PROBLEMS/SOLUTIONS

1. The mixing ratio of oxygen in the atmosphere is 20.95%. Calculate the concentration in mol L^{-1} and in g m^{-3} at P° (101 325 Pa, 1.00 atm) and 25°C.

Solution

The mixing ratio for O_2 (g) is 20.95% (Table 2.1). Use the 'Ideal Gas' law (PV= nRT) to calculate the total number of moles of gas in 1.00 L for the given conditions. Constants are given in Appendices B.1 and C.1.

T = 25°C (298 K), P = 1.01325×10^5 Pa, R = 8.315 J K^{-1} mol^{-1}, and V = 1.00 L = 1.00×10^{-3} m^3

The total number of moles of gas in 1.00 L is

$$n = PV/RT$$
$$n = 0.04089 \text{ mol}$$

The number of moles of oxygen can be calculated from the mole fraction (which is the same as the mixing ratio).

$$\%\ O_2 = 20.95, \text{ mole fraction } = 0.2095$$

The number of moles of O_2 in 1.00 L is: 0.2095 x 0.04089 = 0.00857 mol

The concentration of O_2 (g) is: 8.57×10^{-3} mol L^{-1}.

The concentration of O_2 (g) in units of g m^{-3} is determined as follows:

1 m^3 = 1000 L, therefore, 1000 L contains 8.57 moles of O_2 (g). (M.M. of O_2 is 31.9988 g mol^{-1})

$$31.9988 \text{ g mol}^{-1} \times 8.57 \text{ mol m}^{-3} = 274 \text{ g m}^{-3}$$

The O_2 (g) concentration can be expressed as either 8.57×10^{-3} mol L^{-1} or 274 g m^{-3}.

2. Calculate the atmospheric pressure at the stratopause. What are the concentrations (mol m^{-3}) of dioxygen and dinitrogen at this altitude? How do these concentrations compare with the corresponding values at sea level?

Solution

Use Equation 2.3 to calculate the pressure at 50 km (stratopause).

$$P_h = P^o e^{-\overline{M}_a g}$$

R = 8.315 J K^{-1} mol^{-1}, P° = 101 325 Pa, g = 9.81 m s^{-2}, $\overline{M}_a$ = 0.02896 kg mol^{-1} (average molar mass of air), h = 50 km (50 000 m) and T = –2°C (271 K). Note: these last two parameters are the approximate altitude and temperature at the stratopause.

$$P_h = 101325\,\text{Pa x e}^{-(0.029\,\text{kg mol}^{-1}\,\text{x}\,9.81\,\text{m s}^{-2}\,\text{x}\,50000\,\text{m}) \div (8.315\,\text{J K}^{-1}\,\text{mol}^{-1}\,\text{x}\,271\,\text{K})}$$

The units in the inverse-natural logarithm term completely cancel. (recall that J = kg m^2 s^{-2})

P_h = 101 325 Pa x 0.001812

= 184 Pa (about 0.2 % of atmospheric pressure at sea level)

Next, calculate the concentration of O_2 and N_2 in units of mol m^{-3} using PV = nRT.

Begin by choosing a reasonable volume for the question. In this case assume the volume = 1 m^3.

The mixing ratios of oxygen gas and nitrogen gas at the stratopause are unchanged from the values at sea level, that is 0.2095 and 0.7808, respectively. The partial pressures are then 38.5 and 143.7 Pa, respectively.

The concentration of oxygen is then calculated using n/V = P/RT

$$n/V = 38.5\ \text{Pa} \ / \ 8.315\ \text{J mol}^{-1}\,\text{K}^{-1}\ \text{x}\ 271\ \text{K}$$

$$= 0.0171\ \text{mol m}^{-3}$$

The concentration of nitrogen is similarly found to be = 0.0638 mol m^{-3}

Comparison to sea level conditions:

The answer to Problem 1 gave the O_2 concentration as 8.56 x 10^{-3} mol L^{-1}. Therefore concentration in units of mol m^{-3} at sea level would be 8.56 mol m^{-3}. A similar calculation for N_2 yields 31.9 mol m^{-3} at sea level.

Comparison of sea level concentrations to stratopause concentrations:

$$\text{for } O_2 \qquad \frac{8.56\ \text{mol m}^{-3}}{0.0171\ \text{mol m}^{-3}} = 500 \qquad\qquad \text{for } N_2 \qquad \frac{31.9\ \text{mol m}^{-3}}{0.0638\ \text{mol m}^{-3}} = 500$$

The concentrations for both species are about 500 times greater at sea level than they are at the stratopause.

