CHEMISTRY 253
Spring, 2015 - Dixon
Homework Set 1.3
Solutions – Non-Collected Problems

Problems: 3-2, 3-6, 3-7

3-2. By adding up the three reactions, show that the net result of the photochemical decomposition of NO_2, the formation of ozone from atomic oxygen, and the above reaction constitute no overall reaction, i.e., a null process.

1) $NO_2 + h\nu \rightarrow NO + O$

2) $O + O_2 + M \rightarrow O_3 + M$

3) $NO + O_3 \rightarrow NO_2 + O_2$

all products and reactants can be cancelled to give a net null process

3-6

Using Figure 3-8, again with an intial VOC concentration of 0.50 ppm, estimate the effect on ozone levels of lowering the NO_x concentration from 0.20 to 0.08 ppm. Explain your results in terms of the chemistry discussed above.

By lowering the NO_x concentration from 0.20 to 0.08 ppm, we follow the vertical dashed line shown below. This leads from an initial ozone of 160 ppb to a new concentration (near tip of arrow) of around 190 ppm (interpreting that location based on distance between 160 and 240 ozone contours).

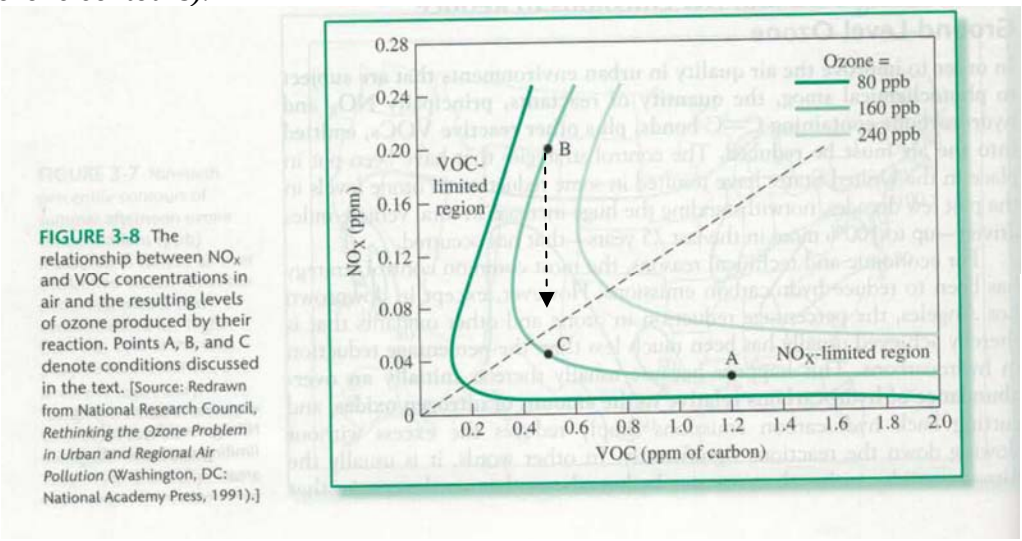

FIGURE 3-8 The relationship between NO_x and VOC concentrations in air and the resulting levels of ozone produced by their reaction. Points A, B, and C denote conditions discussed in the text. [Source: Redrawn from National Research Council, *Rethinking the Ozone Problem in Urban and Regional Air Pollution* (Washington, DC: National Academy Press, 1991).]

In terms of chemistry, greater ozone production occurs at 0.080 ppm NO_x because of the reduction of OH through the OH + NO_2 reaction and limit to ozone through the NO + O_3 reaction.

