Atmospheric chemistry

Attempt the following problems from recent finals papers.

1. *1997 General physical chemistry I, Question 7*

a) The hydroxyl radical, OH, is one of the key intermediates in the homogeneous gas phase chemistry of the troposphere. How is the formation of the free radical promoted by the introduction of urban atmospheric pollutants? [3 marks]

b) What factors control the daytime levels of ozone in urban atmospheres? [3 marks]

c) How do reactions of OH promote the oxidation of hydrocarbons present in urban atmospheres? [8 marks]

d) How may the nitrate radical, NO_3, be generated in urban atmospheres and how does it contribute to:
   i) the oxidation of hydrocarbons; and
   ii) the production of acid rain? [6 marks]

2. *1996 General physical chemistry I, Question 7*

a) Explain how the oxides of nitrogen, NO_X, catalyse the *destruction* of ozone in the stratosphere, yet catalyse the *formation* of ozone in the troposphere (NO_X represents the oxides NO and NO_2). What other chemical constituents must be present for the ozone generation process to occur in the troposphere? What other catalytic species might also be active in the stratosphere? [7 marks]

b) The rate of NO_X-catalysed loss of ozone in the stratosphere is determined by the rate of the process:

$$O + NO_2 \rightarrow NO + O_2 \qquad k_1 = 6\times10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad (1)$$

Explain how this step could be rate limiting. [3 marks]

c) At an altitude of 30 km, the formation and removal of NO_X is dominated by the reactions:

$$O(^1D) + N_2O \rightarrow NO + NO \qquad k_2 = 6\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad (2)$$
$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad k_3 = 2\times10^{-31}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1} \qquad (3)$$

By assuming that the rate of NO formation in reaction (2) is equal to the rate of NO_2 loss in reaction (3), estimate the concentration of NO_2 on the basis of the rate coefficients quoted for the temperature at 30 km, using the concentrations of the other species tabulated below. [6 marks]

Species	Concentration / molecule cm^{-3}
$O(^1D)$	25
OH	1×10^6
O_3	3×10^{12}
N_2O	8×10^{10}
$M(N_2 + O_2)$	4×10^{17}

Then estimate the contribution of the NO_X-catalysed loss of ozone relative to the direct loss in the reaction:

$$O + O_3 \rightarrow O_2 + O_2 \qquad k_4 = 1\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \qquad (4)$$

[4 marks]

3. *1995 General physical chemistry I, Question 4*

Answer any *three* parts of (A)-(E). Each part carries equal weight.

(A) Explain what is meant by the greenhouse effect, and how it can lead to global warming. Indicate which of the following gases found in the exhausts of combustion systems can act as greenhouse gases: CO_2, N_2, CH_4.

(B) NO is oxidised to NO_2 in the polluted troposphere. Explain why the reaction $2NO + O_2 \rightarrow 2NO_2$ is too slow to account for the oxidation rate, and indicate how the presence of hydrocarbons affects the oxidation process and leads to the formation of tropospheric ozone.

(C) The terrestrial temperature falls with altitude until the tropopause at *ca*. 12 km. Above this altitude the temperature rises in the stratosphere. In this region the maximum ozone concentration occurs. Explain these observations.

(D) Chlorofluorocarbons (CFC's) are believed to perturb the ozone layer. Explain the gas-phase chemistry which accounts for this perturbation, and why heterogeneous chemistry is believed to play a major role in the formation of the 'ozone hole' in the Antarctic spring.

(E) Discuss the photolysis of CO_2, and the subsequent reactions of the photolysis products in relation to the composition of the Martian atmosphere.

4. *1994 General physical chemistry I, Question 5*

a) The species O, O^+, O_2^+, O_3 and OH play important roles in various regions of the earth's atmosphere. Explain how the species are formed, what determines the altitudes of their maximum abundance, and how they participate in the chemistry and physics of the atmosphere. [14 marks]

b) Amongst the many species with which the hydroxyl radical (OH) reacts are O_3, CO, CH_4 and SO_2. Mixing ratios and rate constants appropriate to regions near the earth's surface are:

Reactant	O_3	CO	CH_4	SO_2
Mixing ratio / ppbv	50	150	1700	5
k / 10^{-15} cm^3 molecule^{-1} s^{-1}	68	230	7.7	1.5

The units for mixing ratio (ppbv) are parts per billion (10^9) by volume; you may assume that the total number density is 2.5×10^{19} molecule cm^{-3}. What do these data suggest about the relative importance of O_3, CO, CH_4 and SO_2 in removing OH in the troposphere? [6 marks]