3. What is the total mass of the stratosphere (the region between 15 and 50 km above the Earth's surface)? What mass fraction of the atmosphere does this make up?

Solution

The radius of Earth = 6.3782 x 10^6 m and the average molar mass of air = 0.02896 kg mol^{-1}
Using equation 2.3:

$$P_h = P^o e^{-\bar{M}_a\, g}$$

we can calculate the pressure at the 'top and bottom' of the stratosphere.

P at 15 km = 9099 Pa ('bottom' of stratosphere)
P at 50 km = 184 Pa ('top' of stratosphere)

Calculate the following three masses using equation 2.2 (p. 24).
1) the total mass of the atmosphere,
2) the mass of the atmosphere down to the tropopause (h = 15 000 m), and
3) the mass of the atmosphere down to the stratopause (h = 50 000 m).

Mass (of the defined part of the atmosphere) = $P4\pi r^2/g$

pressure / Pa	radius / m	4π	g / m s^{-2}	mass / kg
1) 101 325	6 378 200	12.566	9.81	5.28×10^{18} (mass 1)
2) 9099	6 393 200	12.566	9.81	4.76×10^{17} (mass 2)
3) 184	6 428 200	12.566	9.81	9.74×10^{15} (mass 3)

The radius used in the calculation of mass 2 and mass 3 (above) reflect the increased height of 15 000 m and 50 000 m above the surface of the Earth. The pressures shown are the corresponding pressures calculated at these altitudes.

Mass 1 represents the total mass (mass of entire atmosphere).
Mass 2 represents the mass of the atmosphere minus the troposphere.
Mass 3 represents the mass of the atmosphere minus the sum of the troposphere plus the stratosphere.

The mass of the stratosphere can now be determined by difference.

Mass of troposphere = mass 1 – mass 2 = 4.804×10^{18} kg (mass 4)

Mass of troposphere + mass of stratosphere = mass 1 – mass 3 = 5.270×10^{18} kg (mass 5)

Mass of stratosphere = mass 5 – mass 4 = 4.66×10^{17} kg

The stratospheric mass fraction is

$$4.66 \times 10^{17} \text{ kg} \div 5.28 \times 10^{18} \text{ kg} = 0.08825 \text{ (or} \sim 8.8\%)$$

It is clear from this calculation that the remaining mass of the atmosphere above the stratosphere (> 50 km) would contribute very little to the overall mass of the atmosphere and that most of the mass is contained in the troposphere.

The tropospheric mass fraction is 4.804×10^{18} kg ÷ 5.28×10^{18} kg (x100%) = ~ 91 % of the entire atmosphere.

Together the troposphere and stratosphere account for more than 99 % of the mass of the atmosphere from these calculations.

4. If the mixing ratio of ozone in a polluted urban atmosphere is 50 ppbv, calculate its concentration: (a) in mg m^{-3}; and (b) in molecules cm^{-3}.

Solution

a) Convert 50 ppbv O_3 to units of mg m^{-3}.

Assume 20ºC and 101 325 Pa for a typical polluted urban atmosphere and calculate the total moles of gas for a 1 m^3 volume using PV = nRT.

$$101\,325 \text{ Pa} \times 1 \text{ m}^3 = n \times 8.315 \text{ J mol}^{-1} \text{K}^{-1} \times 293 \text{ K}$$

$$n = 41.59 \text{ mol} \qquad (\text{for } 1 \text{ m}^3)$$

50 ppbv mixing ratio of O_3 represents a mole ratio determined by the formula:

mole ratio

$$(x / 41.59 \text{ mol}) \times 1 \times 10^9 = 50 \text{ ppbv}$$

where x is the number of moles of O_3 in 1 m^3

$$x = 2.08 \times 10^{-6} \text{ mol of } O_3$$

The mass of O_3 in this volume is

$$2.08 \times 10^{-6} \text{ mol} \times 48.0 \text{ g mol}^{-1} \times 1000 \text{ mg g}^{-1} = 0.10 \text{ mg}$$

Therefore the concentration of 50 ppbv O_3 is equivalent to 0.10 mg m^{-3} O_3.

b) Convert 50 ppbv O_3 to molecules per cm^3. Continuing on from the calculation in part (a) from the value 2.08×10^{-6} mol m^{-3} O_3, simply convert the units mol to molecules and cubic meters to cubic centimetres, as shown by the following calculation:

$$2.08 \times 10^{-6} \text{ mol m}^{-3} \times (1 \text{ m}^3 / 1 \times 10^6 \text{ cm}^3) \times 6.022 \times 10^{23} \text{ molecules mol}^{-1}$$

$$= 1.25 \times 10^{12} \text{ molecules cm}^{-3}$$

50 ppbv O_3 can also be expressed as 1.3×10^{12} molecules cm^{-3}.

