

1. (1 point) Is NO_3 a radical (based on the first definition we discussed in class)?
A. yes
B. no

2. (1 point) The relative humidity is measured to be 60% at a temperature of 285 K at sea level. What is the mixing ratio of H_2O in this air? The saturation vapour pressure of H_2O at 285 K is 14 hPa.
A. 23000 ppmv
B. 0.014
C. 8300 ppmv
D. 0.15

3. (1 point) From the options below, choose the one which correctly lists the components of solar radiation in order of **decreasing** wavelength.
A. IR, Visible, UV-A, UV-B, UV-C
B. UV-A, UV-B, UV-C, Visible, IR
C. UV-C, UV-B, UV-A, Visible, IR
D. IR, Visible, UV-C, UV-B, UV-A
E. UV-A, IR, UV-B, Visible, UV-C
F. none of the above

4. (1 point) What is the chemical composition of background aerosols in the stratosphere?
A. ice
B. $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
C. $\text{HNO}_3/\text{H}_2\text{O}$
D. $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$

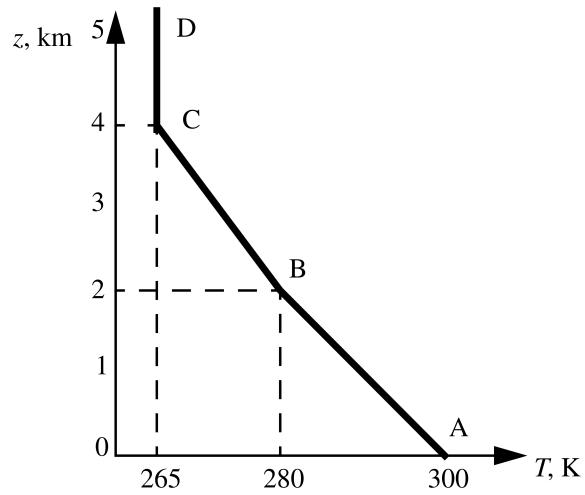
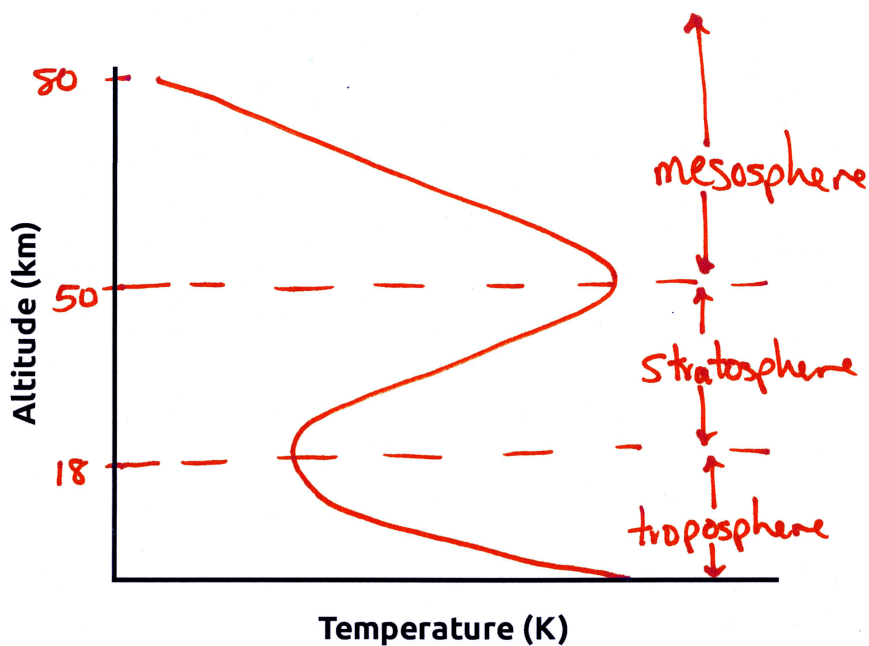


Figure 1

5. (1 point) For the region between C-D shown in Figure 1 (above), which statement is valid?

