Solutions for Selected Exercises

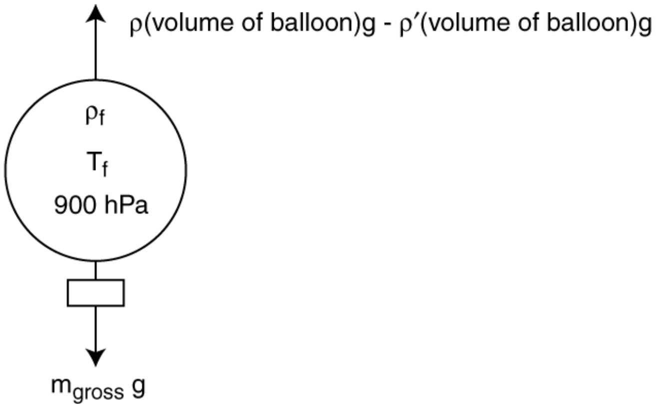
The solutions in this file are intended as a supplement to the solved exercises presented in the body of the text. Solutions to a much broader selection of the exercises at the ends of the chapters are available on the web page for instructors.

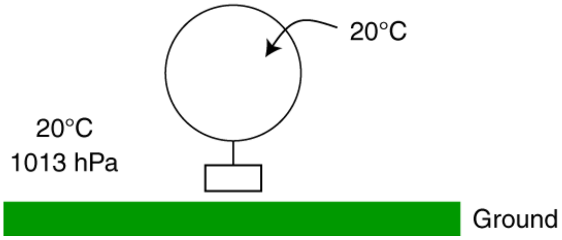
Chapter 3

3.34 If the balloon in Exercise 3.22 is filled with air at the ambient temperature of 20°C at ground level where the pressure is 1013 hPa, estimate how much fuel will need to be burned to lift the balloon to its cruising altitude of 900 hPa. Assume that the balloon is perfectly insulated, and that the fuel releases energy at a rate of 5×10^7 J kg^{-1}.

Answer 5.23 kg

Solution





For the air in balloon at ground level:

$$p_i = 1013 \text{ hPa}$$

$$T_i = 20^\circ\text{C} = 293 \text{ K}$$

For the air in balloon at 900 hPa

$$\begin{aligned} p_f &= 900 \text{ hPa} \\ T_f &= 87.43^\circ\text{C (from solution to Exercise 3.22)} \\ &= 360.43 \text{ K} \end{aligned}$$

Suppose the air in the balloon goes from its initial to its final state in two steps:

1) Heat is added at constant pressure at ground level until the temperature reaches T'_f.
2) Air in the balloon expands adiabatically as p drops from 1013 to 900 hPa, while T drops from T'_f to T_f.

For step (2):

$$pv^\gamma = \text{constant and } \frac{pv}{T} = \text{constant}$$

$$\therefore p^{1-\gamma} T^\gamma = \text{constant}$$

$$\therefore p_i^{1-\gamma} \left(T'_f\right)^\gamma = p_f^{1-\gamma} \left(T_f\right)^\gamma$$

$$\begin{aligned}
\therefore \quad T'_f = {} & \left(\frac{p_f}{p_i}\right)^{\dfrac{1-\gamma}{\gamma}} T_f \\
= {} & \left(\frac{p_f}{p_i}\right)^{\dfrac{1-1.4}{1.4}} T_f \\
= {} & \left(\frac{p_i}{p_f}\right)^{0.286} (360.43) \\
= {} & \left(\frac{1013}{900}\right)^{0.286} (360.43) \\
= {} & (1.034)\,(360.43) = 372.83 \text{ K}
\end{aligned}$$

$$\text{Heat required for heating of air} = (\text{mass of air})\,(c_p)\,(\Delta T) \ \text{ Joules}$$

$$\therefore \left(\begin{array}{c}\text{mass of fuel}\\ \text{needed in kg}\end{array}\right) \left(5 \times 7 \text{ J kg}^{-1}\right) = (\text{mass of air})\,(c_p)\,\Delta T$$

$$\begin{aligned}
\begin{array}{c}\text{Mass of air}\\ \text{in balloon}\\ \text{(in kg)}\end{array} \quad & = \left(\begin{array}{c}\text{volume of air}\\ \text{in balloon}\\ \text{at 900 hPa}\end{array}\right) \left(\begin{array}{c}\text{density of air}\\ \text{at 900 hPa}\\ \text{and 360.43 K}\end{array}\right) \\
& = \left(3000 \text{ m}^3\right) \left(\frac{p}{R_d T}\right) \\
& = \left(3000 \text{ m}^3\right) \left(\frac{900 \times 10^2}{287 \times 360.43}\right) \\
& = 2610.12 \text{ kg}
\end{aligned}$$

$$\begin{aligned}
\therefore \text{Mass of fuel needed (in kg)} \quad & = (2610.12 \text{ kg}) \left(1004 \text{ J K}^{-1} \text{ kg}^{-1}\right) \frac{(372.83 - 273 \text{ K})}{5 \times 10^7 \text{ J kg}^{-1}} \\
& = \frac{(2610.12)\,(1004)\,(99.83)}{5 \times 10^7} \\
& = 52322110.5 \times 10^{-7} \text{ kg} \\
& = \underline{\mathbf{5.23\ kg}}
\end{aligned}$$

3.40 Twenty liters of air at 20°C and a relative humidity of 60% are compressed isothermally to a volume of 4 liters. Calculate the mass of water condensed. The saturation vapor pressure of water at 20°C is 23 hPa. (Density of air at 0°C and 1000 hPa is 1.28 kg m^{-3}.)

Answer 0.14 g

Solution We must find mass vapor in the air before and after the compression.

<u>Mass of water vapor in air initially</u>

$$\begin{aligned}
&\text{Initially, the partial pressure of the vapor}\\
&= \frac{60}{100}\ (\text{SVP of water at } 20^\circ\text{C}\\
&= \frac{60}{100} \times (23.371 \text{ hPa})\\
&= 14.02 \text{ hPa}\\
&\text{Since } p = R\rho T\\
&\rho \propto p/T
\end{aligned}$$

Therefore, for <u>air</u>:

$$\begin{aligned}
\frac{\rho_{20^\circ\text{C}=293 \text{ K and } 14.02 \text{ hPa}}}{\rho_{0^\circ\text{C}=273 \text{ K and } 1000 \text{ hPa}}} &= \frac{14.02/293}{1000/273}\\
&= \frac{14.02}{1000}\,\frac{273}{293}
\end{aligned}$$

Therefore,

$$\rho_{20^\circ\text{C and } 14.02 \text{ hPa}} = \frac{14.02}{1000}\,\frac{273}{293}\,(1.2754)\ \text{ kg m}^{-3}$$

or,

$$\rho_{20^\circ\text{C and } 14.02 \text{ hPa}} = 0.01666 \text{ kg m}^{-3}$$

Provided the water vapor and air are at the same temperature and pressure (i.e., 14.02 hPa and 20°C in this case).

$$\begin{aligned}
\text{Density of water vapor} &= \frac{18.016}{28.97}\ (\text{density of air})\\
&= 0.62\ (\text{density of air})
\end{aligned}$$

Therefore, the mass (in kg) of water vapor that occupies 20 liters under these conditions is

$$\begin{aligned}
(0.62) \times\ &(\text{density of air at } 20^\circ\text{C and } 14.02 \text{ hPa}) \times\\
&\left(\text{volume of 20 liters in m}^3\right)\\
&= \frac{5}{8}\,(0.01666)\left(2{,}0000 \times 10^{-6}\right)\\
&= 2.0825 \times 10^{-4} \text{ kg} \qquad (1)
\end{aligned}$$

Mass of water vapor in air after compression

To saturate air at 20°C it would have to be compressed until the vapor pressure is raised from 60% to 100% of the saturation value. From Boyle's Law, this means that it becomes saturated when its volume is reduced to 60% of initial value. This compression is *exceeded* when volume is reduced from 20 to 4 liters. Therefore, after compression the air is saturated and its partial pressure is equal to the saturation vapor pressure of water at 20°C = 23.37 hPa.