5. The gases from a wood-burning stove are found to contain 1.8% carbon monoxide at a temperature of 65ºC. Express the concentration in units of g m^{-3}.

Solution

Use PV = nRT, assume 101 325 Pa for pressure and use 1 m^3 for volume

$$101\,325 \text{ Pa} \times 1 \text{ m}^3 = n \times 8.315 \text{ J mol}^{-1} \text{K}^{-1} \times 338 \text{ K}$$

$n = 36.05$ mol (total moles of gas for 1 m^3 at 65ºC)

CO (g) moles: 0.018×36.05 mol $= 0.6490$ mol

mass of CO (g): 0.6490 mol $\times$ 28.0 g mol^{-1} $= 18.2$ g of CO (in 1 m^3)

The concentration of CO gas from the wood-burning stove under these conditions is 18.2 g m^{-3} !

6. Using Fig. 8.2 compare the mixing ratio (as %) of water in the atmosphere for a situation in a tropical rain forest in Kinshasa, DRC (T = 36ºC, relative humidity = 92%) with that in Denver, USA (T = 8ºC, relative humidity = 24%).

Solution

Refer to Chapter 8, figure 8.2.

For Kinshasa: The partial pressure of water at 36ºC is approximately 5.5 kPa.

From the relative humidity provided the actual partial pressure of water vapour can be determined.

0.92×5.5 kPa $= 5.06$ kPa (P_{H2O})

The mixing ratio (mole fraction) expressed as a percent is determined by dividing the partial pressure of water vapour by the total pressure and multiplying by 100%.

5.06 kPa $\div 101.325$ kPa $\times$ 100% = 5.0%

For Denver: The partial pressure of water at 8ºC is approximately 1.0 kPa.

The mixing ratio (as %) is

0.24×1.0 kPa $= 0.24$ kPa

0.24 kPa $\div$ 101.325 kPa $\times$ 100% = 0.24%

There is about 21 times more water (as %) in the air in Kinshasa compared with that in Denver under these given conditions.

7. Calculate the maximum wavelength of radiation that could have sufficient energy to effect the dissociation of nitric oxide (NO). In what regions of the atmosphere would such radiation be available? Use data from Appendix B.2.

Solution

Using the ΔH^o_f values (as a measure of bond strength) as given in Appendix B.2, consider the process of

$$N (g) + O (g) \rightarrow NO (g)$$

ΔH^o_{rxn} = 90.25 - (472.70 + 249.17) = - 631.62 kJ mol^{-1}

The NO bond strength is estimated to be 632 kJ mol^{-1} (this value may vary depending on source of data).

Divide the bond strength by Avogadro's number and convert to the energy units to Joules (x 1000 J/kJ). This gives:

E (per NO bond) = 1.049 x 10^{-18} J

Then use: E = hν (where $\nu = c/\lambda$) and rearrange to get λ = h c ÷ E

h = Planck constant = 6.626 x 10^{-34} J s, c = the speed of light = 3.00 x 10^{8} m s^{-1}

The maximum wavelength equivalent to this amount of energy is calculated by:

λ_{max} = (6.626 x 10^{-34} J s x 3.00 x 10^{8} m s^{-1}) ÷ 1.049 x 10^{-18} J
= 1.89 x 10^{-7} m (multiply by 1 x 10^{9} nm m^{-1})
= 189 nm

The radiation that will have sufficient energy to break the NO bond would include those that have wavelengths of approximately 190 nm (maximum) and shorter. These high energy wavelengths are available in the upper region of the atmosphere (mesosphere) and not in the lower regions, i.e. the stratosphere and troposphere.