- A. **The region is stable with respect to vertical motion**
- B. The region is unstable with respect to vertical motion
- C. Stability in this region cannot be determined from the data presented

6. (3 points) On the figure below, graph the temperature vs. altitude for the Earth's atmosphere. Label the different regions of the atmosphere from 0 to 80 km. Indicate the range of altitudes that each region extends.



7. (2 points) The ozone depletion potential (ODP) of CFC-13 (CF_3Cl) is 0.8 while the ODP value of Halon-1301 (CF_3Br) is 10. Explain why Halon-1301 is much more efficient at depleting ozone than CFC-13.

Solution:

- Br compounds photolyze at lower altitudes than Cl compounds in the stratosphere
- Br is a more effective catalyst than Cl for depleting O_3
 - Fewer reservoirs for Br
 - Most of the bromine in the stratosphere exists in its active form (Br and BrO)

8. (4 points) Identify four reservoir species in the atmosphere and, with equations, show from what catalytic species they can be formed.

Solution: Any four of the following (reservoir species are shown in **bold**):

- $\text{OH} + \text{HO}_2 \rightarrow \mathbf{H_2O} + \text{O}_2$
- $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \mathbf{HNO_3} + \text{M}$
- $\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \mathbf{N_2O_5} + \text{M}$
- $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \mathbf{ClONO_2} + \text{M}$
- $\text{Cl} + \text{CH}_4 \rightarrow \mathbf{HCl} + \text{CH}_3$
- $\text{ClO} + \text{HO}_2 \rightarrow \mathbf{HOCl} + \text{O}_2$
- $\text{BrO} + \text{HO}_2 \rightarrow \mathbf{HOBr} + \text{O}_2$

9. (4 points) The absorption cross section for ozone in the middle of the UV-B region (at 305 nm) is $1.9 \times 10^{-19} \text{ cm}^2$. If the intensity of 305 nm radiation measured at the Earth's surface is 17% of the value measured above the ozone layer, what is the amount of ozone present in the atmosphere in Dobson units?

Solution:
$$\frac{I}{I_0} = \exp(-L\sigma_{\text{O}_3}z)$$

$$\begin{aligned} z &= \frac{-\ln \frac{I}{I_0}}{L\sigma_{\text{O}_3}} \\ &= \frac{-\ln 0.17}{(2.69 \times 10^{19} \text{ molec cm}^{-3}) \cdot (1.9 \times 10^{-19} \text{ cm}^2 \text{ molec}^{-1})} \\ &= 0.347 \text{ cm} \\ &= 3.47 \text{ mm} \end{aligned}$$

$$3.47 \text{ mm} \cdot \frac{100 \text{ DU}}{\text{mm}} = 347 \text{ DU}$$

10. (4 points) What is the role of polar stratospheric clouds in the formation of an “ozone hole” over the Antarctic region? Include a statement that describes the role of PSCs and include all necessary chemical equations.

Solution:

- PSCs provide a surface to convert temporary reservoirs of ClO_x into $\text{Cl}_2(\text{g})$
- $\text{ClONO}_2(\text{g}) + \text{HCl}(\text{a}) \rightarrow \text{Cl}_2(\text{g}) + \text{HNO}_3(\text{a})$
- $\text{ClONO}_2(\text{g}) + \text{H}_2\text{O}(\text{a}) \rightarrow \text{HOCl}(\text{g}) + \text{HNO}_3(\text{a})$
- $\text{HOCl}(\text{g}) + \text{HCl}(\text{a}) \rightarrow \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{a})$

(a) - adsorbed on PSC

(g) - gas phase

11. (3 points) The cruising altitudes of subsonic and supersonic aircraft are 12km and 20km respectively. What is the difference in pressure between these two altitudes?

