

Chapter 2:

The Earth's atmosphere

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^0 (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.

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

The total number of moles of gas in 1.00 L is

$$\begin{aligned} n &= PV/RT \\ n &= 0.04089 \text{ mol} \end{aligned}$$

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

$$\% \text{ O}_2 = 20.95, \text{ mole fraction} = 0.2095$$

The number of moles of O_2 in 1.00 L is: $0.2095 \times 0.04089 = 0.00857 \text{ mol}$

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

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

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

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

The O_2 (g) concentration can be expressed as either $8.57 \times 10^{-3} \text{ mol L}^{-1}$ 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).

$$P_h = P^0 e^{-\bar{M}_a g h}$$

$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$, $P^0 = 101\,325 \text{ Pa}$, $g = 9.81 \text{ m s}^{-2}$, $\bar{M}_a = 0.02896 \text{ kg mol}^{-1}$ (average molar mass of air), $h = 50 \text{ km}$ (50 000 m) and $T = -2^\circ\text{C}$ (271 K). Note: these last two parameters are the approximate altitude and temperature at the stratopause.

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

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

$$P_h = 101325 \text{ Pa} \times 0.001812$$

$$= 184 \text{ Pa} \quad (\text{about } 0.2 \% \text{ of atmospheric pressure at sea level})$$

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 $n/V = P/RT$

$$\begin{aligned} n/V &= 38.5 \text{ Pa} / 8.315 \text{ J mol}^{-1} \text{K}^{-1} \times 271 \text{ K} \\ &= 0.0171 \text{ mol m}^{-3} \end{aligned}$$

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

Comparison to sea level conditions:

The answer to Problem 1 gave the O_2 concentration as $8.56 \times 10^{-3} \text{ mol L}^{-1}$. 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:

$$\begin{array}{ll} \text{for } \text{O}_2 & \frac{8.56 \text{ mol m}^{-3}}{0.0171 \text{ mol m}^{-3}} = 500 \\ \text{for } \text{N}_2 & \frac{31.9 \text{ mol m}^{-3}}{0.0638 \text{ mol m}^{-3}} = 500 \end{array}$$

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 = $6.3782 \times 10^6 \text{ m}$ and the average molar mass of air = $0.02896 \text{ kg mol}^{-1}$
Using equation 2.3:

$$P_h = P^0 e^{-\bar{M}_a g}$$

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

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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	$g / \text{m s}^{-2}$	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 $4.804 \times 10^{18} \text{ kg} \div 5.28 \times 10^{18} \text{ kg (x100\%)} = \sim 91 \%$ of the entire atmosphere.

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

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

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

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

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

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

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

$$x = 2.08 \times 10^{-6} \text{ mol of } \text{O}_3$$

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 $0.10 \text{ mg m}^{-3} \text{ O}_3$.

b) Convert 50 ppbv O_3 to molecules per cm^3 . Continuing on from the calculation in part (a) from the value $2.08 \times 10^{-6} \text{ mol m}^{-3} \text{ O}_3$, simply convert the units mol to molecules and cubic meters to cubic centimetres, as shown by the following calculation:

$$\begin{aligned} 2.08 \times 10^{-6} \text{ mol m}^{-3} \times (1 \text{ m}^3 / 1 \times 10^6 \text{ cm}^3) \times 6.022 \times 10^{23} \text{ molecules mol}^{-1} \\ = 1.25 \times 10^{12} \text{ molecules cm}^{-3} \end{aligned}$$

50 ppbv O_3 can also be expressed as $1.3 \times 10^{12} \text{ molecules cm}^{-3}$.

5. The gases from a wood-burning stove are found to contain 1.8% carbon monoxide at a temperature of 65°C. 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

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

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$$n = 36.05 \text{ mol} \quad (\text{total moles of gas for } 1 \text{ m}^3 \text{ at } 65^\circ\text{C})$$

$$\text{CO (g) moles:} \quad 0.018 \times 36.05 \text{ mol} = 0.6490 \text{ mol}$$

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

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 ($T = 36^\circ\text{C}$, relative humidity = 92%) with that in Denver, USA ($T = 8^\circ\text{C}$, relative humidity = 24%).

Solution

Refer to Chapter 8, figure 8.2.