8. The average distance a gas molecule travels before colliding with another (mean free path, S_{mfp}) is given by the relation

$$S_{\text{mfp}} = \frac{kT}{\sqrt{2}P\sigma_{\text{c}}}$$

where T and P are the temperature (K) and pressure (Pa), respectively, *k* is Boltzmann's constant = 1.38 × 10^{-23} J K^{-1}, and σ_c is the collision cross-section of the molecule (m^2). Calculate the mean free path of a dinitrogen molecule at the Earth's surface (P^o and T = 25^{o}C), and at the stratopause. The value of σ_c for dinitrogen is 0.43 nm^2. What does this indicate regarding gas-phase reaction rates in these two locations?

Solution

s_{mfp} = (kT) ÷ ($\sqrt{2}$ x P x σ_c)

where: k = Boltzmann constant 1.38 x 10^{-23} J K^{-1}
T = temperature (298 K)
P = pressure (101 325 Pa)
σ_c = collision cross section 0.43 nm^2 (1 m^2 = 1 x 10^{18} nm^2)
= 4.3 x 10^{-19} m^2

s_{mfp} = 1.38 x 10^{-23} J K^{-1} x 298 K ÷ (1.414 x 101 325 Pa x 4.3 x 10^{-19} m^2)
s_{mfp} = 6.67 x 10^{-8} m (convert to nm, multiply by 1 x 10^{9} nm m^{-1})
s_{mfp} = 67 nm (at the Earth's surface)

The calculation is repeated for conditions at the stratopause:

T = 271 K, and P = 184 Pa (see answer of Problem 2)

$s_{mfp} = 1.38 \times 10^{-23}$ J $K^{-1} \times 271$ K ÷ (1.414 x 184 Pa x 4.3×10^{-19} m^2)

s_{mfp} = 33 423 nm

The mean free path for dinitrogen at the Earth's surface is 67 nm while at the stratopause it is approximately 33.4 µm. These values would suggest that the rate of reactions that occur at the stratopause would be much less than that at the Earth surface, since the mean distant travelled for a collision to occur is almost 500 times greater.

9. Calculate the maximum wavelength of radiation required to bring about dissociation of: (a) a dinitrogen molecule; (b) a dioxygen molecule. Account qualitatively for the difference.

Solution

Bond enthalpies can be found in Appendix B.3 and then use λ_{max} = (h c) / E (as shown in Problem 7, see Example 2.2 as well)

a) for N_2 946 kJ mol^{-1} (= 1.571×10^{-18} J)

λ_{max} = (6.626×10^{-34} J s x 3.00×10^{8} m s^{-1}) ÷ 1.571×10^{-18} J
= 1.27×10^{-7} m (multiply by 1×10^{9} nm m^{-1})
λ_{max} = 127 nm

b) for O_2 497 kJ mol^{-1} (= 8.253×10^{-19} J)

λ_{max} = (6.626×10^{-34} J s x 3.00×10^{8} m s^{-1}) ÷ 8.253×10^{-19} J
= 2.41×10^{-7} m (multiply by 1×10^{9} nm m^{-1})
λ_{max} = 241 nm

The bond enthalpy for the nitrogen is higher (a triple bond, bond order of 3), thus it requires a wavelength of higher energy (a lower wavelength value) for dissociation compared to the dioxygen molecule (a double bond, bond order of 2).

10. Carbon dioxide in the troposphere is a major greenhouse gas. It absorbs infrared radiation, which causes changes in the frequency of carbon–oxygen stretching vibrations. What are the ranges of wavelength (µm), wavenumber (cm^{-1}), and energy (J) associated with this absorption?

Solution

IR absorption characteristics of Carbon dioxide:

Wavelength (µm)

See Chapter 8 (The chemistry of global climate) for information on infrared absorption by CO_2 (g).

Two strong regions include: 14 – 19 μm & 4.0 – 4.3 μm (see Section 8.3 sub section on carbon dioxide)

Wavenumber (cm^{-1})

ν (wavenumber) = $1/\lambda$ (convert λ units from μm to cm)

$\lambda = 14\ \mu m \times 1 \times 10^{-4}\ cm\ \mu m^{-1} = 1.4 \times 10^{-3}\ cm$

$\nu = 1 \div 1.4 \times 10^{-3}\ cm = 714\ cm^{-1}$

similarly, 19 μm yields $\nu = 1 \div 1.9 \times 10^{-3}\ cm = 526\ cm^{-1}$
4 μm $\nu = 1 \div 1.0 \times 10^{-4}\ cm = 2500\ cm^{-1}$
and 4.3 μm $\nu = 1 \div 1.9 \times 10^{-3}\ cm = 2325\ cm^{-1}$