Solution:

$$P(z) = P(0) \exp\left(-\frac{z}{H}\right)$$

$$P(0) = 1.013 \times 10^5 \text{ Pa}$$

$$P(12 \text{ km}) = 1.013 \times 10^5 \text{ Pa} \exp\left(-\frac{12 \text{ km}}{7.4 \text{ km}}\right)$$

$$P(12 \text{ km}) = 20014.6 \text{ Pa}$$

$$P(20 \text{ km}) = 1.013 \times 10^5 \text{ Pa} \exp\left(-\frac{20 \text{ km}}{7.4 \text{ km}}\right)$$

$$P(20 \text{ km}) = 6789.5 \text{ Pa}$$

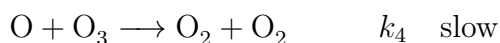
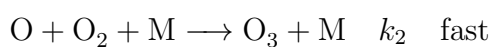
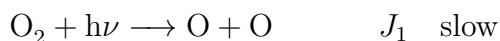
$$20014.6 \text{ Pa} - 6789.5 \text{ Pa} = 13225.1 \text{ Pa} = 13.22 \text{ kPa}$$

12. (4 points) Using the Chapman mechanism given below, show that the $\frac{[O]}{[O_3]}$ concentration ratio in the stratosphere is equal to the following:

$$\frac{[O]}{[O_3]} = \frac{J_3}{k_2 C_{O_2} n_{\text{air}}^2}$$

where n_{air} = number density of air. To get full marks you must show all steps and state all assumptions.

Chapman mechanism:



Solution: Steady state for [O]:

$$\frac{d[O]}{dt} = 0 = 2J_1[O_2] + J_3[O_3] - k_2[O][O_2][M] - k_4[O][O_3]$$

$$\underbrace{2J_1[O_2] + J_3[O_3]}_{\text{rate of formation}} = \underbrace{k_2[O][O_2][M] + k_4[O][O_3]}_{\text{rate of destruction}}$$

since $J_1[O_2] \ll J_3[O_3]$ and $k_2[O][O_2][M] \gg k_4[O]$

equation reduces to:

$$J_3[O_3] = k_2[O][O_2][M]$$

solve for $\frac{[O]}{[O_3]}$

$$\frac{[O]}{[O_3]} = \frac{J_3}{k_2[O_2][M]} = \frac{J_3}{k_2 C_{O_2} [M]^2}$$

or

$$\frac{[O]}{[O_3]} = \frac{J_3}{k_2 C_{O_2} n_{\text{air}}^2}$$

13. (4 points) If a HCFC-151 (C_2H_4FCl) molecule is released into the atmosphere from the Earth's surface will it eventually make it to the stratosphere and then contribute to the depletion of stratospheric ozone? Assume that it takes approximately 2 years for a molecule released at the Earth's surface to make it to the stratosphere and that reaction by OH is the only mechanism for removal in the troposphere. Justify your answer with calculations. Show all work.

Solution:

- Time it takes for a molecule released from the Earth's surface to make it to the stratosphere $\tau_{\text{transport}} = 2 \text{ years}$
- Compare with the lifetime of C_2H_4FCl in the troposphere.

$$\tau_{C_2H_4FCl} = \frac{[C_2H_4FCl]}{\text{rate of removal of } C_2H_4FCl}$$

If the only removal process in the troposphere is reaction with OH



$$\tau_{C_2H_4FCl} = \frac{[C_2H_4FCl]}{k_{OH}[C_2H_4FCl][OH]}$$

$$\tau_{C_2H_4FCl} = \frac{1}{k_{OH}[OH]}$$

$$\tau_{C_2H_4FCl} = \frac{1}{(1.69 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) (1 \times 10^6 \text{ molecules cm}^{-3})}$$

$$\tau_{C_2H_4FCl} = 5.9 \times 10^6 \text{ s}$$

$$\tau_{C_2H_4FCl} = 5.9 \times 10^6 \text{ s} \cdot \left(\frac{1 \text{ min}}{60 \text{ s}}\right) \left(\frac{1 \text{ hr}}{60 \text{ min}}\right) \left(\frac{1 \text{ day}}{24 \text{ hr}}\right)$$

$$\tau_{C_2H_4FCl} = 68 \text{ days} \ll 2 \text{ years}$$

$$\tau_{\text{C}_2\text{H}_4\text{FCl}} \ll \tau_{\text{transport}}$$

therefore, C₂H₄FCl will on average not make it to the stratosphere.