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

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

$$0.92 \times 5.5 \text{ kPa} = 5.06 \text{ kPa (P}_{\text{H}_2\text{O}})$$

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%.

$$5.06 \text{ kPa} \div 101.325 \text{ kPa} \times 100\% = 5.0\%$$

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

The mixing ratio (as %) is

$$0.24 \times 1.0 \text{ kPa} = 0.24 \text{ kPa}$$

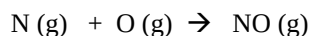
$$0.24 \text{ kPa} \div 101.325 \text{ kPa} \times 100\% = 0.24\%$$

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°_f values (as a measure of bond strength) as given in Appendix B.2, consider the process of



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$$\Delta H^\circ_{\text{rxn}} = 90.25 - (472.70 + 249.17) = -631.62 \text{ kJ mol}^{-1}$$

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 ($\times 1000 \text{ J/kJ}$).

This gives:

$$E (\text{per NO bond}) = 1.049 \times 10^{-18} \text{ J}$$

Then use: $E = h\nu$ (where $\nu = c/\lambda$) and rearrange to get $\lambda = hc \div E$

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

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

$$\begin{aligned} \lambda_{\text{max}} &= (6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}) \div 1.049 \times 10^{-18} \text{ J} \\ &= 1.89 \times 10^{-7} \text{ m} \quad (\text{multiply by } 1 \times 10^9 \text{ nm m}^{-1}) \\ &= 189 \text{ nm} \end{aligned}$$

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

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

where T and P are the temperature (K) and pressure (Pa), respectively, k is Boltzmann's constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$, 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° and $T = 25^\circ\text{C}$), 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

$$S_{\text{mfp}} = (kT) \div (\sqrt{2} \times P \times \sigma_c)$$

where: k = Boltzmann constant $1.38 \times 10^{-23} \text{ J K}^{-1}$

T = temperature (298 K)

P = pressure (101 325 Pa)

σ_c = collision cross section 0.43 nm^2 ($1 \text{ m}^2 = 1 \times 10^{18} \text{ nm}^2$)
 $= 4.3 \times 10^{-19} \text{ m}^2$

$$S_{\text{mfp}} = 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K} \div (1.414 \times 101\,325 \text{ Pa} \times 4.3 \times 10^{-19} \text{ m}^2)$$

$$S_{\text{mfp}} = 6.67 \times 10^{-8} \text{ m} \quad (\text{convert to nm, multiply by } 1 \times 10^9 \text{ nm m}^{-1})$$

$$S_{\text{mfp}} = 67 \text{ nm} \quad (\text{at the Earth's surface})$$

The calculation is repeated for conditions at the stratopause:

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$T = 271 \text{ K}$, and $P = 184 \text{ Pa}$ (see answer of Problem 2)

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

$$s_{\text{mfp}} = 33\,423 \text{ nm}$$

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 distance 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 $\lambda_{\text{max}} = (h c) / E$ (as shown in Problem 7, see Example 2.2 as well)

a) for N_2 946 kJ mol^{-1} ($= 1.571 \times 10^{-18} \text{ J}$)

$$\begin{aligned}\lambda_{\text{max}} &= (6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}) \div 1.571 \times 10^{-18} \text{ J} \\ &= 1.27 \times 10^{-7} \text{ m} \quad (\text{multiply by } 1 \times 10^9 \text{ nm m}^{-1}) \\ \lambda_{\text{max}} &= 127 \text{ nm}\end{aligned}$$

b) for O_2 497 kJ mol^{-1} ($= 8.253 \times 10^{-19} \text{ J}$)

$$\begin{aligned}\lambda_{\text{max}} &= (6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}) \div 8.253 \times 10^{-19} \text{ J} \\ &= 2.41 \times 10^{-7} \text{ m} \quad (\text{multiply by } 1 \times 10^9 \text{ nm m}^{-1}) \\ \lambda_{\text{max}} &= 241 \text{ nm}\end{aligned}$$

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).

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

Wavenumber (cm^{-1})

$$\nu \text{ (wavenumber)} = 1/\lambda \quad (\text{convert } \lambda \text{ units from } \mu\text{m} \text{ to cm})$$

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

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

$$\text{similarly, } 19 \mu\text{m} \text{ yields } \nu = 1 \div 1.9 \times 10^{-3} \text{ cm} = 526 \text{ cm}^{-1}$$

$$4 \mu\text{m} \quad \nu = 1 \div 1.0 \times 10^{-4} \text{ cm} = 2500 \text{ cm}^{-1}$$

$$\text{and } 4.3 \mu\text{m} \quad \nu = 1 \div 1.9 \times 10^{-3} \text{ cm} = 2325 \text{ cm}^{-1}$$

Therefore, the corresponding ranges of absorptions in wavenumbers are:

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

Energy (J)

$$E = (h c)/\lambda \quad (\text{convert to units of Joules})$$

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

$$E \text{ (for } 19 \mu\text{m)} = 1.05 \times 10^{-20} \text{ J}$$

$$E \text{ (for } 4 \mu\text{m)} = 4.97 \times 10^{-20} \text{ J}$$

$$E \text{ (for } 4.5 \mu\text{m)} = 4.42 \times 10^{-20} \text{ J}$$

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.

