your answer in Part (a) to grams per year. (Hint: Average mass of air is 29.0 g/mol)  
c) It is known that  $7.23 \times 10^{16}$  g of this gas is actually emitted to the atmosphere annually. Compare this value to your answer in Part (b). What additional information does this give you about this system?

a) Recall that we rearranged the steady state concentration equation to obtain  $R = t_{\text{avg}}/C_{\text{ss}}$ . We're given residence time ( $t_{\text{avg}}$ ) and  $C_{\text{ss}}$ , so we can just plug in.  
Release rate =  $R = 9 \text{ years} / 37 \text{ ppm} = 4.11 \text{ ppm/yr}$

b) Several ways to attack this, but here's how I did it.  
# moles of air in the atmosphere = (mass of atmosphere)/(average molar mass of air)

The mass of the atmosphere was missing in the question, but is Google-able and provided by an email:  $5.1 \times 10^{21}$  g

$x = (5.1 \times 10^{21} \text{ g}) / (29 \text{ g/mol}) = 1.71 \times 10^{20}$  moles of air

moles of "gas" =  $4.11 \times 10^{-6} \times$  moles of air = 7.24 moles / year

$7.24 \text{ moles / yr} \times 43 \text{ g/mol} = 3.11 \times 10^{16} \text{ g/yr}$

c) The source is  $7.23 \times 10^{16}$  g /yr. The net release is  $3.11 \times 10^{16}$  g/yr. This seems to indicate that there is a sink missing from the calculation, and that the missing sink accounts for  $(7.23 \times 10^{16} \text{ g/yr} - 3.11 \times 10^{16} \text{ g/yr}) = 4.12 \times 10^{16} \text{ g/yr}$ .

- 2) The common tropospheric pollutant gases  $\text{SO}_2$  and  $\text{NO}_2$  have molecular structures similar to  $\text{CO}_2$ . However, these molecules are bent, rather than linear. Their vibrational wavelengths are:

Gas	Symmetric stretch	Asymmetric stretch	Bending
$\text{SO}_2$	8.7 $\mu\text{m}$	7.3 $\mu\text{m}$	19.3 $\mu\text{m}$
$\text{NO}_2$	7.6 $\mu\text{m}$	6.2 $\mu\text{m}$	13.3 $\mu\text{m}$

- a) Which of these vibrations can absorb IR energy?  
b) Which, if any, of these vibrations could contribute significantly to global warming?  
c) What characteristics of these gases could limit their role as greenhouse gases?

a) This is dangerously subtle. It's easy to say that a symmetric stretch doesn't produce a change in dipole, and thus eliminate the symm stretch for both molecules. However, these molecules (unlike CO<sub>2</sub>!) are nonlinear, and thus even the symmetric stretch will change the dipole moment. All six vibrations are IR active – some more so than others.

b) Only the SO<sub>2</sub> symmetric stretch and the NO<sub>2</sub> bend are in the “atmospheric window”, so only those two would contribute strongly.

c) Both gases have short (~ days) lifetimes in the atmosphere, and do not accumulate to an appreciable extent.

3) How can the fact that nitrous oxide has three vibrations that absorb IR light be used to prove that its linear structure is NNO rather than NON?

If the molecule were NON, then the symmetric stretch would not produce a change in dipole moment, and would thus not be IR active. If all three modes are IR active, then the symmetric stretch must be active, which means that the two bonds can't be equivalent – that is, the *molecule itself* must be asymmetric.

4) Calculate the volume of CO<sub>2</sub> produced at 1 atm and 293 K from the complete combustion of 1.00 L of n-octane, a primary component of gasoline (C<sub>8</sub>H<sub>18</sub>, ρ = 0.702g/mL). If an SUV has a fuel efficiency of 19 mpg, what volume of CO<sub>2</sub> is produced in a 100 mile drive? (1 gal = 3.785 L)

The complete combustion of 1 molecule of n-octane produces 8 CO<sub>2</sub> molecules.

How many moles of n-octane are there in 1.00 L?

$$1.00 \text{ L} \times 1000 \text{ mL/L} \times 0.702 \text{ g/mL} \times 1/114.2 \text{ g/mol} = 6.15 \text{ mol}$$

That means  $8 \times 6.15 = 49.2$  moles of CO<sub>2</sub>.

Given the specified T and P,  $V(\text{CO}_2) = nRT/P = (49.2)(0.08206)(293)/(1) = 1180$  L of CO<sub>2</sub> per liter of n-octane.

100 miles /19 mpg = 5.26 gallons of gasoline

5.26 gallons x 3.785 L of gasoline /gallon x 1180 L of CO<sub>2</sub> / L of gasoline = 23500 L CO<sub>2</sub> produced(!).

Reading Analysis #3 (6 points – with 2 points reserved for Discussion)  
Due Tuesday, October 6, 2011

1) The paper by the European Space Agency discusses a dramatic reduction in sea ice in the North Atlantic in 2007. Do some web research, and discuss what's happened to sea ice in the North Atlantic in the years since.

The NA sea ice cover in was significantly higher in 2008-2010 than in 2007. Still, each year lies much below the historical average, and would be truly frightening in the absence of a year (2007) which was even worse. The available data for 2011 suggests that it was the second "worst" year on record, second only to 2007. This stresses the fact that the trend we're looking at is not a straight line. There are many, many variables in play besides simply temperature. There will always be oscillations around the trend from any number of natural and man-made sources. But the fit line is definitely trending down.

2) In the 2007 IPCC report, one of the most controversial figures has been Figure SPM.2. What is Figure 2 attempting to depict? What do the authors think is the take home message? What do critics think is the take home message?

This one's almost an opinion question – I'm not the IPCC and I'm not the critics. But here goes. I think Figure 2 is trying to show that we know a lot more about the problem than critics think we do. In particular, we know what the forcings are from greenhouse gases, AND we know which parts we DON'T understand very well (aerosols), so we can focus our efforts there. I believe the IPCC hoped that they could show that a) the error bars on CO<sub>2</sub> are pretty small, and since that's what we're trying to get governments to regulate, the rest almost is beside the point and b) even with the large error bars in the net result, there is almost zero possibility that there will be no warming, and there is a decent chance that warming will occur *faster* than their model predicts (which was absolutely the case between the last two iterations of the IPCC report). Sadly, I think critics see large error bars and say that this is bad science.

3) In the 2007 IPCC report, one of the most powerful figures has been Figure SPM.4. What is shown in Figure 4? Why is this such a powerful presentation? What are the implications for the power of Figure SPM.5?

Figure 4 shows that the observed historical trends cannot be explained using only natural forcings, but that once we include "known" forcings from Figure 2, the historical data fall exactly in to line. This holds not only when considering the entire planet, but even when breaking that down to one continent at a time. This suggests that the model *works* – and thus, it is a reasonable model to use to make the terrifying predictions shown in Figure 5.