3-7

Write and balance the reactions in which NO is converted to N_2 (a) by CO and (b) by C_6H_{14} [*Hint*: The other reaction product is CO_2 plus H_2O in the latter case.]

a) $2NO + 2CO \rightarrow N_2 + 2CO_2$
b) $NO + C_6H_{14} \rightarrow N_2 + CO_2 + H_2O$ – unbalanced
balance all but O: $2NO + C_6H_{14} \rightarrow N_2 + 6CO_2 + 7H_2O$ [O is now 2 on left, 19 on right]
add NO to balance O: $19NO + C_6H_{14} \rightarrow N_2 + 6CO_2 + 7H_2O$ [N now not balanced/add to right]
$19NO + C_6H_{14} \rightarrow 19/2N_2 + 6CO_2 + 7H_2O$ [finally, multiply all coefficients by 2]
$38NO + 2C_6H_{14} \rightarrow 19N_2 + 12CO_2 + 14H_2O$

Review Questions: 3-2 to 3-5, 3-7 to 3-10, 1-15, 2-1-2-7, 2-9, 2-12
3-2 What chemical substance initiates the air oxidation of stable molecules? How is it initially formed, and how is it reformed?
OH is the chemical compound. It is initially formed through the reaction:

$O^* + H_2O \rightarrow 2OH$ (where O refers to excited – or O(1D) – oxygen atoms produced by photolysis of ozone)*

It is reformed from HO_2 (the most common reaction product of oxidation of stable molecules) in the reaction:

$HO_2 + NO \rightarrow OH + NO_2$

3-3 In general terms, what is meant by photochemical smog? What are the initial reactants in the process? Why is sunlight required?
Photochemical smog is poor quality air formed through a photochemical reactions (including production of ozone).
The initial reactants are nitrogen oxides and hydrocarbons.
Sunlight is needed to convert NO_2 to O atoms needed for formation of ozone.

3-4 What is meant by a *primary pollutant* and by a *secondary pollutant*? Give examples.
A primary pollutant is a pollutant as emitted. A secondary pollutant is formed through atmospheric reactions. An example of a primary pollutant is CO. An example of a secondary pollutant is ozone.

3-5 How does OH react with a stable molecule containing a C=C bond? With an alkane?
OH reacts with alkenes through an addition reaction, while it reacts with alkanes through H atom extraction.

3-7. What is the chemical reaction by which *thermal* NO is produced?

$N_2 + O_2 \rightarrow 2NO$

From which two sources does most urban NO arise?
Vehicle emissions and power plant emissions
What is meant by the term NO_x?
NO is NO_2 + NO – the two forms that exist in the atmosphere which interconvert rapidly between each.
What is meant by *fuel* NO?
Fuel NO is formed from fuel containing nitrogen such as CH_3NO_2 (used in model airplanes and for car racing).

3-8 Describe the strategies by which reduction of urban ozone levels has been attempted.
Historically, the main strategy has been to reduce VOCs. More recently, there has been a greater focus on reduction of NO_x.
What difficulties have been encountered by these efforts?
The main difficulties in limiting hydrocarbons is that greater ozone is produced in down-wind regions and where natural hydrocarbon emissions is high. In using a NO_x reduction strategy, greater ozone can form in urban areas.
Is photochemical smog strictly a localized urban problem?
No. NO is converted to other species such as HNO_3 slowly and can be reconverted back to NO_x through HNO_3 photolysis. This results in regional ozone (a well as other smog components) occurring in rural areas down-wind of urban areas.

3-9 What is meant by geographic regions that are VOC-*limited*? NO_x-*limited*?
VOC-limted and NO_x-limited regions refer to whether reductions in VOCs or NO_x would lead to greater ozone reduction. In many situations, it makes sense to reduce only one pollutant because reducing VOCs in a NO_x-limited situation will have little effect on ozone concentrations, or, in the case of VOC-limted situations could even lead to an increase in ozone concentrations near urban centers.

3-10 Describe the operation of the three-way catalyst in transforming emissions released by an automobile engine.
The catalyst works to reduce NO to N_2 while improving oxidation of CO, H_2, and uncombusted hydrocarbons to CO_2 and H_2O.
Does the catalyst operate when the engine is cold?
No.
Why is it important for convertors that the level of sulfur in gasoline be minimized?
Sulfur degrades catalysts.