Proceeding as before,

For air:

$$\frac{\rho_{293\text{ K and }23.371\text{ hPa}}}{\rho_{273\text{ K and }1000\text{ hPa}}} = \frac{23.371/293}{1000/273}$$

Therefore,

$$\rho_{293\text{ K and }23.371\text{ hPa}} = \frac{23.371}{1000}\,\frac{273}{293}\left(\rho_{273\text{ K and }1000\text{ hPa}}\right)$$

Hence, density of air at 293 K and 23.371 hPa is:

$$\therefore \rho_{293\text{ K and }23.371\text{ hPa}} = \frac{23.371}{1000} \times \frac{273}{293} \times (1.2754)\ \text{kg m}^{-3}$$

Therefore, mass of water vapor that occupies 4 liters when air is saturated is

$$\left(\frac{5}{8} \times \rho_{293\text{ K and }23.371\text{ hPa}}\right) \times \left(4{,}000 \times 10^{-6}\right)\ \text{kg}$$

$$\begin{aligned} &= \left(\frac{5}{8} \times \frac{23.371}{1000} \times \frac{273}{293} \times 1.2754\right) \times \left(4{,}000 \times 10^{-6}\right) \\ &= \underline{6.943\ \times\ 10^{-5}\ \text{kg}} \end{aligned}$$

$$\begin{aligned} \text{Therefore, mass of water condensed} &= (\text{mass of water vapor in air initially}) - \\ &\quad\ (\text{mass of water vapor in air after compression}) \\ &= \left(2.0825 \times 10^{-4}\right) - \left(6.943 \times 10^{-5}\right)\ \text{kg} \\ &= 0.139\text{ grams} = \underline{\mathbf{0.14\ grams}} \end{aligned}$$

An alternative solution:

$$\text{Relative humidity} = \frac{e}{e_s}100$$

Therefore, for initial state:

$$60 = \frac{e}{23.37}100$$

or,

$$e = 14.022 \text{ hPa} = \underline{1402.2 \text{ Pa}}$$

Let us now assume system is compressed isothermally and consider (fictionally) a fixed mass of water vapor (i.e., no condensation), then for vapor:

$(1402.2)20 = p_2 4$

Therefore, $\underline{p_2 = 7011.0 \text{ Pa} = 70.11 \text{ hPa}}$

This exceeds the SVP at 20°C, which is 23.37 hPa, by 46.74 hPa. Therefore, water must condense to bring vapor pressure to saturation at 20°C (= 23.37 hPa). Mass fraction of water that condenses is

$$\frac{70.11 - 23.37}{70.11} = 0.67$$

But, mass of water vapor in air before condensation is (from first solution given above)

$$= 2.0825 \times 10^{-4} \text{ kg}$$

$$\begin{aligned} \text{Therefore, mass of water condensed} &= 0.67 \times (2.0828 \times 10^{-4}) \text{ kg} \\ &= 1.39 \times 10^{-4} \text{ kg} \\ &= \underline{\mathbf{0.14\ grams}} \end{aligned}$$

3.54 *Potential density* D is defined as the density that dry air would attain if it were transformed reversibly and adiabatically from its existing conditions to a standard pressure p_0 (usually 1000 hPa).

a) If the density and pressure of a parcel of the air are ρ and p, respectively, show that

$$D = \rho \left(\frac{p_0}{p} \right)^{c_v/c_p}$$

where c_p and c_v are the specific heats of air at constant pressure and constant volume, respectively.

b) Calculate the potential density of a quantity of air at a pressure of 600 hPa and a temperature of −15°C.

Answer 1.17 kg m^{-3}

c) Show that

$$\frac{1}{D}\frac{dD}{dz} = -\frac{1}{T}(\Gamma_d - \Gamma)$$

where Γ_d is the dry adiabatic lapse rate, Γ the actual lapse rate of the atmosphere, and T the temperature at height z. [Hint: Take the natural logarithms of both sides of the expression given in (a) and then differentiate with respect to height z.]

d) Show that the criteria for stable, neutral, and unstable conditions in the atmosphere are that the potential density decreases with increasing height, is constant with height, and increases with increasing height, respectively. [Hint: Use the expression given in (c).]

e) Compare the criteria given in (d) with those for stable, neutral, and unstable conditions for a liquid.

Solution

(a) For a reversible, adiabatic transformation of an ideal gas

$$pV^\gamma = \text{constant}$$

where, $\gamma = c_p/c_v$. For a unit mass of a gas, $V = 1/\rho$, where ρ is the density of the gas. Therefore,

$$\left(\frac{p}{\rho^\gamma}\right) = \text{constant}$$

Hence, if the initial pressure and density of a gas are p and ρ, and the final pressure and density are p_o and D, and the gas undergoes an adiabatic transformation,

$$\frac{p}{\rho^\gamma} = \frac{p_o}{D^\gamma}$$

or,

$$D = \rho\left(\frac{p_o}{p}\right)^{1/\gamma} = \rho\left(\frac{p_o}{p}\right)^{c_v/c_p} \tag{3.122}$$

(b) From the ideal gas equation for a unit mass of air

$$p = R_d \rho T \tag{3.123}$$

From (3.122) and (3.123)

$$D = \frac{p}{R_d T}\left(\frac{p_o}{p}\right)^{c_v/c_p} \tag{3.124}$$

For $p = 600$ hPa $= 6 \times 10^4$ Pa, $T = (273 - 15)$ K$= 258$ K, $p_o =$ 1000 hPa$= 10^5$ Pa, $R_d = 287$ J deg^{-1} kg^{-1}, $c_v = 717$ J deg^{-1} kg^{-1} and $c_p = 10004$ J deg^{-1} kg^{-1}, we have from (3.124)

$$D = \frac{\left(6 \times 10^4\right)}{(287)\,(258)}\left(\frac{10^5}{6 \times 10^4}\right)^{\dfrac{717}{1004}}$$

$$D = 1.17 \text{ kg m}^{-3}$$

(c) Taking logarithms of (3.122), we have

$$\ln D = \ln \rho + \frac{c_v}{c_p} \ln \left(\frac{p_o}{p} \right)$$

Differentiating with respect to height z,

$$\frac{1}{D}\frac{dD}{dz} = \frac{1}{\rho}\frac{d\rho}{dz} - \frac{c_v}{c_p}\frac{1}{p}\frac{dp}{dz} \tag{3.125}$$

Also, for a unit mass of dry air considered as an ideal gas

$$p = R_d \rho T$$

Therefore,

$$\ln p = \ln R_d + \ln \rho + \ln T$$

and, differentiating this last expression with respect to height z,

$$\frac{1}{p}\frac{dp}{dz} = \frac{1}{\rho}\frac{d\rho}{dz} + \frac{1}{T}\frac{dT}{dz} \tag{3.126}$$

From (3.125) and (3.126)

$$\begin{aligned} \frac{1}{D}\frac{dD}{dz} &= -\frac{1}{T}\frac{dT}{dz} + \frac{1}{p}\frac{dp}{dz}\left(1 - \frac{c_v}{c_p}\right) \\ &= -\frac{1}{T}\frac{dT}{dz} + \frac{R_d}{pc_p}\frac{dp}{dz} \end{aligned} \tag{3.127}$$

where we have used the relation $c_p - c_v = R_d$ (see eqn. (3.45) in text). From the hydrostatic equation and the ideal gas equation,

$$\frac{dp}{dz} = -g\rho = -g\frac{p}{R_d T} \tag{3.128}$$

From (3.127) and (3.128),

$$\frac{1}{D}\frac{dD}{dz} = -\frac{1}{T}\left(\frac{g}{c_p} + \frac{dT}{dz}\right) \tag{3.129}$$

But, the dry adiabatic lapse rate Γ_d is given by (see eqn. (3.53) in the text)

$$\Gamma_d = \frac{g}{c_p} \tag{3.130}$$

From (3.129) and (3.130)

$$\frac{1}{D}\frac{dD}{dz} = -\frac{1}{T}\left(\Gamma_d - \Gamma\right) \tag{3.131}$$

where, $\Gamma = -\dfrac{\partial T}{\partial z}$ is the lapse rate in the atmosphere.

(d) From Section 3.6.1 in the text, we have

for a stable atmosphere: $\Gamma < \Gamma_d$
for an unstable atmosphere: $\Gamma > \Gamma_d$
for a neutral atmosphere: $\Gamma = \Gamma_d$

Hence, from (3.131),

for a stable atmosphere: $\dfrac{dD}{dz}$ is negative
(i.e., D decreases with increasing height)
for an unstable atmosphere: $\dfrac{dD}{dz}$ is positive
(i.e., D increases with increasing height)
for a neutral atmosphere: $\dfrac{dD}{dz} = 0$
(i.e., D is constant with height)

3.55 A necessary condition for the formation of a mirage is that the density of the air increase with increasing height. Show that this condition is realized if the decrease of atmospheric temperature with height exceeds 3.5 Γ_d, where Γ_d is the dry adiabatic lapse rate. [**Hint:** Take the natural logarithm of both sides of the expression for D given in Exercise 3.54a, then differentiate with respect to height z. Follow the same two steps for the gas equation in the form $p = \rho R_d T$. Combine the two expressions so derived with the hydrostatic equation to show that $\frac{1}{\rho}\frac{d\rho}{dt} = -\frac{1}{T}(dT/dz + g/R_d)$. Hence, proceed to the solution.]

