Birla Institute of Technology and Science, Pilani, Rajasthan – 333031
Sem-II, 2022-23 CHEM F430 Atmospheric Chemistry
Comprehensive Examination, Part-A: Closed Book
Maximum Marks: 54 Maximum time: 90 minutes Date: 20-05-2023

Invigilator's signature

Name: **ID.** **Marks obtained:**

Request for recheck:

Useful information: R = 8.31 J K^{-1} mol^{-1}; h = 6.626 × 10^{-34} J s; Surface pressure = 984 hPa; M_{N2} = 28 g/mol; Dew point (P_{H2O} = 11.5 hPa) = 282 K; M_a = 0.029 kg/mol; M_{O2} = 32 g/mol; $\Delta_{vap}H_m$ (ethanol) = 38.9 kJ/mol; C_{CO2} = 365 ppmv; Surface temperature = 288 K; $P_{H2O, SAT}$ (293 K) = 23 hPa; σ_{max} (O_2) = 10^{-17}; M_H = 1.008 amu; ; Dew point (P_{H2O} = 23 hPa) = 290 K; τ_{O2} = 4 × 10^7; M_{Ar} = 40 g/mol; A_v = 6.022 × 10^{23}; 1 amu = 1.660 × 10^{-27} kg; Dew point (P_{H2O} = 20hPa) = 285 K; Hartley bands: < 320 nm; F_S = 1370 W m^{-2}; σ = 5.67 × 10^{-8} W m^{-2} K^{-4}; M_{Cl} = 34.969 amu;

Q1. Assume air is composed of N_2 (C_{N2} = 0.78), O_2 (C_{O2} = 0.21), and Ar (C_{Ar} = 0.0093). Calculate the mean molecular weight of dry air. **[2]**

Q2. The normal boiling point of ethanol is 78.3 °C. We want to boil ethanol at 25 °C under vacuum distillation condition. Determine the magnitude of reduced pressure to achieve this condition. **[3]**

Q3. What are the forces important for Geostrophic flow in atmosphere? **[2]**

Q4. State whether following statements are True (T) or False (F) with explanation. **[2]**
(i) Flows in atmosphere are generally laminar.

(ii) Diurnal cycle of surface heating/cooling leads to ventilation of urban pollution.

Q5. Does growth of corals ($Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3\ (s)$) cause atmospheric CO_2 to increase or decrease? Explain briefly. **[2]**

Q6. Calculate atmospheric transmittance as a result of absorption by O_2. Comment whether O_2 is optically thick or thin based on your result. **[3]**

Q7. An inert molecule (X) with initial concentration $C_i(0)$ is emitted at a rate of q_i = 200 μg m^{-2} h^{-1}, calculate its steady-state concentration over a city characterized by an average wind-speed of 3 m s^{-1}. Assume that the city has dimensions of 100 × 100 km, a constant mixing height of 1000 m, and background concentration of X is 1 μg m^{-3}. You may use following relation for concentration: $C_i(t) = C_i(0)e^{-t/\tau_r} + \left(\frac{q_i \times \tau_r}{H} + C_i^0\right)\left(1 - e^{-t/\tau_r}\right)$. Symbols are having usual meaning. You may consider flushing time (τ_r) to be 10 h. **[4]**

Q8. Determine number density of CO_2 (in molecule m^{-3}) at the sea level for P = 1013 hPa and T = 25°C with C_{CO2} = 365 ppmv **[3]**

Q9. The concepts of lifetime can be applied to reactions of any order. Determine the lifetime of NO in the following second order reaction: $NO + O_3 \rightarrow NO_2 + O_2$, k (298 K) = 1.9×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. At the Earth's surface at 298 K, the O_3 mixing ratio is 50 ppbv, NO mixing ratio is 10 ppbv. **[4]**

Q10. GWP of H_2O is higher compared to that of CO_2. Explain the reasons from molecular level understanding. **[4]**

Q11. World population is ever growing along with an increase in the food consumption. "Consequently, the CO_2 level in the atmosphere is also increasing". Comment on this statement. **[2]**