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ΔH_f° / kJ mol ⁻¹		ΔH_f° / kJ mol ⁻¹	
HF (g)	- 271	Cl ₂ (g)	0
HCl (g)	- 92	Br ₂ (g)	0
HBr (g)	- 36	F (g)	79
H ₂ (g)	0	H (g)	218
F ₂ (g)	0	Cl (g)	122
Br (g)	112		

Calculation of HF dissociation energy:

	ΔH_f° / kJ mol ⁻¹
HF (g) → ½ H ₂ (g) + ½ F ₂ (g)	+ 271
½ H ₂ (g) → H (g)	+ 218
½ F ₂ (g) → F (g)	+ 79
Net: HF (g) → H (g) + F (g)	+ 568

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

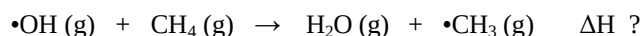
Similar calculations for HCl and HBr yield the bond energy values of 432 kJ mol⁻¹ and 366 kJ mol⁻¹ respectively. As expected, these values are similar to those provided in Appendix B.3 (mean bond enthalpies).

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.



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)

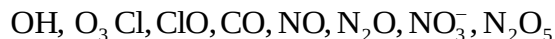
$$\begin{aligned} \Delta H &= \Sigma E (\text{bonds broken}) - \Sigma E (\text{bonds formed}) \\ &= (1 \text{ mol} \times 412 \text{ kJ mol}^{-1}) - (1 \text{ mol} \times 463 \text{ kJ mol}^{-1}) \\ &= - 51 \text{ kJ} \end{aligned}$$

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

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



Solution

The following species are free radicals and typically shown as:



The single nitrogen species NO and NO₂ despite being free radicals, are often shown without the 'dot'.

14. In an indoor atmosphere, for NO₂ the value of the first-order rate constant has been estimated to be 1.28 h⁻¹. Calculate its residence time.

Solution

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

Let x represent the steady state amount of [NO₂].

Let the flux = rate of change = k[NO₂] therefore, flux = 1.28 h⁻¹ x

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

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, k₂ and k₃? Calculate the conversion factor for converting k₂ values obtained in the units above to ones using molecules per cm³ 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

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Calculation of conversion factor for k_2 ($\text{L mol}^{-1} \text{s}^{-1}$) from units of mol L^{-1} to molecules cm^{-3} .

$1 \text{ L} = 1000 \text{ cm}^3$, therefore $1 \text{ mol L}^{-1} = 0.001 \text{ mol cm}^{-3}$

convert to molecules using $1 \text{ mol} = 6.022 \times 10^{23} \text{ molecules}$

$$0.001 \text{ mol cm}^{-3} \times 6.022 \times 10^{23} \text{ molecules mol}^{-1} = 6.022 \times 10^{20} \text{ molecules cm}^{-3}$$

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

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

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

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

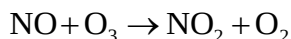
$$1 \text{ Pa} = 9.869 \times 10^{-6} \text{ atm} \quad (1.00 \text{ atm} = 101\,325 \text{ Pa})$$

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

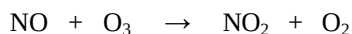
The conversion factor is $101\,325 \text{ atm}^{-1} \text{s}^{-1} / \text{Pa}^{-1} \text{s}^{-1}$

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

16. For the reaction



the second-order rate constant has a value of $1.8 \times 10^{-14} \text{ molecule}^{-1} \text{cm}^3 \text{s}^{-1}$ at 25°C . 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

$$k_2 = 1.8 \times 10^{-14} \text{ molecules}^{-1} \text{cm}^3 \text{s}^{-1} \quad \text{at} \quad 298 \text{ K}$$

$$\text{NO} = 0.10 \text{ ppbv} \quad \text{O}_3 = 15 \text{ ppbv}$$

Unit conversion:

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

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

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

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

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

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

Let y = mol of O₃ $(y/4.09 \times 10^{-5} \text{ mol}) \times 1 \times 10^9 = 15 \text{ ppbv}$

$$y = 6.13 \times 10^{-13} \text{ mol of O}_3 \text{ (in } 1 \text{ cm}^3\text{)}$$

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

$$\text{rate}_{\text{NO}} = k_2[\text{NO}][\text{O}_3]$$

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

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

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

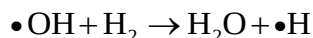
If we assume that the concentration of O₃ is unchanging during the reaction we can treat this value as a constant. This is reasonable, since its concentration is more than 100 times that of the NO. We can then combine the two constants and derive a new rate constant k' (pseudo first-order constant with units of s⁻¹).

