Birla Institute of Technology and Science, Pilani, Rajasthan – 333031
Sem-II, 2021-22   CHEM F430   Atmospheric Chemistry
Comprehensive Examination, Part-A: Closed Book

Invigilator's signature

Maximum Marks: 25   Maximum time: 60 minutes   Date:19-05-2022
Attempt all questions. Circle the correct answer(s) for MCQ ($\sqrt{}$ or any other mark will not be considered)

Name: ID.   Marks obtained:

Request for recheck:

Useful information: R = 8.31 J K^{-1} mol^{-1}; Surface pressure = 984 hPa; Dew point (P_{H2O} = 11.5 hPa) = 282 K; M_a = 0.029 kg/mol; C_{CO2} = 365 ppmv; Surface temperature = 288 K; $P_{H2O, SAT}$ (293 K) = 23 hPa; Chappuis bands: 400 – 600 nm; Dew point (P_{H2O} = 23 hPa) = 290 K; A_v = 6.022 $\times$ 10^{23}; Dew point (P_{H2O} = 20hPa) = 285 K; Hartley bands: < 320 nm; F_S = 1370 W m^{-2}; σ = 5.67 $\times$ 10^{-8} W m^{-2} K^{-4}.

Q1. Number density of CO_2 (in molecules m^{-3}) at the sea level for P = 1013 hPa and T = 25°C is

(A) 9.81 $\times$ 10^{21} (B) 8.97 $\times$ 10^{21} (C) 9.81 $\times$ 10^{27} (D) 8.97 $\times$ 10^{27}

Q2. At sunset, T = 293 K, RH = 50%. Assume, P_{H2O} remains constant till next morning. Fog formation during night may happen if the temperature (in K) of air cool to

(A) 290   (B) 285   (C) 282   (D) 280

Q3. Mass density of air (in kg m^{-3}) at the surface of the Earth is

(A) 1.19   (B) 1.31   (C) 0.50   (D) 2.23

Q4. Some of the following concepts could be used to design an instrument for the direct measurement of the size distribution of particulate matter in the atmosphere

(A) Mass-spectrometry   (B) Scattering   (C) UV spectroscopy   (D) Chemical separation

Q5. Among the following, the incorrect statement(s) is

(A) Temperature increases with altitude in thermosphere and stratosphere.

(B) UV radiation is absorbed by O_2/N_2 in thermosphere and O_2 in stratosphere.

(C) Temperature decreases with altitude in thermosphere and increases with altitude in stratosphere.

(D) Altitude of 18-50 km is known as stratosphere and 50-80 km is known as mesosphere.

Q6. The vapor pressure of a substance at 20°C is 58 kPa and its enthalpy of vaporization is 32.7 kJ/mol. Vapor of the substance may be assumed to behave like a perfect gas and enthalpy of vaporization is independent of temperature. Estimate the temperature (in K) at which its vapor pressure is 66 kPa

(A) 290   (B) 316   (C) 306   (D) 297

Q7. 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

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

Q8. The incorrect statement(s) on atmospheric composition (mol/mol) of Earth, Venus, and Mars is

(A) Maximum CO_2 is Earth (B) Maximum N_2 on Earth (C) Maximum O_2 on Earth (D) Maximum H_2O on Earth

Q9. Identify the IR active modes from the following

(A) Stretching of N_2 (B) Symmetric stretching of CO_2 (C) Stretching of H_2O (D) Bending of CO_2

Q10. Incorrect statement(s) among the following about actinic flux is

(A) Drives the chemistry in atmosphere   (B) Flux from direct solar radiation

(C) Unit: photons cm^{-2} s^{-1} (D) Unit for spectral actinic flux: photons cm^2 s^{-1} nm^{-1}

Q11. Identify the correct statement(s) for the following reaction: $O_3 + h\nu \rightarrow O + O_2$

(A) Chappuis band produce O (^{3}P) and O_2 ($^3\Sigma$)

(B) Hartley band produce O (^{3}P) and O_2 ($^3\Delta$)

(C) Hartley band produce O (^{1}D) and O_2 ($^1\Delta$)

(D) Chappuis band produce O (^{1}D) and O_2 ($^1\Sigma$)

Q12. Reservoir of ClOx is

(A) $ClNO_3$ (B) CF_2Cl_2 (C) ClOOCl   (D) ClOO

Q13. One of the major sources of the OH radical in the stratosphere is

(A) Photolysis of H_2O (B) Oxidation of H_2O by O   (C) HO_2 (D) Collisional cleavage of H_2O

Q14. According the Chapman mechanism, $[O_3]_{SS}$ does not depend on

(A) $[N_2]$ (B) Rate constant of O_2 dissociation   (C) Rate of O (^{1}D) to O (^{3}P) conversion   (D) Temperature

Q15. The correct statement about ClO dimer

(A) Leading to null cycle for ozone loss

(B) Photolysis takes place at the O-O bond

(C) Photolysis takes place at Cl-O bond

(D) Leads to catalytic cycle of ozone loss

Q16. GWP of a substance is defined with respect to

(A) CO_2 (B) CH_4 (C) H_2O (D) N_2O

Q17. A simulation is performed by removing all ozone above 30 km. The expected result would be

