CHEM 302: Atmospheric Environmental Chemistry

Total Marks = [45]

1. The *Threshold Limit Value* (TLV) for formaldehyde (**H_2CO**) in indoor air has been set at 1.5 mg/m^3. Express this concentration as molecules cm^{-3} and ppmv. State any assumptions. [3]

2. The reaction below has a measured rate constant k = 1.1 x 10^{-33} molecules^{-2} cm^6 s^{-1} in the stratosphere (220K, P_T = 0.010 atm, [**O**(g)] = 0.21 ppbv).

$$\mathbf{O}(g) + \mathbf{O_2}(g) + M(g) \rightarrow \mathbf{O_3}(g) + M(g)$$

Show that this reaction can be expressed as a pseudo first order process and calculate the *pseudo first order* rate constant. [4]

3. Referring to s*tratospheric reaction chemistry,* account for TWO of the following. [4]

(i) **HO_x** catalytic ozone destruction

(ii) CFC-115 is a source of stratospheric chlorine

(iii) **N_2O_5** and **HNO_3** are resevoirs for **NO_x** species

4. Identify TWO of the following providing a chemical reaction leading to its formation or loss and indicating the significance to *tropospheric environmental chemistry. [6]*

(i) PAN

(ii) **O**(^{1}D)

(iii) **CO**

5. A natural decomposition route for **N_2O** is a stratospheric photochemical reaction:

$$\mathbf{N_2O}(g) + h\nu \rightarrow \mathbf{N_2}(g) + \mathbf{O^*}(g)$$

ΔH^o_f (**N_2O**, g) = 82 kJ mol^{-1}

ΔH^o_f (**N_2**, g) = 0 kJ mol^{-1}

ΔH^o_f (**O**, g) = 247 kJ mol^{-1}

Excitation energy of **O*** = 188 kJ mol^{-1}

a) Calculate the maximum wavelength of photons energetically capable of causing photodissociation and suggest an explanation for the fact that this reaction does not occur in the troposphere. [4]

b) The atmospheric lifetime of **N_2O** is estimated to be 100 years. Assuming it's concentration in the atmosphere is roughly constant at 310 ppbv, at what rate (kg yr^{-1}) is **N_2O** being released into the atmosphere? [4]

6. Describe the thermal structure of the atmosphere and explain its origin and significance to atmospheric environmental chemistry. [6]

OR

Use the Chapman reactions to explain why the concentration of ozone goes through a maximum in the stratosphere. [6]

7. Hydroxyl radicals are powerful hydrogen atom abstractors as depicted by the reactions below. The concentration of methane (**CH_4**) is roughly constant throughout the troposphere and is estimated at 1.7 ppmv. In a typical polluted urban air environment the mixing ratio of hexane (**C_6H_{14}**) is approximately 100 times lower than that of methane.

OH + **CH_4** $\rightarrow$ **H_2O** + products $\quad k_1 = 8.4 \times 10^{-15}$ cm^3 molec^{-1} s^{-1}

OH + **C_6H_{14}** $\rightarrow$ **H_2O** + products $\quad k_2 = 5.6\ 10^{-12}$ cm^3 molec^{-1} s^{-1}

Considering only the reactions of **OH** with methane and hexane, calculate the fraction of **OH** lost by reaction with methane. [4]

8. The following three reactions represent a simplification of the chemistry of **NO**, **NO_2** and **O_3** in the troposphere.

(i) **NO** + **O_3** $\rightarrow$ **NO_2** + **O_2** $\quad k_1$

(ii) **NO_2** + hv $\rightarrow$ **NO** + **O** $\quad f_2$

(iii) **O** + **O_2** + M $\rightarrow$ **O_3** + M $\quad k_3$

Each of these reactions is rapid and **NO_2** is depleted by reaction (ii) at roughly the same rate as it is formed by reaction (i).

a) Assuming a *steady state* concentration for nitrogen dioxide, derive an expression for the concentration of **O_3** in terms of the concentration of **NO_2**, **NO** and appropriate rate constants. [3]

b) Explain why urban ground level ozone concentrations peak in mid- to late afternoon, several hours after the morning rush hour. [2]

9. An article published a recent edition of the *New Scientist* suggests that a mass extinction event on Earth some 443 million years ago may have been the result of an interstellar burst of gamma rays (high energy photons). The authors describe the effect of a gamma ray burst on the Earths atmosphere as the 'splitting the nitrogen and oxygen' resulting in the formation of nitrogen oxides, which 'block' visible light. The result was a massive shift in the solar irradiance reaching the Earth's surface as depicted in the diagram below.

a) Suggest chemical reactions leading to the 'splitting of nitrogen and oxygen' and the formation of nitrogen oxides? [2]

b) What chemical species is responsible for the 'blocking' the visible light spectrum and how? [2]

c) What chemical process (or cycle of reactions) is responsible for the increased penetration of UV light? [2]