Q12. The molecular diffusion coefficient of air at the sea level is 0.2 $cm^2\ s^{-1}$. The average time (in hours) for an air molecule to travel 1 m by molecular diffusion is **[2]**

(A) 0.01 (B) 2.8 (C) 6.9 (D) 4.5

Q13. Explain the effect of clouds at higher altitude on the Earth's temperature. **[3]**

Q14. The CO_2 mixing ratio in the stratosphere is always less (by 1-2 ppmv) compared to that in the troposphere. Although, stratosphere does not have any sink of CO_2. Explain this observation. **[3]**

Q15. Evaluate the rotational constant of $^{1}H^{35}Cl$ molecule in Hz. Equilibrium bond length of $^{1}H^{35}Cl$ molecule is 127.4 pm. **[4]**

Q16. Few billion years ago, the solar radiation was 25% less than today. Assume A = 0.28 and f = 0.77. Calculate the surface temperature (in K) of Earth during that period. **[4]**

Q17. Consider the mechanism for oxidation of CH_4 to CO_2:

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O \quad (1)$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \quad (2a)$$

$$CH_3O_2 + NO \xrightarrow{O_2} CH_2O + NO_2 \quad (2b)$$

$$CH_3OOH + h\nu \xrightarrow{O_2} CH_2O + HO_2 + OH \quad (3a)$$

$$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O \quad (3b)$$

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \quad (3c)$$

$$CH_2O + h\nu \xrightarrow{O_2} CO + 2HO_2 \quad (4a)$$

$$CH_2O + h\nu \rightarrow CO + H_2 \quad (4b)$$

$$CH_2O + OH \xrightarrow{O_2} CO + HO_2 + H_2O \quad (4c)$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \quad (5)$$

Assume the following branching ratios: 2:1 for loss of CH_3O_2 by (2a):(2b), 1:1:1 loss of CH_3OOH by (3a):(3b):(3c), and 2:1:1 for loss of CH_2O by (4a):(4b):(4c).

(a) How many molecules of CH_3O_2 are produced in the oxidation of one molecule of CH_4 to CO_2? **[4]**

(b) Which reactions in the mechanism consume OH? Which reaction produces OH? What is the net numbers of OH molecules consumed in the oxidation of one molecule of CH_4 to CO_2? **[3]**

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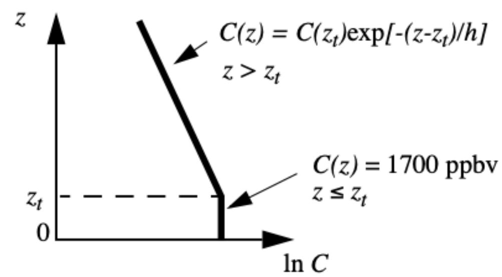
Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
II Semester, 2022-2023

CHEM F430	**Atmospheric Chemistry**	**Date: 20-05-2023**
Comprehensive Examination (Open book)	**Max. Time: 90 minutes**	**Max. marks: 40**

Q1. (a) Methane is removed from the troposphere by oxidation, and the corresponding lifetime of methane is estimated to be 9 years. Based on this lifetime, would you expect methane to be well mixed in the troposphere?

(b) The present day methane concentration in the troposphere is 1700 ppbv and is rising at the rate of 10 ppbv/yr. Determine the present day emission of methane using a mass balance equation. Pressure at the top of the troposphere is assumed to be 150 hPa. Moreover, transport of methane to stratosphere may be neglected for this calculation.

(c) Now, assume that chemical loss of methane is possible in the stratosphere. The mixing ratio C of the methane above the troposphere (altitude z) decreases exponentially with z, with a scale height, h = 60 km, as shown in the figure. Using a turbulent diffusion formulation for the vertical flux and assuming steady state for methane in the stratosphere, show that $-A\left[K_z\, n_a\, \frac{dc}{dz}\right]_{troposphere} = L_{stratosphere}$;



where K_z is the turbulent diffusion coefficient, the air density is n_a, and the methane mixing ratio is determined just above the troposphere. A is the surface area of the Earth, and $L_{stratosphere}$ is the total chemical loss of methane in the stratosphere.