Solution From the solution to Exercise 3.54(a)

$$D = \rho\left(\frac{p_0}{p}\right)^{c_v/c_p}$$

Therefore,

$$\ln D = \ln\rho + \frac{c_v}{c_p}\ln\left(\frac{p_0}{p}\right)$$

and, differentiating with respect to height z,

$$\frac{1}{D}\frac{dD}{dz} = \frac{1}{\rho}\frac{d\rho}{dz} - \frac{c_v}{c_p}\frac{1}{p}\frac{dp}{dz} \tag{3.132}$$

From the ideal gas equation for a unit mass of dry air,

$$p = R_d\rho T$$

therefore,

$$\ln p = \ln R_d + \ln\rho + \ln T$$

and, differentiating with respect to height z,

$$\frac{1}{p}\frac{dp}{dz} = \frac{1}{\rho}\frac{d\rho}{dz} + \frac{1}{T}\frac{dT}{dz} \tag{3.133}$$

From (3.132) and (3.133),

$$\frac{1}{D}\frac{dD}{dz} = -\frac{1}{T}\frac{dT}{dz} + \frac{R_d}{pc_p}\frac{dp}{dz} \tag{3.134}$$

From the hydrostatic equation and the ideal gas equation,

$$\frac{dp}{dz} = -g\rho = -\frac{gp}{R_d T} \tag{3.135}$$

From (3.133) and (3.135),

$$\frac{1}{\rho}\frac{d\rho}{dz} = -\frac{1}{T}\left(\frac{dT}{dz} + \frac{g}{R_d}\right) \tag{3.136}$$

For a mirage to occur, $\frac{d\rho}{dz}$ must be positive. Therefore, from (3.136), for a mirage to occur

$$\frac{dT}{dz} + \frac{g}{R_d} < 0$$

or,

$$-\frac{dT}{dz} > \frac{g}{R_d} = \frac{c_p}{R_d}\frac{g}{c_p} = \frac{c_p}{R_d}\Gamma_d \tag{3.137}$$

where, in the last step, we have used eqn. (3.53) in the text, that is, $\frac{g}{c_p} = \Gamma_d$. Substituting $c_p = 1004$ J deg^{-1} kg^{-1} and $R_d = 287$ J deg^{-1} kg^{-1} into (3.137), we find that a necessary condition for a mirage to occur is that

$$-\frac{dT}{dz} > 3.5\ \Gamma_d$$

That is, the temperature of the air must decrease with height at more than $3.5\ \Gamma_d = 3.5\left(9.8^\circ\text{C km}^{-1}\right) = 34^\circ\text{C km}^{-1}$. Such a steep lapse rate generally occurs only over strongly heated surfaces, such as deserts and roads.

3.60 A Carnot engine operating in reverse (i.e., as an air conditioner) is used to cool a house. The indoor temperature of the house is maintained at T_i and the outdoor temperature is T_o ($T_o > T_i$). Because the walls of the house are not perfectly insulating, heat is transferred into the house at a constant rate given by

$$\left(\frac{dq}{dt}\right)_{\text{leakage}} = K(T_o - T_i)$$

where K (> 0) is a constant.

a) Derive an expression for the power (i.e., energy used per second) required to drive the Carnot engine in reverse in terms of T_o, T_i and K.

b) During the afternoon, the outdoor temperature increases from 27 to 30°C. What percentage increase in power is required to drive the Carnot engine in reverse to maintain the interior temperature of the house at 21°C?

Answer (a) $K(T_o - T_i)^2/T_i$; (b) 125%

Solution

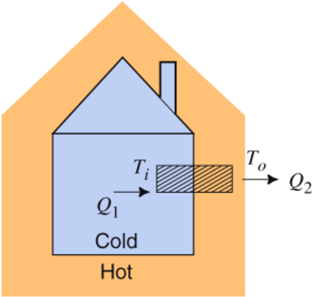


Figure 3.27

(a) See Figure 3.27. Let Q_1 and Q_2 be the heats that a Carnot engine running in reverse (i.e., serving as an air conditioner) takes in and rejects, respectively, in one cycle to keep a house at a temperature T_i that is below the outside temperature of T_o.

If T_i is to remain constant,

$$\left(\frac{dq}{dt}\right)_{\substack{\text{pumped out}\\ \text{of house by}\\ \text{air conditioner}}} = \left(\frac{dq}{dt}\right)_{\substack{\text{heat leakage}\\ \text{into house}}}$$

Hence,

$$\frac{Q_1}{\Delta t} = K\,(T_o - T_i) \tag{3.138}$$

where, Δt is the time period for one cycle of the air conditioner. The power (i.e., work per unit time) needed to drive the air conditioner is

$$\begin{aligned} P &= \frac{\text{Work done to drive air conditioner per cycle}}{\Delta t} \\ &= \frac{Q_2 - Q_1}{\Delta t} \end{aligned} \tag{3.139}$$

Since the air conditioner is ideal

$$\frac{Q_2}{Q_1} = \frac{T_o}{T_i}$$

or

$$\frac{Q_2 - Q_1}{Q_1} = \frac{T_o - T_i}{T_i}$$

Therefore,

$$Q_2 - Q_1 = Q_1 \left(\frac{T_o - T_i}{T_i} \right) \tag{3.140}$$

From (3.139) and (3.140)

$$P = \frac{Q_1}{\Delta t} \left(\frac{T_o - T_i}{T_i} \right) \tag{3.141}$$

From (3.138) and (3.141)

$$P = K \left(T_o - T_i \right)^2 \diagup T_i \tag{3.142}$$

(b) For outside temperatures of T_{o1} and T_{o2}, the powers P_2 and P_1, respectively, needed to drive the air conditioner to maintain the house at temperature T_i are, from (3.142) in (a) above,

$$\begin{aligned} \frac{P_2}{P_1} &= \frac{K \left(T_{o2} - T_i \right)^2 \diagup T_i}{K \left(T_{o1} - T_i \right)^2 \diagup T_i} \\ &= \frac{\left(T_{o2} - T_i \right)^2}{\left(T_{o1} - T_i \right)^2} \end{aligned}$$

For $T_i = 294$ K, $T_{01} = 300$ K and $T_{o2} = 303$ K,

$$\frac{P_2}{P_1} = \frac{9^2}{6^2} = 2.25$$

Therefore, the increase in power needed to keep the house at 21°C or 294 K is **125%**.

3.63 Show that the expression numbered (3.118) in the solution to Exercise 3.50 above can be written as

$$\Gamma_s = \Gamma_d \frac{(1 + w_s L_v / R_d T)}{(1 + w_s L_v^2 / c_p R_v T^2)}$$

Solution Comparing expression (3.118) in Exercise 3.50 with the expression given in the statement of this exercise, we see that we have to prove (a) $-\rho L_v \left(\frac{dw_s}{dp} \right)_T = \frac{w_s L_v}{R_d T}$, and (b) $\frac{L_v}{c_p} \left(\frac{dw_s}{dT} \right)_p = \frac{w_s L_v^2}{c_p R_v T^2}$

(a) To show:

$$-\rho L_v \left(\frac{dw_s}{dp}\right)_T = \frac{w_s L_v}{R_d T}$$

From eqn. (3.63)

$$w_s \simeq 0.622 \frac{e_s}{p} \tag{3.143}$$

Also,

$$p = R_d \ \rho \ T \tag{3.144}$$

From (3.143) and (3.144),

$$\left(\frac{dw_s}{dp}\right)_T = \left[\frac{dw_s}{d\left(R_d \ \rho \ T\right)}\right]_T$$

or, since T is constant,

$$\left(\frac{dw_s}{dp}\right)_T = \frac{1}{R_d T} \frac{dw_s}{dp} \tag{3.145}$$

But,

$$w_s = \frac{\rho_{sv}}{\rho}$$

Therefore,

$$\frac{dw_s}{d\rho} = \rho_{sv} \frac{d}{d\rho}\left(\rho^{-1}\right) = -\frac{\rho_{sv}}{\rho^2} \tag{3.146}$$