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

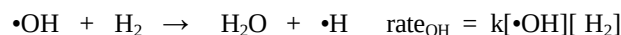
$$k' = 3.69 \times 10^{11} \text{ molecules cm}^{-3} \times 1.8 \times 10^{-14} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1} = 6.64 \times 10^{-3} \text{ s}^{-1}$$

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

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



are $A = 8 \times 10^{10} \text{ s}^{-1}$, and $E_a = 42 \text{ kJ mol}^{-1}$. Given that the concentration of hydroxyl radical in the atmosphere is $7 \times 10^5 \text{ molecules cm}^{-3}$ and that of H₂ is 530 ppbv, calculate the rate of reaction (units of molecule cm⁻³ s⁻¹) for this process.

Solution

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

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

$$[\text{H}_2] = 530 \text{ ppbv} \quad (\text{convert to molecules cm}^{-3})$$

Use $PV = nRT$ $P = 101\,325 \text{ Pa}$, $V = 1 \times 10^{-6} \text{ m}^3$ (1 cm³), $T = 298 \text{ K}$

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

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

$$\text{Let } x = \text{mol of H}_2 \quad (x/4.09 \times 10^{-5}\text{ mol}) \times 1 \times 10^9 = 530\text{ ppbv}$$

$$x = 2.17 \times 10^{-11}\text{ mol of H}_2 \text{ (in } 1\text{ cm}^3)$$

$$\text{gives } 1.31 \times 10^{13}\text{ molecules cm}^{-3} \quad (\text{for H}_2)$$

$$\text{Arrhenius equation} \quad k = Ae^{-E_a/RT}$$

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

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

$$\text{rate}_{\text{OH}} = k_2[\bullet\text{OH}][\text{H}_2] \quad \text{H}_2 \text{ concentration is high and constant compared to } [\bullet\text{OH}]$$

$$\text{so } k_2[\text{H}_2] = k \text{ and}$$

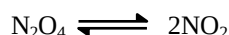
$$\text{rate}_{\text{OH}} = k[\bullet\text{OH}] \quad (\text{pseudo first-order, as expected})$$

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

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

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

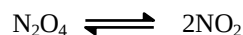
18. The equilibrium constant for the reaction



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

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

Solution



$$K_c = 4.65 \times 10^{-3}\text{ mol L}^{-1} \text{ at } 298\text{K}, \Delta H^\circ = 57\text{ kJ}$$

$$K_c = -[\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$$

Calculation of enthalpy ($\Delta H^\circ_{\text{rxn}}$)

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

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

$$\Delta H^\circ_{\text{rxn}} = 56.7 \text{ kJ}$$

Convert the concentration of NO₂ to mol L⁻¹

$$\text{NO}_2 = 200 \mu\text{g m}^{-3} \quad 1 \text{ m}^3 = 1000 \text{ L} \quad 1 \text{ g} = 10^6 \mu\text{g} \quad (\text{M.M. } 46.0 \text{ g mol}^{-1} \text{ NO}_2)$$

$$[\text{NO}_2] = 4.35 \times 10^{-9} \text{ mol L}^{-1}$$

Note that this is the equilibrium concentration of NO₂. It is now straight-forward to calculate the corresponding concentration of N₂O₄ using the equilibrium relation.

$$K_c = [\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$$

$$4.65 \times 10^{-3} = (4.35 \times 10^{-9})^2 / [\text{N}_2\text{O}_4]$$

$$[\text{N}_2\text{O}_4] = 4.06 \times 10^{-15} \text{ mol L}^{-1}$$

Earlier, in problems 16 and 17, we found that the total moles of gas at P^o and 298 K is 4.09 × 10⁻² in 1 L. Therefore, the mixing ratio of N₂O₄ is calculated to be = 1 × 10⁻⁴ ppbv.

If the temperature were to be increased for the reaction the relative concentration of N₂O₄ 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 NO₂.

19. It is postulated¹ that the hydroxyl radical concentration in the tropical atmosphere is directly proportional to the rate constant for photolysis of O₃ to O^{*}, and to the concentration of O₃ and H₂O. It is inversely proportional to (C_{CO} + 0.03 × C_{CH₄}); 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 / °C	25–30	20–25
Cloudiness / %	50–75	25–50
O ₃ / ppbv	10	19
H ₂ O / kPa	> 25	20
CO / ppbv	38	50
CH ₄ / ppmv	1560	1580
J(O ₃) / s ⁻¹	1.3	0.68

Solution

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.

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