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

Set 1.3

Problems: 3-1, 3-3, 3-5, 3-8

3-1 In one study, the concentration of OH in air at the time was found to be 8.7 x 10^{11} molec/cm^3. Calculate its molar concentrations and its concentrations in parts per trillion, assuming that the total air pressure is 1.0 atm and the temperature is 15°C.

n/V = (8.7 x 10^6 molec/cm^3)(1000 cm/L)(1 mol/6.02 x 10^{23} molec) = ***1.4 x 10^{-14} mol/L***

parts per trillion is equivalent to n_{OH}/n_{air}

n_{OH}/n_{air} = (1.45 x 10^{-14} mol/L)/(n_{air}/V) = (1.45 x 10^{-14} mol/L)/(P/RT)

n_{OH}/n_{air} = (1.45 x 10^{-14} mol/L)/(1.0 atm/[(0.0821 L atm/mol K)(273.15 + 15)]

n_{OH}/n_{air} = (1.45 x 10^{-14} mol/L)/(0.04227 mol/L)10^{12} = ***0.34 parts per trillion***

3-3 Convert into ppb units the EU ozone standard of 120 μg m^{-3} and the WHO standard of 100 μg m^{-3}, assuming summertime air temperature of 27°C.

EU ozone = (120 μg m^{-3})(1 μmol/48.0 μg)(m^3/1000 L)(1 mol/10^6 μmol) = 2.50 x 10^{-9} mol/L

n_{ozone}/n_{air} = (2.50 x 10^{-9} mol/L)/[(1.0 atm)/[0.0821 L atm/mol K)(273.15 + 27)] = 6.16 x 10^{-8}

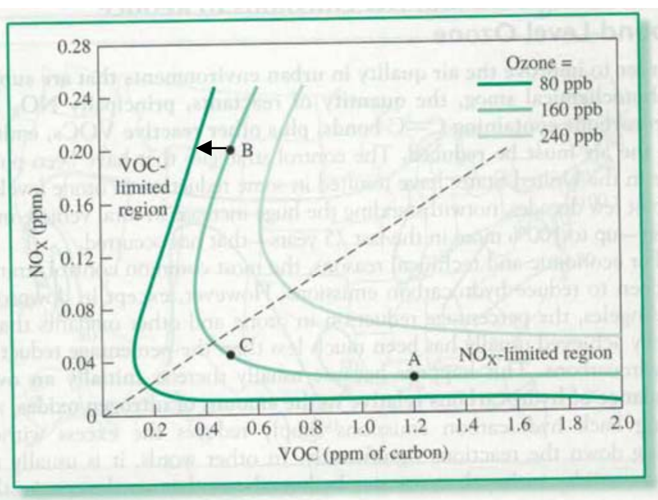
mixing ratio = (6.16 x 10^{-8})(*10^9*) = **62 ppb**

WHO standard = (62 ppb)(100/120) = **51 ppb**

3-5 Using Figure 3-8, and assuming a NO_x concentration of 0.20 ppm, estimate the effect on ozone levels of reducing the VOC concentration from 0.5 to 0.4 ppm. Do your results support the characterization of that zone of the graph as VOC limited?

By looking at the arrow on the plot below (starting at B and moving to the left), it is seen that ozone did decrease indicating ***that the conditions were in the VOC limited region****.*

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).]



3-8 Deduce the balanced redox equation that converts urea and nitric oxide into N_2, CO_2, and water.

Urea = $NH_2CONH_2 = CN_2H_4O + NO \rightarrow N_2 + CO_2 + H_2O$ (unbalanced)
Redox part: O is -2, C is +4, H is -1, and N is: +2 in NO, 0 in N_2, and -3 in each N in CN_2H_4O
Oxidation half reaction: $CN_2H_4O + 3/2O_2 \rightarrow N_2 + CO_2 + 2H_2O + 6e^-$
Reduction half reaction: $2NO + 4e^- \rightarrow N_2 + O_2$
We now combine the two half reactions (but also must eliminate O as it would otherwise require redox reactions): 2[oxidation] + 3[reduction]

$$2CN_2H_4O + 3O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O + 12e^-$$
$$6NO + 12e^- \rightarrow 3N_2 + 3O_2$$

Net: $$2CN_2H_4O + 6NO \rightarrow 5N_2 + 2CO_2 + 4H_2O$$

Additional Problems: 3-1, 3-2

3-1 The rate constant for the oxidation of nitric oxide by ozone is 2 x 10^{-14} $molec^{-1}$ cm^3 s^{-1}, whereas that for the competing reaction in which it is oxidized by oxygen, i.e.

$$2NO + O_2 \rightarrow 2NO_2$$

Is 2 x 10^{-38} $molec^{-2}$ cm^6 s^{-1}. For typical concentrations encountered in morning smog episodes, namely 40 ppb for ozone and 80 ppb for nitric oxide, deduce the rates of these two reactions and decide which one is the dominant process.

Conversion to molec cm^{-3}: O_3 at 40 ppb is $P_{O3} = 4 \times 10^{-8}$ atm and n/V = P/RT
$= (4 \times 10^{-8}$ atm$)/[(0.0821$ L atm mol^{-1} $K^{-1})(298K)]$
$= (1.635 \times 10^{-9}$ mol $L^{-1})(6.02 \times 10^{23}$ molec/mol$)($L/1000 $cm^3)$
$= 9.84 \times 10^{11}$ molec cm^{-3}. NO (twice the concentration) $= 1.968 \times 10^{12}$ molec cm^{-3}.
O_2: (0.21 atm)/[(0.0821 L atm mol^{-1} K^{-1})(298K)] $= 5.167 \times 10^{18}$ molec cm^{-3}
NO + O_3 rate: rate = k[NO][O_3]
$= (2 \times 10^{-14}$ $molec^{-1}$ cm^3 $s^{-1})(9.84 \times 10^{11}$ molec $cm^{-3})(1.968 \times 10^{12}$ molec $cm^{-3})$
$= 3.9 \times 10^{10}$ molec cm^3 s^{-1}.
For $2NO + O_2 \rightarrow 2NO_2$ reaction, rate = k[NO]^2[O_2]
$= (2 \times 10^{-38}$ $molec^{-2}$ cm^6 $s^{-1})(1.968 \times 10^{12}$ molec $cm^{-3})^2(5.167 \times 10^{18}$ molec $cm^{-3})$
= 40,000 molec cm^{-3} s^{-1}
The NO + O_3 is the dominant reaction.

3-2 In a particular air mass, the concentration of OH was found to 8.7 x 10^6 molec cm^{-3}, and that of carbon monoxide was 20 ppm.

a) Calculate the rate of the reaction of OH with atmospheric CO at 30ºC, given that the rate constant for the process is 5 x 10^{-13} $e^{-300/T}$ $molec^{-1}$ cm^3 s^{-1}.

CO conc. from mixing ratio: n/V = P/RT = $(2 \times 10^{-5}$ atm$)/[(0.0821$ L atm mol^{-1} $K^{-1})(303K)]$
$= 8.04 \times 10^{-7}$ mol/L $= 4.84 \times 10^{14}$ molec cm^{-3}
Rate = k[OH][CO] = ***7.84×10^8 molec cm^{-3} s^{-1}***

b) Estimate the half-life of an OH molecule in air, assuming that its lifetime is determined by its reaction with CO. [Hint: re-express the rate law as a pseudo-first-order process with the level of CO fixed at 20 ppm].

τ = 1/k[CO] = 0.011 s $t_{1/2}$ = τln2 = **0.0077 s**