Name _____

CHEM/ATOC 5151: Atmospheric Chemistry
Final Exam - December 15, 2014

1. (20 pts) Large and complicated models are common tools these days for studying air pollution chemistry. In part, this is simply due to the power of computers. However, simple 'box' models can often be quite useful for exploring some basic principles of proposed chemical schemes.

   In the 1980s and 1990s, scientists from NOAA measuring ozone in the Arctic noticed a strange and rapid loss of ozone from normal wintertime values of 40 parts per billion (ppb) to the limit of detection (below 1 ppb) when the sun rose in springtime. These losses soon became known as "ozone depletion events", or ODEs, and it wasn't long before researchers found that BrO was somehow involved. A key problem, however, was that modelers noted the presence of NOx emitted from the snowpack would react with BrO to form bromine nitrate ($BrONO_2$), stopping the ozone-depletion chemistry. A group led by Daniel Jacob at Harvard discovered a 'solution' to this problem, noting that heterogeneous reactions of $BrONO_2$ could regenerate BrO, so that the presence of NOx was actually a requirement for maintaining the high levels of BrO needed to destroy ozone.

   This chemistry can be explored with a simple model (which is, in fact, how the group at Harvard examined the problem). Here are some simple reactions that are included in an Excel spreadsheet that you can download from the following link:

   http://storm.colorado.edu/~toohey/Final_Brox-surface.xlsx

$Br + O_3 \rightarrow BrO + O_2$	R1 _____
$BrO + BrO \rightarrow Br + Br + O_2$	R2_____
$BrO + HO_2 \rightarrow HOBr + O_2$	R3_____
$OH + HOBr \rightarrow BrO + H_2O$	R4_____
$BrO + NO \rightarrow Br + NO_2$	R5_____
$BrO + NO_2 \rightarrow BrONO_2$	R6_____
$BrONO_2 + h\nu \rightarrow Br + NO_3$	R7_____
$NO + O_3 \rightarrow NO_2 + O_2$	R8_____
$NO_2 + hn \rightarrow NO + O$	R9_____
$HOBr + BrONO_2 \rightarrow Br_2O + HNO_3$	R10_____

(a) (2 pts) In the underlined space given after each of the reactions above, write the type of reaction (i.e., bimolecular, photolysis, etc.).

(b) (2 pts) Calculate the mixing ratio of HO_2 (T6, the blue grid box), and give a probable reason why the concentrations of OH and HO_2 are fixed in this model, and not calculated explicitly for every time step?

(c) (4 pts) An observation that is often made in the late winter/early spring in the polar boundary layer is that NOx abundances are very low – around a part per billion or less. Our box model is currently set up with an initial abundance of NO_2 of 1 part per billion (Cell P2, colored yellow). Decrease this value in increments of 1/10 (i.e., 0.1 ppb, 0.01 ppb, etc.) and note the behavior of ozone, BrO, $BrONO_2$, and final NO_2 (Cell P3).

NOx (ppb)	Ozone (final)	BrO (final)	$BrONO_2$(final)	NO_2(final)
1				
0.1				
0.01				
0.001				
0.0001				

(d) (4 pts) Researchers studying the ODE phenomenon quickly realized that gas phase bromine chemistry alone could not explain the total loss of ozone observed in just a few days in springtime during these events. They noted that heterogeneous reactions of stable bromine reservoirs could better mimic the behavior of ozone and other observable quantities (like BrO). Starting with 0.1 ppb of NO_2 (Cell P2), increase the surface area density (Cell N2) as noted in the first column in the table below and note the behavior of ozone, BrO, $BroNO_2$, and final NO_2 (Cell P3)

SAD (ppb)	Ozone (final)	BrO (final)	$BrONO_2$(final)	NO_2(final)
1e-8				
4e-8				
8e-8				
1.2e-7				
1.6e-7				
2.0e-7				
2.4e-7				

(e) (2 pts) Based on the behavior you observed in Part (b), and the fact that the troposphere is usually filled with particles, speculate on whether or not ultra- low abundances of NOx are a requirement for ozone losses in the springtime polar boundary layer. Note that this phenomenon has also been called the “bromine explosion.”