Therefore, the corresponding ranges of absorptions in wavenumbers are:

526 – 714 cm^{-1} and 2325 – 2500 cm^{-1} (compare these values to those absorptions shown in Fig. 8.8)

Energy (J)

$E = (h\ c)/\lambda$ (convert to units of Joules)

$E = 6.626 \times 10^{-34}\ J\ s \times 3.00 \times 10^{8}\ m\ s^{-1} \div (14\ \mu m \times 1 \times 10^{-6}\ m\ \mu m^{-1})$
$= 1.42 \times 10^{-20}\ J$

E (for 19 μm) = 1.05×10^{-20} J
E (for 4 μm) = 4.97×10^{-20} J
E (for 4.5 μm) = 4.42×10^{-20} J

The corresponding ranges of energy are 1.05×10^{-20} to 1.42×10^{-20} J and 4.42×10^{-20} J to 4.97×10^{-20} J

11. The stability of compounds in the stratosphere depends on the magnitude of the bond energies of the reactive part of the molecules. Using Appendix B.2 calculate bond energies of HF (g), HCl (g), and HBr (g), in order to determine the relative ability of these molecules to act as reservoirs for the respective halogen atoms.

Solution

Stability of HF (g), HCl (g), HBr (g) in stratosphere.

Note: most of the data required is in Appendix B.2. A more comprehensive set of thermodynamic tables will be required.

	ΔH_f^o / kJ mol^{-1}
HF (g)	– 271
HCl (g)	– 92
HBr (g)	– 36
H_2 (g)	0
F_2 (g)	0
Br (g)	112

	ΔH_f^o / kJ mol^{-1}
Cl_2 (g)	0
Br_2 (g)	0
F (g)	79
H (g)	218
Cl (g)	122

Calculation of HF dissociation energy: ΔH_f^o / kJ mol^{-1}

$$
\begin{array}{lr}
HF (g) \rightarrow \tfrac{1}{2} H_2 (g) + \tfrac{1}{2} F_2 (g) & +271 \\
\tfrac{1}{2} H_2 (g) \rightarrow H (g) & +218 \\
\tfrac{1}{2} F_2 (g) \rightarrow F (g) & +79 \\
\hline
\text{Net: } HF (g) \rightarrow H (g) + F (g) & +568
\end{array}
$$

For a diatomic molecule, the bond strength is can be considered equal to the dissociation energy.

Similar calculations for HCl and HBr yield the bond energy values of 432 kJ mol^{-1} and 366 kJ mol^{-1} respectively. As expected, these values are similar to those provided in Appendix B.3 (mean bond enthalpies).

Since the bond energy for HF is the largest, relatively speaking it will require higher energy radiation to bring about its dissociation, and is therefore a more stable molecule in the stratosphere.

12. Use the tabulated bond energy data in Appendix B.3 to estimate the enthalpy change of the gas-phase reaction between hydroxyl radical and methane.

Solution

Enthalpy change for the reaction between hydroxyl radical and methane.

$$\bullet OH (g) + CH_4 (g) \rightarrow H_2O (g) + \bullet CH_3 (g) \quad \Delta H \ ?$$

Mean bond enthalpies are found in Appendix B.3.

Essentially, one hydrogen is removed from carbon and attached to oxygen.

C – H	412 kJ mol^{-1}	(energy (E) needed to break one bond)
O – H	463 kJ mol^{-1}	(energy (E) produced from forming one bond)

$$
\begin{aligned}
\Delta H &= \Sigma\, E \text{ (bonds broken)} - \Sigma\, E \text{ (bonds formed)} \\
&= (1 \text{ mol} \times 412 \text{ kJ mol}^{-1}) - (1 \text{ mol} \times 463 \text{ kJ mol}^{-1}) \\
&= -51 \text{ kJ}
\end{aligned}
$$

The enthalpy change (ΔH) for the reaction is – 51 kJ mol^{-1}, an energetically favourable process.

13. Which of the following atmospheric species are free radicals?

$$OH,\ O_3\ Cl, ClO, CO, NO, N_2O, NO_3^-, N_2O_5$$

Solution

The following species are free radicals and typically shown as:

•OH •Cl ClO• and NO

The single nitrogen species NO and NO_2 despite being free radicals, are often shown without the 'dot'.

14. In an indoor atmosphere, for NO_2 the value of the first-order rate constant has been estimated to be $1.28\ h^{-1}$. Calculate its residence time.