From (3.145) and (3.146),

$$\left(\frac{dw_s}{dp}\right)_T = -\frac{1}{R_d T} \frac{\rho_{sv}}{\rho^2} \tag{3.147}$$

From (3.146) and (3.147),

$$\left(\frac{dw_s}{dp}\right)_T = -\frac{w_s}{R_d T \rho} \tag{3.148}$$

Therefore,

$$\underline{-\boldsymbol{\rho} L_v \left(\frac{dw_s}{dp}\right)_T = L_v \frac{w_s}{R_d T}} \qquad QED$$

(b) To show:

$$\frac{L_v}{c_p} \left(\frac{dw_s}{dT}\right)_p = \frac{w_s L_v^2}{c_p R_v T^2}$$

From (3.143) in (a) above:

$$\begin{aligned} \left(\frac{dw_s}{dT}\right)_p &= \frac{d}{dT}\left[\left(0.622 \frac{e_s}{p}\right)\right]_p \\ &= \frac{0.622}{p} \frac{de_s}{dT} \end{aligned} \tag{3.149}$$

Using the Clausius-Clapeyron eqn. (3.93) and the ideal gas equation for saturated water vapor,

$$\frac{de_s}{dT} = \frac{L_v}{T\alpha_2} = \frac{L_v}{T\frac{R_vT}{e_s}} = \frac{L_v e_s}{T^2 R_v} \tag{3.150}$$

From (3.149) and (3.150)

$$\left(\frac{dw_s}{dT}\right)_p = \frac{0.622}{p}\ \frac{L_v e_s}{T^2 R_v}$$

and using (3.143)

$$= \frac{w_s L_v}{T^2 R_v}$$

Therefore,

$$\frac{L_v}{c_p}\left(\frac{dw_s}{dT}\right)_p = \frac{w_s L_v^2}{c_p R_v T^2}$$

Chapter 4

4.44 Show that for overhead parallel beam radiation incident on an isothermal atmosphere, in which the mixing ratio of the absorbing gas, r, and the volume absorption coefficient, k_λ, are both independent of height, the absorption per unit volume (i.e., dI_λ/dz) is strongest at the level of unit optical depth.

Solution: From Eq. (4.17) if r and k_λ are both independent of height,

$$\frac{dI_\lambda}{dz} = I_{\lambda\infty} T_\lambda k_\lambda \rho r \tag{1}$$

where $I_{\lambda\infty}$ is the intensity of the radiation incident on the top of the atmosphere, $T_\lambda = I_\lambda / I_{\lambda\infty}$ is the transmissivity of the overlying layer, and ρ is the density of the ambient air. From (4.28) for an overhead beam

$$T_\lambda = e^{-\tau_\lambda} \tag{2}$$

For an isothermal atmosphere, $p \propto \rho$, therefore from (3.26)

$$\rho = \rho_0 e^{-z/H} \tag{3}$$

where, H is the scale height. Substituting (2) and (3) into (1) we obtain,

$$\frac{dI_\lambda}{dz} = I_{\lambda\infty} k_\lambda r \rho_0 e^{-z/H} e^{-\tau_\lambda} \tag{4}$$

From (4.32)

$$\begin{aligned} \tau_\lambda &= (k_\lambda \rho_0 r) \int_z^\infty e^{-z/H} dz \\ &= H(k_\lambda r \rho_0) e^{-z/H} \end{aligned} \tag{5}$$

Using (5) to express $e^{-z/H}$ in (4) in terms of optical depth, we obtain

$$\frac{dI_\lambda}{dz} = \frac{I_{\lambda\infty}}{H} \tau_\lambda e^{-\tau_\lambda}$$

At the level where the absorption is strongest,

$$\frac{d}{dz}\left(\frac{dI_\lambda}{dz}\right) = \frac{I_{\lambda\infty}}{H} \frac{d}{dz}(\tau_\lambda e^{-\tau_\lambda}) = 0 \tag{6}$$

Performing the differentiation on the right-hand side of (6), we obtain

$$e^{-\tau_\lambda} \frac{d\tau_\lambda}{dz}(1 - \tau_\lambda) = 0$$

from which it follows that $\tau_\lambda = 1$. Although this result is strictly applicable only to an isothermal atmosphere in which k_λ and r are independent of height, it is qualitatively representative of conditions in planetary atmospheres in which the mixing ratios of the principal absorbing constituents do not change rapidly with height. It was originally developed by Sidney Chapman for understanding radiative and photochemical processes related to the stratospheric ozone layer (see Section 5.7).

4.48 Prove that the expression for the heating rate, as approximated by cooling to space, namely, eqn. (4.54) in text:

$$\left(\frac{dT}{dt}\right)_\nu = -\frac{2\pi}{c_p}\int_0^1 k_\nu r B_\nu(z) e^{-\tau_\nu/\mu} d\mu \tag{1}$$

can be integrated over solid angle to obtain eqn. (4.56) in the text, that is:

$$\left(\frac{dT}{dt}\right)_\nu = -\frac{\pi}{c_p} k_\nu r B_\nu(z) \frac{e^{-\tau_\nu/\overline{\mu}}}{\overline{\mu}} \tag{2}$$

where is as defined in Eq. (4.47) in the text.

Solution: Equation (1) can be rewritten in the form

$$\left(\frac{dT}{dt}\right)_\nu = -\frac{\pi}{c_p} k_\nu r B_\nu(z) \times 2\int_0^1 e^{-\tau_\nu/\mu} d\mu \tag{3}$$

The integral in (3) can be rewritten

$$\begin{aligned} 2\int_0^1 e^{-\tau_\nu/\mu} d\mu &= 2\int_0^1 \frac{de^{-\tau_\nu/\mu}}{d\tau_\nu}(-\mu)\, d\mu \\ &= -2\int_0^1 \frac{d\left(e^{-\tau_\nu/\mu}\mu\right)}{d\tau_\nu} d\mu \end{aligned}$$

Exchanging the order of the differentiation and the intergration yields

$$\begin{aligned} 2\int_0^1 e^{-\tau_\nu/\mu} d\mu &= \frac{d}{d\tau_\nu}\left[2\int_0^1 e^{-\tau_\nu/\mu} \mu d\mu\right] \\ &= e^{-\tau_\nu/\overline{\mu}}/\overline{\mu} \end{aligned}$$

Substituting for the integral in (3) yields (2).

4.51 Show that Schwarszchild's equation [(4.41) in the text, which is

$$dI_\lambda = -(I_\lambda - B_\lambda(T)) k_\lambda \rho r ds \tag{1}$$

can be integrated along a path extending from 0 to s_1 in Fig. 4.26 in the text to obtain

$$I_\lambda(s_1) = I_{\lambda 0} e^{-\tau_\lambda(s_1,0)} + \int_0^{s_1} k_\lambda \rho r B_\lambda\left[T\left(s\right)\right] e^{-\tau_\lambda(s_1,s)} ds$$

which appears as Eq. (4.42) in the text.

Solution: The differential form of the slant path optical depth is

$$d\tau_{\lambda,s} = -k_{\lambda,s}\rho r ds \tag{2}$$

where ds, which is directed along the path of the radiation, may be either upward or downward, as depicted in Fig. 4.26 The minus sign appears in this expression because ds and $d\tau_{\lambda,s}$ are in opposite directions. Incorporating this relationship into eqn. (4.36) in the text yields

$$dI_\lambda(s) = I_\lambda d\tau_{\lambda,s} - B_\lambda[T(s)]d\tau_{\lambda,s} \tag{3}$$

Multiplying (3) by the factor $e^{-\tau_{\lambda,s}}$, where $\tau_{\lambda,s}$ is the optical thickness along the path length from s to s_1, we have

$$e^{-\tau_{\lambda,s}}dI_\lambda(s) = I_\lambda e^{-\tau_{\lambda,s}}d\tau_{\lambda,s} - B_\lambda[T(s)]e^{-\tau_{\lambda,s}}d\tau_{\lambda,s}$$

Moving the first term on the right hand side to the left hand side and combining it with the other term yields

$$d\left[I_\lambda(s)e^{-\tau_{\lambda,s}}\right] = -B_\lambda[T(s)]e^{-\tau_{\lambda,s}}d\tau_{\lambda,s}$$

Integrating along the path from $s = 0$ to $s = s_1$ we have

$$\left[I_\lambda(s)e^{-\tau_{\lambda,s}}\right]_0^s = -\int_0^{s_1} B_\lambda[T(s)]e^{-\tau_{\lambda,s}}d\tau_{\lambda,s}$$

Moving the second term on the left hand side to the right hand side and combining with (2), we obtain

$$I_\lambda(s_1) = I_{\lambda 0}e^{-\tau_\lambda(s_1,0)} + \int_0^{s_1} k_\lambda \rho r B_\lambda\left[T\left(s\right)\right]e^{-\tau_\lambda(s_1,s)}ds$$

Chapter 5

5.12 (a) As discussed in Section 5.2.1(a), the earth's atmosphere is strongly affected by biota (i.e., plants). For example, VOCs and HCs are emitted by plants. Therefore, statement has some truth.