(A) Cooling of troposphere and stratosphere

(B) Tropospheric warming and stratospheric cooling

(C) Warming of troposphere and stratosphere

(D) Tropospheric cooling and stratospheric warming

Q18. Few billion years ago, the solar radiation was 25% less than today. Assume A = 0.28 and f = 0.77. The surface temperature (in K) of Earth at that time was

(A) 270   (B) 305   (C) 285   (D) 325

Q19. Identify the correct statement(s) about greenhouse gases

(A) Absorbs IR   (B) Absorbs VIS   (C) Absorbs UV   (D) Absorbs Microwave

Q20. Fluorescence process among the following reactions of X is

(A) $X^* \rightarrow B1 + B2$ (B) $X^* + M \rightarrow X + M$ (C) $X^* \rightarrow X + h\nu$ (D) $X + h\nu \rightarrow X^*$

Q21. The major sink of peroxyacetylnitrate in the troposphere is

(A) Dry deposition   (B) Wet deposition   (C) Photolysis   (D) Thermal decomposition

Q22. Ozone production efficiency is defined with respect to

(A) RH   (B) NOx   (C) ClOx   (D) SO_2

Q23. Principle source of CO to atmosphere is oxidation of CH_4. The rate constants for oxidation of CH_4 and CO by OH in the troposphere are $k_1 = 2.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $k_2 = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. Global uniform CH_4 concentration is 1700 ppbv. Concentration of CO (in ppbv) is …………………………

Q24. Net reaction for oxidation of CO to CO_2 and CH_4 to CO_2 produces one and four molecules of ozone, respectively. Emission rate of CH_4 and CO are 3×10^{13} moles yr^{-1} and 4×10^{13} moles yr^{-1}, respectively. Global production rate of ozone in moles yr^{-1} is ……………………………………………..

Q25. The most abundant gaseous selenium species in marine environment is

(A) $CH_3SeSeCH_3$ (B) C_6H_5SeH (C) CH_3SeH (D) CH_3SeCH_3

********END********

Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
II Semester, 2021-2022

CHEM F430	Atmospheric Chemistry	Date: 19-05-2022
Comprehensive Examination	**Max. Time: 120 minutes**	**Max. marks: 55**

Q1. Emission of CFCs was controlled by the Montreal protocol (1987). The protocol was further amended in 1990 (London) and 1992 (Copenhagen) to respond to the increased urgency created by the antartic ozone hole. CFC-12 was used to compare the effectiveness of the original and amended protocols. Atmospheric lifetime of CFC-12 is 100 years against loss by photolysis in the stratosphere. Data were collected from 1989 when the Montreal protocol was implemented. In 1989 the mass of CFC-12 in the atmosphere was 1×10^{10} kg and the emission rate was 4×10^8 kg yr^{-1}.

(a) The Montreal protocol (1987) called for a 50% reduction of CFC emission by 1999 and a stabilization of emission henceforth. Consider a future scenario when CFC-12 emission are held constant at 50% of 1989 values. Calculate the mass of CFC-12 in the atmosphere considering a steady-state situation. Compare your result with the mass of CFC-12 in 1989 and comment. **[6]**

(b) The subsequent amendments to the Montreal protocol banned CFC-12 production completely as of 1996. Consider a scenario where CFC-12 emission are held constant from 1989 to 1996 and then drop to zero as of 1996. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Compare your results with the CFC-12 mass in the atmosphere in 1989. **[5]**

(c) What would have happened if the Montreal protocol had been delayed by 10 years? Consider a scenario where emission are held constant at 1989 levels from 1989 to 2006 and then drop to zero as of 2006. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Briefly comment on the consequence of the delayed action of the Montreal protocol. **[5]**

Q2. (a) Write down the catalytic ozone loss cycle that is initiated by the self-reaction of ClO and is a key cycle for the loss of polar ozone. **[3]**

(b) The ozone abundance at 20 km altitude fell from 2.0 ppm on August 23 to 0.8 ppm on September 22. Assume that the self-reaction of ClO is the rate-limiting step (k = 1.74×10^{-13} cm^3 molecule^{-1} s^{-1}) for ozone loss at 20 km. Calculate the mixing ratio of ClO (in ppb) required to account for the observed loss of ozone. Between August 23 and September 22, air in the polar vortex experiences roughly 8 h of sunlight per day. Assume T = 200 K, p = 60 mbar, and [M] = 2.175×10^{18} molecules cm^{-3}. **[13]**

Q3. Consider that the CH_4 + OH reaction (k = 2.45×10^{-12} exp(-1755/T) cm^3 molecules^{-1} s^{-1}) is the rate-limiting step in tropospheric ozone production from CH_4. Assume [OH] = 10^6 molecules cm^{-3}, p = 1 atm, T = 298 K, global CH_4 mixing ratio is 1.8 ppm, and average height of troposphere ~ 12 km. Calculate the theoretical maximum rate at which ozone could be produced from CH_4 oxidation (in Tg/year) in the troposphere. **[16]**

Q4. The radiative forcing due to an increase of the atmospheric CO_2 mixing ratio by a factor β can be approximated by $\Delta F = 5.3 \ln \beta$ (W m^{-2}).
(a) For a sustained increase in the CO_2 mixing ratio of 1% per year, that is $\Delta F = bt$, calculate the value of the constant b. **[3]**

(b) At this rate of increase, how many years would be required for the CO_2 mixing ratio to increase from the level of 400 ppm to 560 ppm? **[4]**

********************************End********************************