Solution

$$\text{Residence time} = \tau = \frac{\text{steady state amount}}{\text{flux}} \qquad \text{(see Chapter 1, Example 1.1)}$$

Let $\boldsymbol{x}$ represent the steady state amount of $[NO_2]$.

Let the flux = rate of change = $k[NO_2]$ therefore, flux = $1.28\ h^{-1}\ \boldsymbol{x}$

$$\tau = \frac{\boldsymbol{x}}{1.28\ h^{-1}\ \boldsymbol{x}} = \frac{1}{1.28\ h^{-1}} = 0.781\ h\ \ (x\ 60\ min\ h^{-1}) = 46.9\ min$$

The residence time based on the first-order rate constant would be about 47 minutes (the reciprocal of the first-order rate constant). If there are several removal processes, the residence time is calculated as the reciprocal of the sum of all the first-order rate constants involved.

15. If the rate laws are expressed using mol L^{-1} for concentrations, and Pa for pressure, what are the units of the second- and third-order rate constants, k_2 and k_3? Calculate the conversion factor for converting k_2 values obtained in the units above to ones using molecules per cm^3 for concentration and atm for pressure.

Solution

second-order rate constants	i) for mol L^{-1}	k_2 units are:	i) L $mol^{-1}\ s^{-1}$
	ii) for Pa		ii) $Pa^{-1}\ s^{-1}$
third-order rate constants	i) for mol L^{-1}	k_3 units are:	i) $L^2\ mol^{-2}\ s^{-1}$
	ii) for Pa		ii) $Pa^{-2}\ s^{-1}$

Calculation of conversion factor for k_2 (L mol^{-1} s^{-1}) from units of mol L^{-1} to molecules cm^{-3}.
1L = 1000 cm^3, therefore 1 mol L^{-1} = 0.001 mol cm^{-3}
convert to molecules using 1 mol = 6.022×10^{23} molecules

0.001 mol cm^{-3} x 6.022×10^{23} molecules mol^{-1} = 6.022×10^{20} molecules cm^{-3}

and, $(6.022 \times 10^{20}$ molecules $cm^{-3})^{-1}$ = 1.661×10^{-21} cm^3 $molecule^{-1}$

The conversion factor is 1.661×10^{-21} cm^3 $molecule^{-1}$ s^{-1} / L mol^{-1} s^{-1}

Therefore, multiply the original rate constant (having units L mol^{-1} s^{-1}) by 1.661×10^{-21} cm^3 $molecule^{-1}$ s^{-1} / L mol^{-1} s^{-1} to give the correct numerical value and units of cm^3 $molecule^{-1}$ s^{-1}.

Calculation of conversion factor for k_2 (Pa^{-1} s^{-1}), from units of Pa to atm.

1 Pa = 9.869×10^{-6} atm (1.00 atm = 101 325 Pa)

$(9.869 \times 10^{-6}$ atm$)^{-1}$ = 101 325 atm^{-1} which gives 101 325 atm^{-1} s^{-1}

The conversion factor is 101 325 atm^{-1} s^{-1} / Pa^{-1} s^{-1}

Therefore, multiply the original rate constant (with units Pa^{-1} s^{-1}) by 101 325 atm^{-1} s^{-1} / Pa^{-1} s^{-1} to give the correct numerical value and units of atm^{-1} s^{-1}.

16. For the reaction

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

the second-order rate constant has a value of 1.8×10^{-14} $molecule^{-1}$ cm^3 s^{-1} at 25ºC. The concentration of NO in a relatively clean atmosphere is 0.10 ppbv and that of O_3 is 15 ppbv. Calculate these two concentrations in units of molecule per cm^3. Calculate the rate of the NO oxidation using concentration units of molecule cm^{-3}. Show how the rate law may be expressed in pseudo first-order terms and calculate the corresponding pseudo first-order rate constant.