(b) (See Section 5.3.5.) O_3 production is enhanced by NO_x from industrial and car emissions (eqns. (5.15)–(5.16) and (5.22)).

(c) Residence time of CO_2 is 3–4 years, whereas for H_2S it is 1–5 days (Table 5.1).

(d) OH production requires $h\nu$ (see eqn. (5.6)), and OH has very short residence time ($\sim$1 s).

(e) OH, HO_2, H_2O_2, NO_x (Note: O_2 and O_3 have large bond energies and are therefore relatively unreactive except with radicals—O_2 is reactive only with highly unstable radicals.

(f) Since O_3 is involved in production of OH (eqn. (5.6)), and O_3 is increasing due to emissions of NO_2, source of OH could be increasing. However some of the maximum sinks of OH are oxidation by CO (to form CO_2) and HC, and concentrations of CO and HC are increasing due to industrial activities. Hence, concentration of OH may not be changing much. (Prinn et al. (1995) derived an OH trend of $0 \pm 0.2\%$ yr^{-1} based on model analysis of CH_3CCl_3 data for the period 1978–1994.)

(g) Because of scattering of sun's rays by particles in the air (compare with scattering from the beam of a slide projector).

(h) Because of less attenuation of light by pollutants.

(i) Due to flow around collectors, which biases against the collection of smaller particles.

(j) Due to salt particles and humidity.

(k) Due to thermal phoretic effect.

(l) Due to g-to-p conversion.

(m) If rate at which chemical is emitted is less than rate of removal, the amount of the chemical in the atmosphere would eventually decrease to essentially zero.

(n) Clouds and precipitation (sinks for water vapor) are much more common in tropics than in polar regions.

(o) Because at high temperatures N_2 is oxidized to NO (thermal NO)—see Section 5.5.1.

(p) Because most of UV radiation is absorbed in the stratosphere.

(q) At very high altitudes $h\nu$ is intense but the concentration of O_2 is too low to produce much atomic oxygen via eqn. (5.47). At low altitudes there is plenty of O_2, but $h\nu$ is reduced. At some intermediate height O_3 will peak.

(r) The sink reactions for atomic oxygen (5.48) and (5.50) remain, but the source reactions (5.47) and (5.49) are removed.

(s) More stratospheric O_3 would lower $h\nu$ in the troposphere. With less $h\nu$ there would be less OH and therefore higher concentrations of tropospheric pollutants.

(t) Because NaCl particles are relatively large and therefore confined to lower troposphere.

(u) Because of lack of sunlight and isolation of polar vortex.

(v) ClO (chlorine monoxide)—see eqns. (5.88).

(w) ClO is formed by photolysis of Cl_2 when sun rises (only weak sunlight is needed) via eqns. (5.83) and (5.86).

(x) In lower stratosphere of the polar vortex HCl condenses onto PSCs which sediment.

(y) In the lower stratosphere HCl condenses to form PSCs. CH_4 is transported into stratosphere, hence it is present in higher concentrations in lower stratosphere. (CH_4 is depleted in low stratosphere by OH, and in upper stratosphere by $O(^1D)$ and Cl. Oxidation of CH_4 is the main source of $H_2O(g)$ in the stratosphere.

(z) Because low temperatures might cause more PSCs.

5.13 The reverse of the photosynthesis reaction (5.2) in this chapter is

$$CH_2O(s) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

which is the respiration reaction. If x is the oxidation number of C in CH_2O we have

$$x + 2(+1) + (-2) = 0$$

Therefore,

$$x = 0$$

If y is the oxidation number of C in CO_2 we have

$$y + 2(-2) = 0$$

Therefore,

$$y = 4$$

Change in oxidation number of C for the above *reaction is +4*. Since the oxidation number of C is increased, **C is *oxidized.*** (NOTE: "burning" = "oxidation").

5.14 Molecular weight of NH_3 is 14 + 3(1.01) = 17.03. Therefore, the number of moles of NH_3 in 1 m^3 of air at 0°C and 1 atm is $\frac{0.456 \times 10^{-6}}{17.03}$, and number of molecules of NH_3 in 1 m^3 of air is $\frac{0.456 \times 10^{-6}}{17.03}$ (Avogadros' number)

$$= \left(\frac{0.456 \times 10^{-6}}{17.03}\right)\left(6.022 \times 10^{23}\right).$$

The total number of molecules in 1 m^3 of air at 1 atm and 0°C is Loschmidt's number which, from Ex. 5.1, is 2.687×10^{25} molecules m^{-3}. Therefore, the fraction of NH_3 molecules in air (and therefore the fraction of NH_3 by volume in air) is

$$\begin{aligned} & \frac{\frac{0.456 \times 10^{-6}}{17.03}\left(6.022 \times 10^{23}\right)}{2.687 \times 10^{25}} \\ = & \ 6.00 \times 10^{-10} \\ = & \ \underline{\mathbf{0.600\ ppbv}} \end{aligned}$$

5.15 Since it is an adiabatic expression, we have for the air in the chamber

$$\frac{p_1 \mathrm{v}_1}{T_1} = \frac{p_2 \mathrm{v}_2}{T_2}$$

and

$$p_1 \mathrm{v}_1^{\gamma} = p_2 \mathrm{v}_2^{\gamma}$$

Therefore

$$T_2 = \left(\frac{\mathrm{v}_1}{\mathrm{v}_2}\right)^{\gamma-1} T_1$$

with $\frac{\mathrm{v}_2}{\mathrm{v}_1} = 1.2$ and $T_1 = 288°\mathrm{K}$

$$\begin{aligned} T_2 &= (0.8333)^{1.4-1}\,288 \\ &= (0.8333)^{0.4}\,288 \\ &= 0.9297 \times 288 \\ &= 267.74\ \mathrm{K} = -5.26°\mathrm{C} \\ \text{Maximum saturation ratio} &= \frac{e(T_2)}{e_s(T_2)} \end{aligned}$$

For the water vapor itself

$$\frac{e_s(T_1)\mathrm{v}_1}{T_1} = \frac{e(T_2)\mathrm{v}_2}{T_2}$$

Therefore,

$$\begin{aligned} e(T_2) &= \frac{T_2}{T_1}\frac{\mathrm{v}_1}{\mathrm{v}_2} e_s(T_1) \\ &= \frac{267.74}{288}\frac{1}{1.2} 17\ \mathrm{hPa}\ \ [e_s(15°\mathrm{C}) = 17\ \mathrm{hPa\ from\ Fig.\ 3.9}] \\ &= 13.17\ \mathrm{hPa} \end{aligned}$$

Therefore,

$$\begin{aligned}
\text{Maximum saturation ratio} &= \frac{13.17}{e_s(-5.26°\text{C})} = \frac{13.17}{4} \; [e_s(\text{-}5.26°\text{C}) = 4 \text{ hPa from Fig. 3.9}] \\
&= 3.29 \\
\text{Maximum supersaturation (\%)} &= (\text{saturation ratio} - 1)100 \\
&= (3.29 - 1)100 \\
&= \underline{\mathbf{229\%}}
\end{aligned}$$

5.16 (a) If particles are spherical

$$dS = \pi D^2 \; dN$$

Therefore,

$$\frac{dS}{d(\log D)} = \pi D^2 \; \frac{dN}{d(\log D)}$$

Hence, using (5.31),

$$\frac{dS}{d(\log D)} = \pi C D^{2-\beta}$$

(b) For spherical particles,

$$dV = \frac{\pi}{6} D^3 \; dN$$

Therefore,

$$\frac{dV}{d(\log D)} = \frac{\pi}{6} D^3 \; \frac{dN}{d(\log D)}$$

Hence, using (5.31),

$$\frac{dV}{d(\log D)} = \frac{\pi}{6} C D^{3-\beta}$$

From the expression derived in (a) we see that $dS/d(\log D)$ is an increasing function of D for $\beta < 2$ and a decreasing function of D for $\beta > 2$. Hence, the surface area distribution will reach a peak value when β passes through a value of 2. Similarly, from the expression derived in (b) above, we see that the volume distribution will attain a peak value when β passes through a value of 3.

