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

	CHEM F430	Atmospheric Chemistry				
Mid-Sem	Time: 90 mins.	Date: 18.03.2023	[50 M]			
Useful information: M_a (Earth) = 28.96 × 10 ⁻³ kg; ρ_{H20} = 1000 kg/m ³ ; Radius of earth = 6400 km; Density						
of air = $2.5 \times 10^{\circ}$	D^{19} molecules/cm ³ ; K _z = 1 × 10 ⁴	5 cm ² s ⁻¹ ; 1 amu = 1.66054 × 10 ⁻²⁷	kg; h = 6.626×10^{-34} J s; 1			
$Tg = 1 \times 10^{12} g;$; R = 8.314 J K ⁻¹ mol ⁻¹ ; Γ = 9.8	K km ⁻¹ ; Molar mass (g/mol): Ar = 4	40, $C = 12$, $O = 16$, $N = 14$;			
General solutior	n of $\frac{dx}{dy} = A - kB$ is $B(y) = B(0) e^{-k}$	$x^{y} + (1 - e^{-ky}) \frac{A}{\kappa}$; h = 6.626 × 10 ⁻³⁴ J	s; N_A = 6.022 \times 10 23 mol $^{-1}$;			

Q1. (a) Determine the scale height for the atmosphere of Venus and Mars based on the relevant information provided below: [8]

Planet	T _s (°C)	g (m s ⁻²)	Composition
Venus	464	8.9	0.965 CO ₂ , 0.035 N ₂
Mars	-63	3.7	0.953 CO ₂ , 0.027 N ₂ , 0.016 Ar

Compare the scale height of Mars and Earth considering the surface temperature of the two planets and the molecular weight of the atmospheres.

(b) The normal boiling point of ethanol is 78.3 °C and at this temperature $\Delta_{vap}H_m = 38.9$ kJ/mol. With decrease in the pressure the boiling point will also decrease. Determine the value of pressure P (in Torr) for boiling of ethanol at 25 °C. [2]

Q2. The 1987 Montreal protocol was the first international agreement to control the emission of chlorofluorocarbons (CFCs) harmful to ozone layer. It was subsequently amended (London 1990, Copenhagen 1992) to respond to the increased urgency created by the Antarctic ozone hole. In this problem we compare the effectiveness of the original and amended protocols. We focus on CFC-12, which has an atmospheric life-time of 100 years against loss by photolysis in the stratosphere. We start our analysis in 1989 when the Montreal protocol entered into force. In 1989 the mass of CFC-12 in the atmosphere was $m = 1 \times 10^{10}$ kg and the emission rate was $E = 4 \times 10^8$ kg/year.

(i) The initial Montreal protocol called for a 50% reduction of CFC emissions by 1999 and a stabilization of emission henceforth. Consider a future scenario where CFC-12 emissions are held constant at 50% of 1989 values. Show that the mass of CFC-12 in the atmosphere would eventually approach a steady-state value that is higher than the 1989 value. Determine the steady-state value and explain briefly why the CFC-12 abundance would increase even though the emission decreases.

(ii) The subsequent amendments to the Montreal protocol banned CFC production completely as of 1996. Consider a scenario where CFC-12 emissions 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 with the 1989 value.

(iii) What would have happened if the Montreal protocol had been delayed by 10 years? Consider a scenario where emissions 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 conclude as to the consequence of delayed action.

Q3. (a) A town suffers from severe nighttime smoke pollution during the winter months because of domestic wood burning and strong temperature inversions. Consider the temperature profile measured at dawn as shown in Figure. Determine the minimum temperature rise required to ventilate the town. **[4]**



(b) Consider the global cycle of carbon between the atmosphere, the terrestrial vegetation,



and the soli as shown in the Figure. Reservoirs are in units of Pg C (1 Ph = 1×10^{15} g) and flows are in units of Pg C year⁻¹. [6]

(i) The three reservoirs "ground vegetation", "tree leaves", and "tree wood" collectively represent the "the terrestrial vegetation reservoir". Calculate the lifetime of carbon in the terrestrial vegetation reservoir against transfer to litter and soil.

(ii) Tree leaves eventually fall to produce litter. What is the dominant fate of carbon in the litter? What fraction

is incorporated into the soil?

(iii) Acid rain causes a decrease of microbial activity in the litter and in the soil. How is the atmosphere of CO₂ affected?

Q4. (a) Consider the propagation of radiation of wavelength λ in the atmosphere through a layer of thickness dx and perpendicular to beam of intensity $F(\lambda)$. Derive an expression of Beer-Lambert law. [3]

(b) Estimate the maximum wavelength of light at which the photodissociation of O₂ into two ground state oxygen atoms. Photodissociation energy is 498.4 kJ/mol. [2]

(c) Cloud formation releases latent heat. Explain this observation at the molecular level. [2]

(d) We wish to determine the emission flux of the hydrocarbone isoprene from a forest canopy. Measurements from a tower above the canopy indicate mean isoprene concentrations of 1.5 ppbv at 20 m altitude and 1.2 ppbv at 30 m altitude. The $k_z = 1 \times 10^5$ cm² s⁻¹ and air density is 2.5×10^{19} molecules cm⁻³. Calculate the emission flux of isoprene. [3]