Solution

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

k_2 = 1.8×10^{-14} $molecules^{-1}$ cm^3 s^{-1} at 298 K

NO = 0.10 ppbv O_3 = 15 ppbv

Unit conversion:

Use PV = nRT P = 101 325 Pa, V = 1×10^{-6} m^3 (1 cm^3), T = 298 K

101 325 Pa x 1×10^{-6} m^3 = n x 8.315 J mol^{-1} K^{-1} x 298 K

n = 4.09×10^{-5} mol (total number of moles of gas in 1 cm^3)

Let x = mol of NO, $(x/4.09 \times 10^{-5}\text{ mol}) \times 1 \times 10^{9} = 0.10$ ppbv

$x = 4.09 \times 10^{-15}$ mol of NO (in 1 cm^3)

$= 2.46 \times 10^{9}$ molecules cm^{-3} (NO)

Let y = mol of O_3 $(y/4.09 \times 10^{-5}\text{ mol}) \times 1 \times 10^{9} = 15$ ppbv

$y = 6.13 \times 10^{-13}$ mol of O_3 (in 1 cm^3)

$= 3.69 \times 10^{11}$ molecules cm^{-3}

$\text{rate}_{NO} = k_2[NO][O_3]$

$\text{rate}_{NO} = 1.8 \times 10^{-14}\text{ molecules}^{-1}\text{ cm}^3\text{ s}^{-1} \times 2.46 \times 10^{9}\text{ molecules cm}^{-3} \times 3.69 \times 10^{11}\text{ molecules cm}^{-3}$

$\text{rate}_{NO} = 1.63 \times 10^{7}\text{ molecules cm}^{-3}\text{ s}^{-1}$

The rate of oxidation of NO is 1.63×10^{7} molecules $cm^{-3}\ s^{-1}$.

If we assume that the concentration of O_3 is unchanging during the reaction we can treat this value as a constant. This is reasonable, since its concentration is more than 100 times that of the NO. We can then combine the two constants and derive a new rate constant k' (pseudo first-order constant with units of s^{-1}).

$\text{rate}_{NO} = k'[NO]$

$k' = 3.69 \times 10^{11}\text{ molecules cm}^{-3} \times 1.8 \times 10^{-14}\text{ molecules}^{-1}\text{ cm}^3\text{ s}^{-1} = 6.64 \times 10^{-3}\text{ s}^{-1}$

The pseudo first-order rate constant (k') = $6.64 \times 10^{-3}\ s^{-1}$.

17. At a particular temperature, the Arrhenius parameters for the reaction

$$\bullet OH + H_2 \rightarrow H_2O + \bullet H$$

are $A = 8 \times 10^{10}\ s^{-1}$, and $E_a = 42\ \text{kJ mol}^{-1}$. Given that the concentration of hydroxyl radical in the atmosphere is 7×10^{5} molecules cm^{-3} and that of H_2 is 530 ppbv, calculate the rate of reaction (units of molecule $cm^{-3}\ s^{-1}$) for this process.

<u>Solution</u>

$\bullet OH + H_2 \rightarrow H_2O + \bullet H \qquad \text{rate}_{OH} = k[\bullet OH][H_2]$

A = $8 \times 10^{10}\ s^{-1}$ (note that these units indicate that the rate constant will be a pseudo first-order rate constant)

$E_a = 42\ \text{kJ mol}^{-1}$ & $[\bullet OH] = 7 \times 10^{5}$ molecules cm^{-3}

$[H_2] = 530$ ppbv (convert to molecules cm^{-3})

Use PV = nRT P = 101 325 Pa, V = $1 \times 10^{-6}\ m^3$ (1 cm^3), T = 298 K

$101\ 325\ \text{Pa}\ \ 1 \times 10^{-6}\ \text{m}^3 = n \times 8.315\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}$

$n = 4.09\text{x}10^{-5}\ \text{mol}$ (total number of moles of gas in 1 cm^3)

Let $\boldsymbol{x}$ = mol of H_2 $(\boldsymbol{x}/4.09 \times 10^{-5}\ \text{mol}) \times 1 \times 10^9 = 530$ ppbv

$\boldsymbol{x} = 2.17 \times 10^{-11}$ mol of H_2 (in 1 cm^3)

gives 1.31×10^{13} molecules cm^{-3} (for H_2)

Arrhenius equation $k = Ae^{-Ea/RT}$

Therefore $k = 8 \times 10^{10}\ \text{s}^{-1}\ e^{-(42\ 000\ \text{J/mol}\ \div\ (8.315\ \text{J/mol K} \times 298\ \text{K}))}$

$k = 3481\ \text{s}^{-1}$ (a first-order rate constant)

$\text{rate}_{OH} = k_2[\bullet OH][H_2]$ H_2 concentration is high and constant compared to $[^\bullet OH]$

so $k_2[H_2] = k$ and

$\text{rate}_{OH} = k\,[\bullet OH]$ (pseudo first-order, as expected)

$\text{rate}_{OH} = 3481\ \text{s}^{-1} \times 7 \times 10^5$ molecules cm^{-3}

$\text{rate}_{OH} = 2.43 \times 10^9$ molecules $\text{cm}^{-3}\ \text{s}^{-1}$

The rate of reaction for this process is 2.43×10^9 molecules $\text{cm}^{-3}\ \text{s}^{-1}$.