5.17

$$m\frac{d\text{v}}{dt} = 6\pi\eta \; r \; \text{v}$$

Therefore,

$$\frac{d\text{v}}{\text{v}} = -\frac{6\pi\eta \; r}{m} dt$$

and,

$$\begin{aligned}\int_{\mathrm{v}_o}^{\mathrm{v}} \frac{d\mathrm{v}}{\mathrm{v}} &= -\frac{6\pi\eta\, r}{m}\int_o^t dt \\ \ln\frac{\mathrm{v}}{\mathrm{v}_o} &= -\frac{6\pi\eta\, r}{m}t\end{aligned}$$

or,

$$\mathbf{v} = \mathbf{v_0}\,\mathbf{exp}\left(-\frac{\boldsymbol{6\pi\eta\, r}}{\boldsymbol{m}}\boldsymbol{t}\right)$$

Therefore,

$$\begin{aligned}\frac{dx}{dt} &= \mathrm{v}_0 \exp\left(-\frac{6\pi\eta\, r}{m}t\right) \\ \int_0^L dx &= \mathrm{v}_0\int_0^\infty \exp\left(-\frac{6\pi\eta\, r}{m}t\right) dt\end{aligned}$$

or,

$$\boldsymbol{L = v_0\frac{m}{6\pi\eta\, r}}$$

5.18 The residence time τ is given by

$$\tau = \frac{M}{F}$$

where M is the quantity of chemical in the atmosphere, and F the efflux. For NH_3.

$$M = \frac{1\times10^{-8}}{100}\left(5\times10^{18}\right)\ \mathrm{kg}$$

and $F = 5\times10^{10}$ kg per year, therefore, $\tau_{\mathrm{NH_3}} = 0.01\mathrm{a} =$ **4 days**. For N_2O,

$$M = \frac{\left(3\times10^{-5}\right)}{100}\left(5\times10^{18}\right)\ \mathrm{kg}$$

and $F = 1\times10^{10}$ kg per year, therefore, $\tau_{\mathrm{N_2O}} =$ **150 years**. For CH_4,

$$M = \frac{\left(7\times10^{-5}\right)}{100}\left(5\times10^{18}\right)\ \mathrm{kg}$$

and $F = 4\times10^{11}$ kg per year, therefore, $\tau_{\mathrm{CH_4}} =$ **9 years**.

5.19 We can imagine the deposition velocity as the rate at which a column of gas is deposited onto the ground. Hence, the time required to deplete a 5 km high column at 0.4 cm s^{-1} is

$$\begin{aligned}\frac{5\ \mathrm{km}}{0.40\times10^{-5}\ \mathrm{km\ s^{-1}}} &= 12.5\times10^5\ \mathrm{s} \\ &= 14.47\ \mathrm{days} \\ &\simeq \underline{\mathbf{14\ days}}\end{aligned}$$

This calculation gives an upper limit to the residence time of O_3 because other (*in situ*) removal mechanisms have not been considered. Compare this estimate to "days to weeks" for the residence time of O_3 given in Table 5.1.

5.20 (a)

$$\begin{aligned}
&\mathrm{NO} + \mathrm{O_3} \overset{k_1}{\to} \mathrm{NO_2} + \mathrm{O_2}\\
&\mathrm{NO} + \mathrm{HO_2} \overset{k_2}{\to} \mathrm{NO_2} + \mathrm{OH}\\
&\mathrm{NO_2} + hv \overset{j}{\to} \mathrm{NO} + \mathrm{O}\\
&\mathrm{O} + \mathrm{O_2} + \mathrm{M} \overset{k_3}{\to} \mathrm{O_3} + \mathrm{M}
\end{aligned}$$

(b)

$$\begin{aligned}
\frac{d[\mathrm{NO}]}{dt} &= -k_1[\mathrm{NO}][\mathrm{O_3}] - k_2[\mathrm{NO}][\mathrm{HO_2}] + j[\mathrm{NO_2}]\\
\frac{d[\mathrm{O_3}]}{dt} &= -k_1[\mathrm{NO}][\mathrm{O_3}] + k_3[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]\\
\frac{d[\mathrm{NO_2}]}{dt} &= -\frac{d[\mathrm{NO}]}{dt}\\
\frac{d[\mathrm{HO_2}]}{dt} &= -k_2[\mathrm{NO}][\mathrm{HO_2}]\\
\frac{d[\mathrm{HO}]}{dt} &= k_2[\mathrm{NO}][\mathrm{HO_2}]\\
\frac{d[\mathrm{O}]}{dt} &= j[\mathrm{NO_2}] - k_3[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]
\end{aligned}$$

(c) Under steady-state conditions

$$\frac{d[\mathrm{NO}]}{dt} = 0$$

and, if $[\mathrm{HO_2}] = 0$, the first equation in (b) above becomes

$$\boldsymbol{[\mathrm{O_3}] = \frac{j[\mathrm{NO_2}]}{k_1[\mathrm{NO}]}}$$

5.21 Some of the increase in atmospheric CO_2 over, say, the past 50 years may be due to an increase in the average temperature of the oceans, which would cause a decrease in the solubility of CO_2 in the oceans and therefore release CO_2 into the atmosphere. Estimate the percentage change in the CO_2 content of the atmosphere due to an average warming of 0.5°C in the upper (mixed) layer of the world's oceans over the past 50 years. (Assume that the average temperatures of the mixed layer of all the oceans has increased from 15.0°C to 15.5°C. You may treat the ocean water as pure water.)

Based on your calculation, does it appear likely that the measured increase in atmospheric CO_2 over the past 50 years ($\sim$20%) is due to warming of the oceans?

You will need to use the following information. The solubility, C_g, of a gas in a liquid is given by Henry's law:

$$C_g = k_H p_g$$

where k_H is the Henry's law constant, and p_g the partial pressure of the gas over the solution. For CO_2 in pure water, $k_H = 4.5 \times 10^{-2}$ M atm^{-1} at 15°C. The temperature dependence of k_H is given by

$$\ln \frac{k_H(T_2)}{k_H(T_1)} = \frac{\Delta H}{R^*}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where for CO_2 in water $\Delta H = -20.4 \times 10^3$ J mol^{-1}, and R^* is the universal gas constant (8.31 J K^{-1} mol^{-1}). The total mass of carbon in the form of CO_2 in the mixed layer of the world's oceans is $\sim 6.7 \times 10^5$ Tg, which is about the same as the mass of CO_2 in the atmosphere.

Answer +7.5% of the observed increase in CO_2. No.

Solution

$$C_g = k_H\ p$$

Therefore,

$$\Delta C_g = p\ \Delta\ k_H$$

We can determine $\Delta\ k_H$ from

$$\begin{aligned}\ln \frac{k_H\,(288.5°\mathrm{K})}{k_H\,(288°\mathrm{K})} &= \frac{-20.4 \times 10^3}{8.3}\left(\frac{1}{288} - \frac{1}{288.5}\right)\\ &= -2.459\,(3.472 - 3.466)\end{aligned}$$

Therefore,

$$\begin{aligned}\ln \frac{k_H\,(288.5\ \mathrm{K})}{k_H(288\ \mathrm{K})} &= \left(-14.7 \times 10^{-3}\right)\\ &= -0.0147\end{aligned}$$

Therefore,

$$\frac{k_H\,(288.5°\mathrm{K})}{k_H(288°\mathrm{K})} = 0.985$$

or,

$$\begin{aligned}k_H\,(288.5°\mathrm{K}) &= 0.985\,[k_H(288°)]\\ &= 0.985\left(4.5 \times 10^{-2}\right)\\ &= 4.433 \times 10^{-2}\ \mathrm{mol\ L^{-1}\ atm^{-1}}\end{aligned}$$

Therefore,

$$\Delta\, k_H = (4.433 - 4.5)\, 10^{-2} = -6.7 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$$

Hence,

$\Delta\, C_g = -6.7{\times}10^{-4}$ mol L^{-1} (at 1 atm for T changing from 288 K to 288.5 K)

Therefore,

$$\text{Percentage change in } C_g = \frac{-6.7 \times 10^{-4}}{4.5 \times 10^{-2}} \times 100 = -1.5\%$$

Therefore, percentage decrease in CO_2 in mixed layer of oceans is 1.5%. Since the CO_2 capacity of the atmosphere is about the same as the mixed layer of the oceans, the percentage increase in CO_2 in atmosphere due to 0.5°C warming of oceans will be ~1.5%.