Information that you may require (however, you may not need all of this information):

Avogadro's number = 6.022×10^{23} molecules mol⁻¹

Gas constant = $R = 8.134$ J mol⁻¹ K⁻¹

Speed of light in vacuum = $c = 2.998 \times 10^8$ m s⁻¹

Planck constant = $h = 6.626 \times 10^{-34}$ J s

Scale height = $H = 7.4$ km

Mixing ratio of O₂ in the atmosphere = $C_{O_2} = 0.21$

Total pressure at sea level = 1.013×10^5 Pa

Loschmidt's number = $L = 2.69 \times 10^{19}$ molecules cm⁻³

Average concentration of OH in the atmosphere is 1×10^6 molecules cm⁻³

Adiabatic lapse rate in the stratosphere is 9.8 K km⁻¹

$C_2H_4FCl + OH \longrightarrow C_2H_3FCl + H_2O$; rate constant = $k = 1.69 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹

PERIODIC TABLE OF THE ELEMENTS

| | | | | | | | | | | | | | | | | | |
|---------------------------|---------------------------|--------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 1 H 1.0079 | | | | | | | | | | | | | | | | | 2 He 4.0026 |
| 3 Li 6.941 | 4 Be 9.012 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.007 | 8 O 16.00 | 9 F 19.00 | 10 Ne 20.179 |
| 11 Na 22.99 | 12 Mg 24.30 | | | | | | | | | | | 13 Al 26.98 | 14 Si 28.09 | 15 P 30.974 | 16 S 32.06 | 17 Cl 35.453 | 18 Ar 39.948 |
| 19 K 39.10 | 20 Ca 40.08 | 21 Sc 44.96 | 22 Ti 47.90 | 23 V 50.94 | 24 Cr 52.00 | 25 Mn 54.938 | 26 Fe 55.85 | 27 Co 58.93 | 28 Ni 58.69 | 29 Cu 63.55 | 30 Zn 65.39 | 31 Ga 69.72 | 32 Ge 72.59 | 33 As 74.92 | 34 Se 78.96 | 35 Br 79.90 | 36 Kr 83.80 |
| 37 Rb 85.47 | 38 Sr 87.62 | 39 Y 88.91 | 40 Zr 91.22 | 41 Nb 92.91 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.1 | 45 Rh 102.91 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.75 | 52 Te 127.60 | 53 I 126.91 | 54 Xe 131.29 |
| 55 Cs 132.91 | 56 Ba 137.33 | 57 * La 138.91 | 72 Hf 178.49 | 73 Ta 180.95 | 74 W 183.85 | 75 Re 186.21 | 76 Os 190.2 | 77 Ir 192.2 | 78 Pt 195.08 | 79 Au 196.97 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.2 | 83 Bi 208.98 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra 226.02 | 89 † Ac 227.03 | 104 Rf (261) | 105 Db (262) | 106 Sg (266) | 107 Bh (264) | 108 Hs (277) | 109 Mt (268) | 110 Ds (271) | 111 Rg (272) | | | | | | | |

*
Lanthanides

†
Actinides

| | | | | | | | | | | | | | |
|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 151.97 | 64 Gd 157.25 | 65 Tb 158.93 | 66 Dy 162.50 | 67 Ho 164.93 | 68 Er 167.26 | 69 Tm 168.93 | 70 Yb 173.04 | 71 Lu 174.97 |
| 90 Th 232.04 | 91 Pa 231.04 | 92 U 238.03 | 93 Np (237) | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (262) |