18. The equilibrium constant for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

has a value of $K_c = 4.65 \times 10^{-3}$ mol L^{-1} at 25°C and the corresponding standard enthalpy change is $\Delta H^o = +57$ kJ .

Calculate the equilibrium concentration of N_2O_4 in an atmosphere where the concentration of NO_2 is 200 µg m^{-3}. If the temperature were to increase would you expect the relative concentration of N_2O_4 to increase or decrease?

Solution

$$N_2O_4 \rightleftharpoons 2NO_2$$

$K_c = 4.65 \times 10^{-3}\ \text{mol L}^{-1}$ at 298K, $\Delta H^o = 57$ kJ
$K_c = -\,[NO_2]^2 / [N_2O_4]$

Calculation of enthalpy (ΔH^o_{rxn})

$$\Delta H^o_{rxn} = \Sigma(\Delta H^o_f\ \text{products}) - \Sigma(\Delta H^o_f\ \text{reactants})$$

$$\Delta H^o_{rxn} = (2\ \text{mol} \times 33.2\ \text{kJ mol}^{-1}) - (1\ \text{mol} \times 9.7\ \text{kJ mol}^{-1})$$
$$\Delta H^o_{rxn} = 56.7\ \text{kJ}$$

Convert the concentration of NO_2 to mol L^{-1}

$NO_2 = 200\ \mu g\ m^{-3}$ $1\ m^3 = 1000\ L$ $1\ g = 10^6\ \mu g$ (M.M. $46.0\ g\ mol^{-1}$ NO_2)

$$[NO_2] = 4.35 \times 10^{-9}\ \text{mol L}^{-1}$$

Note that this is the equilibrium concentration of NO_2. It is now straight-forward to calculate the corresponding concentration of N_2O_4 using the equilibrium relation.

$$K_c = [NO_2]^2 / [N_2O_4]$$
$$4.65 \times 10^{-3} = (4.35 \times 10^{-9})^2 / [N_2O_4]$$
$$[N_2O_4] = 4.06 \times 10^{-15}\ \text{mol L}^{-1}$$

Earlier, in problems 16 and 17, we found that the total moles of gas at P° and 298 K is 4.09×10^{-2} in 1 L. Therefore, the mixing ratio of N_2O_4 is calculated to be = 1×10^{-4} ppbv.

If the temperature were to be increased for the reaction the relative concentration of N_2O_4 would be expected to decrease because it is an endothermic process and Le Chatelier principle predicts the equilibrium to shift to reduce heat and drive the reaction forward to produce more NO_2.

19. It is postulated[1] that the hydroxyl radical concentration in the tropical atmosphere is directly proportional to the rate constant for photolysis of O_3 to O^*, and to the concentration of O_3 and H_2O. It is inversely proportional to $(C_{CO} + 0.03 \times C_{CH_4})$; concentrations are expressed as mixing ratios. Use this hypothesis to predict the relative hydroxyl concentrations in two tropical atmospheres with the following conditions.

Air temperature / ºC	25–30	20–25
Cloudiness / %	50–75	25–50
O_3 / ppbv	10	19
H_2O / kPa	> 25	20
CO / ppbv	38	50
CH_4 / ppmv	1560	1580
$J(O_3)$ / s^{-1}	1.3	0.68

<u>Solution</u>

The first column in the table refers to wet season conditions (higher water content, greater cloudiness) and the second column refers to dry season conditions. Water vapour and ozone are both precursors to the production of hydroxyl radicals. The comparative levels shown here would have opposing effects on rate of production of this species. However, the larger value of the photochemical rate constant for photolysis of ozone (we use the symbol *f* in the text) indicates a greater rate of production of hydroxyl under the humid conditions. The inverse proportionality to carbon monoxide levels is another reason why levels are higher in the wet season.

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[1] Data taken from H. Rodhe and R. Herrera, *Acidification in tropical countries* (Scope 36), John Wiley and Sons, Chichester; 1988.