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 NO₂, the formation of ozone from atomic oxygen, and the above reaction 
constitute no overall reaction, i.e., a null process.  
1) \[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]  
2) \[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]  
3) \[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
all products and reactants can be cancelled to give a net null process

3-6  
Using Figure 3-8, again with an initial VOC concentration of 0.50 ppm, estimate the effect on 
ozone levels of lowering the NOₓ concentration from 0.20 to 0.08 ppm. Explain your results in 
terms of the chemistry discussed above.  
By lowering the NOₓ 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](image)  

In terms of chemistry, greater ozone production occurs at 0.080 ppm NOₓ because of the 
reduction of OH through the OH + NO₂ reaction and limit to ozone through the NO + O₃ 
reaction.

3-7  
Write and balance the reactions in which NO is converted to N₂ (a) by CO and (b) by C₆H₁₄  
[Hint: The other reaction product is CO₂ plus H₂O in the latter case.]
a) 2NO + 2CO \rightarrow N_2 + 2CO_2 \\
b) NO + C_6H_{14} \rightarrow N_2 + CO_2 + H_2O \quad \text{unbalanced} \\
\text{balance all but O: } 2NO + C_6H_{14} \rightarrow N_2 + 6CO_2 + 7H_2O [O \text{ is now 2 on left, 19 on right}] \\
\text{add NO to balance O: } 19NO + C_6H_{14} \rightarrow N_2 + 6CO_2 + 7H_2O [N \text{ now not balanced/add to right}] \\
19NO + C_6H_{14} \rightarrow 19N_2 + 6CO_2 + 7H_2O \quad \text{[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? 

\textit{Vehicle emissions and power plant emissions} 

What is meant by the term NO_x? 

NO is NO_2 + N\O – 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).
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 NOx.

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 NOx 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 $\text{HNO}_3$ slowly and can be reconverted back to NOx through $\text{HNO}_3$ photolysis. This results in regional ozone (as well as other smog components) occurring in rural areas down-wind of urban areas.

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

Describe the operation of the three-way catalyst in transforming emissions released by an automobile engine. The catalyst works to reduce NO to $\text{N}_2$ while improving oxidation of CO, H2, and uncombusted hydrocarbons to CO2 and H2O.

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.