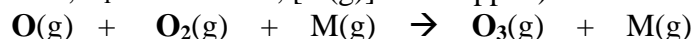


1. The *Threshold Limit Value* (TLV) for formaldehyde (H_2CO) in indoor air has been set at 1.5 mg/m^3 . Express this concentration as molecules cm^{-3} and ppmv. State any assumptions. [3]

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



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

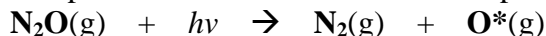
3. Referring to *stratospheric reaction chemistry*, account for TWO of the following. [4]

- (i) HO_x catalytic ozone destruction
- (ii) CFC-115 is a source of stratospheric chlorine
- (iii) N_2O_5 and HNO_3 are reservoirs 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) $\text{O}(^1\text{D})$
- (iii) CO

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



$$\Delta H_f^\circ(\text{N}_2\text{O}, \text{g}) = 82 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{N}_2, \text{g}) = 0 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{O}, \text{g}) = 247 \text{ kJ mol}^{-1}$$

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

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]

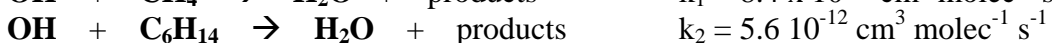
b) The atmospheric lifetime of N_2O is estimated to be 100 years. Assuming it's concentration in the atmosphere is roughly constant at 310 ppbv, at what rate (kg yr^{-1}) is N_2O being released into the atmosphere? [4]

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.



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.



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 Earth's 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.

- Suggest chemical reactions leading to the 'splitting of nitrogen and oxygen' and the formation of nitrogen oxides? [2]
- What chemical species is responsible for the 'blocking' the visible light spectrum and how? [2]
- What chemical process (or cycle of reactions) is responsible for the increased penetration of UV light? [2]

DOOMSDAY SCENARIO

Is this what caused the Ordovician extinction?

A nearby gamma-ray burst splits nitrogen and oxygen molecules in the atmosphere, forming nitrogen dioxide. NO_2 is a toxic brown gas, and it blocks out visible light from the sun. It also destroys the ozone layer, letting through dangerous levels of ultraviolet light.

Life on land and in shallow water is devastated, while deep-sea creatures are relatively unharmed