(d) Calculate $L_{stratosphere}$ assuming a turbulent diffusion coefficient K_z = 7 × 10^3 cm^2 s^{-1} and an air density n_a = 5 × 10^{18} molecules cm^{-3} just above the troposphere. Derive an improved estimate of the present-day emission of methane. **[1 + 4 + 7 + 4 = 16]**

Q2. Ozone depletion over Antarctica is catalyzed by chlorine radicals. Ozone depletion could be prevented by the injection of ethane (C_2H_6) into the Antarctic stratosphere. Ethane reacts quickly with Cl to form HCl. Consider the following ensemble of reactions taking place in the Antarctic stratosphere.

$$HCl + ClNO_3 \xrightarrow{\text{aerosol}} Cl_2 + HNO_3 \quad (1)$$

$$HCl + N_2O_5 \xrightarrow{\text{aerosol}} ClNO_2 + HNO_3 \quad (2)$$

$$N_2O_5 + H_2O \xrightarrow{\text{aerosol}} 2HNO_3 \quad (3)$$

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (4)$$

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \quad (5)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (6)$$

$$ClO + NO_2 + M \rightarrow ClNO_3 + M \quad (7)$$

$$ClO + ClO \xrightarrow{h\nu,\ M} 2Cl + O_2 \quad (8)$$

Assume the following concentrations in the Antarctic stratosphere when the polar vortex forms: HCl = 3.0 ppbv, $ClNO_3$ = 0.5 ppbv, and N_2O_5 = 2.0 ppbv. Condensation of PSCs in the polar winter allows aerosol reactions (1)-(3) to proceed. Assume that all of the $ClNO_3$ reacts by reaction (1) , that the excess HCl reacts by reaction (2), and that the leftover N_2O_5 then reacts by (3). Both Cl_2 and $ClNO_2$ photolyze quickly (reaction (4) & (5)) after the end of the polar night. The NO_2 formed by (5) reacts with ClO by reaction (7) to reform $ClNO_3$.

(a) Determine the partitioning of chlorine (Cl + ClO), $ClNO_3$, and HCl after reaction (1) – (7) have taken place. **[6]**

(b) The reaction of ethane with Cl is:

$C_2H_6 + Cl \rightarrow C_2H_5 + HCl$

If 2.0 ppbv ethane were injected into the poral stratosphere after reactions (1) - (7) have taken place, determine the partitioning of chlorine (Cl + ClO), $ClNO_3$, and HCl. Would such an injection of ethane reduce O_3 loss? **[4]**

(c) How much ethane must actually be injected to convert all the chlorine present to HCl? **[2]**

Q3. (a) Cycling of HO_x chemical family ($HO_x = H + OH + HO_2$) can catalyze O_3 loss in a number of ways. Consider the following reactions, each of the reaction is important in at least some regions of stratosphere:

$OH + O \rightarrow O_2 + H$ (1)
$OH + HO_2 \rightarrow H_2O + O_2$ (2)
$OH + O_3 \rightarrow HO_2 + O_2$ (3)
$H + O_2 + M \rightarrow HO_2 + M$ (4)
$H + O_3 \rightarrow O_2 + OH$ (5)
$HO_2 + O \rightarrow OH + O_2$ (6)
$HO_2 + O_3 \rightarrow OH + 2O_2$ (7)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (8)

(i) Find five different catalytic O_3 loss cycles starting with reactions of OH. **[5]**
(ii) Which of the reactions represent sinks for HO_x? **[2]**
(b) In an experiment to determine the quantum yield of a photochemical reaction, the absorbing substance was exposed to 490 nm light from 100 W source for 2700 s, with 60% of incident light being absorbed. As a result of irradiation, 0.344 mol of absorbing substance decomposed. Determine the primary quantum yield. **[5]**

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