題號: 89

國立臺灣大學101學年度碩士班招生考試試題

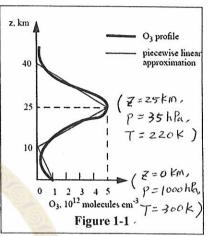
科目:大氣化學

節次: 4

題號: 89 共 | 頁之第 | 頁

Constants or equations that you might need	
PV= nRT for all gases discussed in this test	1 atm = 760 Torr = 101300 Pa = 1013 hPa
$R (gas constant) = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, 0.082 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$	The radius of the Earth: 6400 km
k (Boltzmann constant) = $1.381 \times 10^{-23} \text{ J K}^{-1}$	1 ppmv = 1 x 10^{-6} mol/mol=1 x 10^{-6} atm/atm
$N_{av} = 6.02 \times 10^{23} \text{ molecule mol}^{-1}$	1 ppbv = 1 x 10^{-9} mol/mol=1 x 10^{-9} atm/atm
$Pa = Nm^{-2}$	1 pptv = 1 x 10^{-12} mol/mol=1 x 10^{-12} atm/atm

- 1. Consider the following typical vertical profile of ozone (O₃) number densities measured as shown in Figure 1. The ozone concentration is 5 times higher than the concentration over the surface layer.
 - (1) (12 pts) The ozone formation over the stratosphere is based on the Chapman mechanism. Please describe in detail the major four reactions in Chapman mechanism.
 - (2) (12 pts) The ozone concentration derived from Chapman mechanism is higher than observed profile. Please describe in detail the major three sinks for the ozone reactions.
 - (3) (12 pts) There is ozone over the troposphere as shown in Figure 1. The sources of tropospheric ozone can be contributed via transferring from stratosphere and chemical reactions happening in troposphere. Please describe in detail the chemical production of tropospheric ozone. (Please use CO or CH₄ as the pollutant for the initial reactant)



- (4) (10 pts) Please calculate the ozone concentration in the unit of ppmv for z = 0 km and 25 km.
- (5) (12 pts) Ozone in the stratosphere can shield UV radiation for all organisms on the Earth. As the ozone concentration decreases, ozone hole is formed. Please describe in detail where, when and how the ozone hole is formed.
- 2. Measurement of the long-term trend in atmospheric O₂ has been used to determine the fate of fossil fuel CO₂ in the atmosphere and the relative importance of uptake by the ocean and by the biosphere. We describe here the principle of the method.
 - A. We first examine the O₂:CO₂ stoichiometry of the individual CO₂ sources and sinks.
 - (a) (5 pts) The mean stoichiometric composition of fossil fuel burned is CH_{1.6} (1 part carbon for 1.6 parts hydrogen). We view fossil fuel combustion as a stoichiometric reaction where CH_{1.6} is oxidized by O₂ to yield CO₂ and H₂O. How many moles of O₂ are consumed per mole of CO₂ emitted by fossil fuel combustion?
 - (b) (5 pts) How many moles of O₂ are produced per mole of CO₂ taken up by the biosphere?
 - (c) (5 pts) What is the net reaction when CO₂ dissolves into the ocean? Is there any O₂ produced or consumed when CO₂ dissolves into the ocean?

We are now equipped to use the method. Observations from July 1991 to July 1994 (3 years) indicate a 3.2 ppmv increase in atmospheric CO_2 and a 8.8 ppmv decrease in atmospheric O_2 . Global fossil fuel combustion during this period was 6.3×10^{12} kg C yr⁻¹. (The total number of air in the atmosphere is 1.8×10^{20} moles)

- (d) (5 pts) If fossil fuel were the only process affecting CO_2 and O_2 concentrations during the 1991-1994 period, by how much would these concentrations have changed?
- (e) (12 pts) From the observed trends of atmospheric CO₂ and O₂, determine the fraction of CO₂ emitted from fossil fuel combustion over the 3-year period that (i) was taken up by the biosphere, (ii) dissolved in the oceans, (iii) accumulated in the atmosphere.
- (f) (10 pts) In general, pure water has pH value of 7. However, due to the presence of CO₂, the water is slightly acidified through the following reactions.

$$\begin{array}{c} H_2O \\ CO_2(g) \; \Leftrightarrow \; CO_2 \cdot H_2O \end{array} \tag{H}$$

$$GO_2 \cdot H_2O \Leftrightarrow HCO_3 + H^+$$
 (1)

$$HCO_3^- \Leftrightarrow CO_3^{2^-} + H^+$$
 (2)

with equilibrium constants $K_H = 3.0 \times 10^{-2}$ M atm⁻¹, $K_I = 4.3 \times 10^{-7}$ M, $K_2 = 4.7 \times 10^{-11}$ M. The present atmosphere contains 380 ppmv CO₂. Please calculate the pH of the rain at equilibrium with this concentration of CO₂.

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