The above calculation shows that percentage increase in CO_2 in atmosphere due to 0.5°C increase in the average temperature of the mixed layers of the world's oceans over the past 50 years is ~1.5%. However, measured percentage increase in atmospheric CO_2 over past 50 years is ~20%. Therefore, warming of oceans can account for only ~7.5% of observed increase in CO_2 content of atmosphere.

Answer: No.

5.22 This exercise is a follow-on to Exercise 5.8.

(a) In reality, combustion in cars converts most of the hydrogen in the fuel to H_2O and most of the carbon in the fuel to varying amounts of CO_2 and CO depending on the availability of oxygen.

If a fraction f of the C_xH_y fuel is provided in excess of that required for ideal combustion, derive an expression in terms of f, x, and y for the mole fraction of CO in the emissions (i.e., the ratio of the number of moles of CO to the total number of moles in the emissions). Assume that oxygen is made available to the fuel at the rate required for ideal combustion (even though ideal combustion is not achieved), and that the only effect of the excess C_xH_y is to add CO to the emissions and to change the amount of CO_2 emitted.

(b) Assuming that CH_2 is a reasonable approximation for a general hydrocarbon fuel, use the result from (a) to determine the concentrations (in ppmv and percent) of CO in the emissions from an engine for the following values of f: 0.0010, 0.010, and 0.10.

Answer (a) $$\frac{f\left(2x + \frac{y}{2}\right)}{x\,(4.7 + f) + \frac{y}{2}\,(2.85 + f)}$$

(b) 397 ppmv (= 0.0397%); 3960 ppmv (0.396%); 38700 ppmv (3.87%). (The last concentration of CO would kill you in a closed garage in ~17 mins.)

Solution

(a) If we include the (unreacting) nitrogen in the balanced chemical equation for *complete* combustion, we have from an extension of eqn. (5.34) in Chapter 5

$$\mathrm{C}_x\mathrm{H}_y+\left(x+\frac{y}{4}\right)\mathrm{O}_2+3.7\left(x+\frac{y}{4}\right)\mathrm{N}_2 \rightarrow x\mathrm{CO}_2+\frac{y}{2}\mathrm{H}_2\mathrm{O}+3.7\left(x+\frac{y}{4}\right)\mathrm{N}_2$$

However, if a fraction f of fuel is provided in excess of that needed for complete combustion and, as a consequence, m moles of CO_2 and n moles of CO are contained in the emissions, the chemical equation for combustion becomes

$$\begin{aligned}(1+f)\,\mathrm{C}_x\mathrm{H}_y+\left(x+\frac{y}{4}\right)\mathrm{O}_2+3.7\left(x+\frac{y}{4}\right)\mathrm{N}_2 \quad &\rightarrow \\ m\mathrm{CO}_2+n\mathrm{CO}+(1+f)\,\frac{y}{2}\mathrm{H}_2\mathrm{O}+3.7\left(x+\frac{y}{4}\right)\mathrm{N}_2&\end{aligned}$$

Balancing the carbon atoms for this reaction yields

$$x\,(1+f)=m+n \tag{1}$$

and, balancing the oxygen atoms, gives

$$2x+\frac{y}{2}=(1+f)\,\frac{y}{2}+2m+n \tag{2}$$

Solving (1) and (2) for m and n yields

$$m=x-xf-f\frac{y}{2}$$

and,

$$n=f\frac{y}{2}+2fx$$

Therefore, the mole fraction of CO in the emissions is

$$\frac{f\frac{y}{2}+2fx}{\underbrace{\left(x-xf-f\frac{y}{2}\right)}_{CO_2}+\underbrace{\left[3.7\left(x+\frac{y}{4}\right)\right]}_{N_2}+\underbrace{\left(f\frac{y}{2}+2fx\right)}_{CO}+\underbrace{(1+f)\,\frac{y}{2}}_{H_2O}}$$

$$=\frac{\boldsymbol{f\left(2x+\frac{y}{2}\right)}}{\boldsymbol{x\,(4.7+f)+\frac{y}{2}\,(2.85+f)}}$$

(b) If the fuel is CH_2, $x = 1$ and $y = 2$. Therefore, from the answer to (a) above, the mole fraction of CO in the emissions is

$$\frac{3f}{7.55 + 2f}$$

Therefore, for $\boldsymbol{f = 0.001}$ the mole fraction of unburned CO is $\boldsymbol{3.97 \times 10^{-4}}$ or 397 ppmv (= 0.0397%). For $\boldsymbol{f = 0.01}$ it is $\boldsymbol{3.96 \times 10^{-3}}$ or 3960 ppmv (= 0.396%). For $\boldsymbol{f = 0.1}$ it is $\boldsymbol{3.87 \times 10^{-2}}$or 38700 ppmv (= 3.87%). This last concentration of CO is enough to kill you in a closed garage in about 17 minutes!

5.23 (a) Write down the rate law for the production of NO_2 by reaction (5.36). Does this rate law explain why the production of NO_2 by (5.36) increases sharply with increasing concentration of NO? (b) Another route for the production of NO_2 from NO is reaction (5.17). If the rate coefficients for the production of NO_2 by (5.36) and (5.17) are $\sim 2\times10^{-38}$ cm^6 $molecule^{-1}$ s^{-1} and $\sim 2\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, and the concentrations of NO, O_3 and O_2 are 80 ppbv, 50 ppbv, and 209460 ppmv, respectively, compare the rates of production of NO_2 by these two reactions.

Answer (a) $\frac{1}{2}\frac{d[NO_2]}{dt} = k_1 [NO]^2 [O_2]$. Yes, because production of NO_2 varies at $[NO]^2$.

(b) Reaction (5.17) produces NO_2 at a rate 5.8×10^4 faster than reaction (5.36).

Solution

(a) From (5.36)

$$\boldsymbol{\frac{1}{2}\frac{d\,[NO_2]}{dt} = k_1\,[NO]^2\,[O_2]}$$

Production of NO_2 increases sharply with increasing concentration of NO because it varies as the square of [NO].

(b) For reaction (5.36) we are given that $k = 2 \times 10^{-38}$ cm^6 $molecule^{-1}$ s^{-1} and $[NO] = 80$ ppbv and $[O_2] = 309460$ ppmv. However, the gas concentrations need to be converted to molecules cm^{-3} by multiplying them by Loschmidt's number which, from Exercise 5.1 is 2.687×10^{25} molecules m^{-3} = 2.687×10^{19} molecules cm^{-3}. Therefore, from (a) above

$$\begin{aligned}\frac{1}{2}\frac{d\,[NO_2]}{dt} &= \left(2 \times 10^{-38}\right) \times \\ &\quad \left(80 \times 10^{-9} \times 2.687 \times 10^{19}\right)^2 \times \\ &\quad \left(209460 \times 10^{-6} \times 2.687 \times 10^{19}\right) \text{ molecules cm}^{-3}\text{ s}^{-1} \\ \frac{d\,[NO_2]}{dt} &\simeq \underline{10^6 \text{ molecules cm}^{-3}\text{ s}^{-1}}\end{aligned}$$

For reaction (5.17)

$$O_3 + NO \overset{k_2}{\rightarrow} NO_2 + O_2$$

$$\begin{aligned} \frac{d\,[NO_2]}{dt} &= k_2\,[O_3]\,[NO] \\ &= \left(2 \times 10^{-14}\right)\left(50 \times 10^{-9} \times 2.687 \times 10^{19}\right) \\ &\quad \left(80 \times 10^{-9} \times 2.687 \times 10^{19}\right) \\ &= \underline{5.8 \times 10^{10} \text{ molecules cm}^{-3} \text{ s}^{-1}} \end{aligned}$$

Therefore, reaction (5.17) produces NO_2 at a rate $\frac{5.8 \times 10^{10}}{10^6}$ = $\underline{5.8 \times 10^4 \text{ times as fast}}$ as reaction (5.36).

