

CHEM/TOX 336 Environmental Chemistry and Toxicology
Spring Semester 2004
Midterm Examination: Model Answers

1.

Name of problem	Principal primary contaminant(s)	Region of atmosphere	Local, regional or global problem	Name of accord, if relevant
<i>acid rain</i>	SO ₂ ; NO	<i>troposphere</i>	<i>regional</i>	none
<i>stratospheric ozone depletion</i>	<i>CFCs</i>	<i>stratosphere</i>	<i>global</i>	Montreal Protocol
Photochemical smog	<i>VOCs and NO_x</i>	<i>troposphere</i>	<i>regional</i>	<i>none</i>
<i>global warming</i>	CO ₂ ; CH ₄ ; N ₂ O	<i>troposphere</i>	global	<i>Kyoto Accord</i>

2. True; False; Greens

3. Threshold Limit Value; Short term Exposure Limit

Sum the ratios actual concentration/TLV, which all have the same units, so they cancel
 $(17/30) + (250/375) = 0.57 + 0.67 = 1.23 \therefore$ TLV is exceeded

- 4.
1. $\text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O}$
 2. $\text{O} + \text{O}_2 \longrightarrow \text{O}_3$
 3. $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$

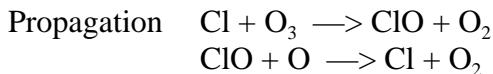
Not at \rightleftharpoons ; steady state maintained away from \rightleftharpoons by sunlight as external energy source.

Once the sun sets, no more ozone is formed, as Reaction 1 stops. In a city centre, NO continues to be emitted during the night hours and reacts with ozone by Reaction 3.

VOCs; NO_x; sunlight; temperature > approx 18°C

NO₂ is the source of ozone (Reactions 1 and 2). When NO reacts with R-O-O it forms NO₂ without using up ozone. The NO₂ formed can then produce more ozone.

5. Initiation $\text{CF}_2\text{Cl}_2 + h\nu \longrightarrow \text{CF}_2\text{Cl} + \text{Cl}$



$134 + 90 = 224$. Digits represents number of C, H, F atoms $\therefore \text{C}_2\text{H}_2\text{F}_4$

Refrigerant fluid; CFC-11

No; HFC-134a contains no Cl atoms OR HFC-134a contains C-H bonds that make it reactive in the troposphere

$$\text{POCP} = \frac{k(\text{substrate})}{k(\text{ethene})} \times \frac{M(\text{ethene})}{M(\text{substrate})} \times 100$$

$$M(\text{C}_2\text{H}_4) = 28 \text{ g/mol}; M(\text{C}_2\text{H}_2\text{F}_4) = 102 \text{ g/mol}$$

$$\text{POCP} = \frac{8.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \times 28 \text{ g/mol} \times 100}{8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \times 102 \text{ g/mol}} = 0.028$$

No; HFC-134a is nearly 4 orders of magnitude less reactive than ethene

6. $n(\text{Na}_2\text{S}_2\text{O}_3) = 0.01136 \text{ mol/L} \times 8.11 \times 10^{-3} \text{ L} = 9.21 \times 10^{-5} \text{ mol}$
 $n(\text{I}_2) = n(\text{Na}_2\text{S}_2\text{O}_3) \times (1 \text{ mol I}_2 / 2 \text{ mol Na}_2\text{S}_2\text{O}_3) = 4.61 \times 10^{-5} \text{ mol}$
 $n(\text{MnO}_2) = n(\text{I}_2)$
 $n(\text{O}_2) = n(\text{MnO}_2) \times (1/2 \text{ mol O}_2 / 1 \text{ mol MnO}_2) = 2.30 \times 10^{-5} \text{ mol}$

$$c(\text{O}_2) = 2.30 \times 10^{-5} \text{ mol} / 0.0500 \text{ L} = 4.61 \times 10^{-4} \text{ mol/L}$$

$$M(\text{O}_2) = 32,000 \text{ mg/mol} \longrightarrow c(\text{O}_2) = 14.7 \text{ mg/L}$$

7. The water contains bases such as HCO_3^- ; if it did not its pH would be near pH 5.5 because of the acidity of dissolved CO_2



$$\Delta H^\circ(\text{rxn}) = (-1206.9) + (-393.5) + (-285.8) - (-542.8) - 2 \times (-692.0) = +40.6 \text{ kJ/mol}$$

$$\Delta S^\circ(\text{rxn}) = 92.9 + 213.6 + 69.9 - (-53.1) - 2 \times 91.2 = +247.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\circ(\text{rxn}) = \Delta H^\circ(\text{rxn}) - T\Delta S^\circ(\text{rxn}) = 40.6 \text{ kJ mol}^{-1} - (333 \text{ K})(0.2471 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -41.7 \text{ kJ mol}^{-1}$$

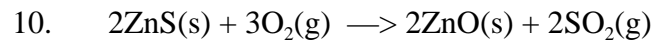
8. $p(\text{OH}) = 9.7 \times 10^5 \text{ molec/cm}^3 \times 1.36 \times 10^{-22} \text{ cm}^3 \text{ atm/molec. K} \times 274 \text{ K}$
 $= 3.6 \times 10^{-14} \text{ atm}$
 $c(\text{OH, aq}) = K_{\text{H}} \times p(\text{OH, g}) = 25 \text{ mol/L atm} \times 3.6 \times 10^{-14} \text{ atm} = 9.0 \times 10^{-13} \text{ mol/L}$

assumes no depletion of OH,g from the gas phase

9. $\text{Rate} = k [\text{SO}_2] [\text{OH}] = k' [\text{SO}_2]$

$$k' = 9 \times 10^{-13} \text{ cm}^3/\text{molec s} \times 9.7 \times 10^5 \text{ molec/cm}^3 = 8.7 \times 10^{-7} \text{ s}^{-1}$$

$$t_{1/2} = 0.693/k' = 0.693/8.7 \times 10^{-7} \text{ s}^{-1} = 7.9 \times 10^5 \text{ s} \rightarrow 9 \text{ days}$$



They are acidic, therefore harmful to plant and aquatic life

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