5.24

$$\tau_{CH_4} = \frac{\text{Abundance of } CH_4}{\text{Removal rate of } CH_4}$$

Since

$$CH_4 + OH \xrightarrow{k} CH_3 + H_2O$$

$$\tau_{CH_4} = \frac{[CH_4]}{k\,[CH_4]\,[OH]} = \frac{1}{k\,[OH]}$$

$$\begin{aligned} \therefore \tau_{CH_4} &= \frac{1}{\left(3.5 \times 10^{-15} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}\right) \times \left(1 \times 10^6 \text{ molecule cm}^{-3}\right)} \\ &= 0.29 \times 10^9 \text{ s} \\ &= \underline{\textbf{9 years}} \end{aligned}$$

5.25 (a) As in Exercise (5.24) above,

$$\begin{aligned} \tau_{C_3H_8} &= \frac{1}{k\,[OH]} \\ &= \frac{1}{(6.1 \times 10^{-13})\,(1 \times 10^6)} \\ &= 0.16 \times 10^7 \text{ s} \\ &= \underline{\textbf{19 days}} \end{aligned}$$

(b) **NMHC**, because their residence time is so much shorter so that they react much quicker before dispersion than does CH_4.

(c) **Because of its relatively long residence time in troposphere.**

5.26 (a) Adding the two reaction steps we get

$$O_3 \overset{k_1}{\rightleftarrows} O_2 + O \qquad (1)$$

$$\underline{O_3 + O \overset{k_2}{\rightleftarrows} 2O_2} \qquad (2)$$

$$\text{Net: } \mathbf{2O_3 \rightarrow 3O_2}$$

which is the overall reaction.

(b) The intermediate is **O(g)**.

(c) **Rate law for step (i) is: Rate = $\boldsymbol{k_1[O_3]}$.**
Rate law for step (ii) is: Rate = $\boldsymbol{k_2[O_3]\ [O]}$.

(d) If overall rate law is: Rate = $k[O_3]^2\ [O_2]^{-1}$, step (1) cannot be rate controlling because it depends only on $[O_3]$. Therefore, **step (2) must be rate controlling**.

(e) If step (2) is rate controlling:

$$[O_3]\,[O] \propto [O_3]^2\,[O_2]^{-1}$$

Therefore,

$$\mathbf{[O] \propto [O_3]\,[O_2]^{-1}}$$

5.27

$$k = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{T}\right)$$

At $T = -20°\text{C} = 253$ K

$$k_{253} = 8.0 \times 10^{-12} \exp\left(-\frac{2060}{253}\right)$$

$$\begin{aligned} At\ T = -30°C &= 243° K \\ k_{243} &= 8.0 \times 10^{-12} \exp\left(-\frac{2060}{243}\right) \end{aligned}$$

Therefore,

$$\begin{aligned} \frac{k_{253}}{k_{243}} &= \frac{\exp\left(-\frac{2060}{253}\right)}{\exp\left(-\frac{2060}{243}\right)} \\ &= \exp\left[-2060\left(\frac{1}{253} - \frac{1}{243}\right)\right] \\ &= \exp\left[-2060\,(0.00395 - 0.00412)\right] \\ &= \exp\left(2060 \times 0.00017\right) \\ &= \exp\left(0.3502\right) \\ &= 1.419 \end{aligned}$$

So, the rate of depletion of O_3 will increase by 42% if temperature falls from −20 to −30°C

$$\therefore k_{243} = k_{253}/1.420$$
$$= 0.704\ k_{253}$$

Therefore, rate of depletion of O_3 will decrease by ∼30% if temperature falls from 253 K to 243 K.

5.28 In the middle and upper stratosphere, O_3 concentrations are maintained at roughly steady values by a number of chemical reactions. Assume that at around a temperature of 220 K

$$\frac{dX}{dt} = k_1 - k_2\mathrm{X}^2$$

where

$$X = \frac{\text{concentration of } O_3 \text{ molecules}}{\text{concentration of all molecules}}$$

$$k_1 = (\text{constant}) \exp\left(\frac{300}{T}\right) \mathrm{s}^{-1}$$

$$k_2 = 10.0 \exp\left(\frac{-1,100}{T}\right) \mathrm{s}^{-1}$$

(a) Doubling the concentration of CO_2 in the atmosphere is predicted to cool the middle stratosphere by about 2°C. What fractional change in X would you expect from this temperature perturbation?

(b) If X were temporarily raised by 1.0% above its steady-state value of 5.0×10^{-7}, how long would it take for this perturbation to fall to exp(–1) of 1.0% at 220 K? (exp 1 = 2.7)

Answers (a) 2.9%, (b) 172 days

Solution

(a)

$$\frac{dX}{dt} = k_1 - k_2\ X^2 \qquad (1)$$

At steady-state, $X = X_{ss}$ and

$$\frac{dX}{dt} = \mathrm{O}$$

Therefore,

$$X_{ss} = \left(\frac{k_1}{k_2}\right)^{\frac{1}{2}} = (\text{constant}) \exp\left[\frac{1}{2}\left(\frac{300}{T} + \frac{1100}{T}\right)\right]$$

and,

$$\ln\ X_{ss} = \text{constant} + \frac{1}{2}\left(\frac{300}{T} + \frac{1100}{T}\right)$$

Hence,

$$\begin{aligned}\frac{1}{X_{ss}}\frac{dX_{ss}}{dT} &= \frac{d}{dT}\left(\frac{700}{T}\right)\\ \frac{dX_{ss}}{X_{ss}} &= \frac{-700}{T^2}dT\end{aligned}$$

For $dT = -2°\text{C}$,

$$\frac{dX_{ss}}{X_{ss}} = \frac{1400}{(220)^2} = 0.029 \text{ or } \mathbf{2.9\%}$$

(b) Substitute $Y = X - X_{ss}$ into (1) yields

$$\begin{aligned}\frac{dY}{dt} &= k_1 - k_2\left(Y + X_{ss}\right)^2\\ &= X_{ss}^2\ k_2 - k_2\left(Y + X_{ss}\right)^2\\ &= -\left(2k_2\ X_{ss}\ Y\right) + \text{ term in } Y_2 \text{ (which is small)}\end{aligned}$$

Therefore,

$$\frac{dY}{Y} = -\left(2k_2\ X_{ss}\right)dt$$

and,

$$\begin{aligned}\left[\ln Y\right]_{Y_O}^{Y} &= -2k_2\ X_{ss}\int_o^t dt\\ \ln\left(\frac{Y}{Y_o}\right) &= -2k_2\ X_{ss}\ t\end{aligned}$$

or,

$$Y = Y_o \exp\left(-2k_2\ X_{ss}\ t\right)$$

The relaxation time (τ) is the time for y to decline to exp(−1) of an initial value Y_o. Therefore, from the last expression

$$\begin{aligned}\tau &= \frac{1}{2k_2\ X_{ss}} = \frac{1}{2\left\{10\exp\left(\frac{-1100}{220}\right)\left(5\times10^{-7}\right)\right\}} = 1.48\times10^{7}\text{ s}\\ &= \underline{\mathbf{172\ days}}\end{aligned}$$

5.29 (a) **If (iia) dominates net effect is**

$$\mathbf{2O_3\ +\ }hv \rightarrow \mathbf{3O_2}$$

If (iib) dominate there is no net effect (ClO never gets to Cl).

(b) $$\boldsymbol{\frac{d\,[\mathrm{O_3}]}{dt} = -k_4\,[\mathrm{Cl}]\,[\mathrm{O_3}]}$$

$$\boldsymbol{\frac{d\,[\mathrm{Cl}]}{dt} = j_2\,[(\mathrm{ClO})_2] + k_3\,[\mathrm{ClOO}]\,[\mathrm{M}] - k_4\,[\mathrm{Cl}]\,[\mathrm{O_3}]}$$

$$\boldsymbol{\frac{d\,[(\mathrm{ClO})_2]}{dt} = k_1\,[\mathrm{ClO}]^2\,[\mathrm{M}] - j_2\,[(\mathrm{ClO})_2]}$$

$$\boldsymbol{\frac{d\,[\mathrm{ClOO}]}{dt} = j_2\,[(\mathrm{ClO})_2] - k_3\,[\mathrm{ClOO}]\,[\mathrm{M}]}$$

(c) If $\frac{d\,[\mathrm{Cl}]}{dt} = \frac{d\,[(\mathrm{ClO})_2]}{dt} = \frac{d\,[\mathrm{ClOO}]}{dt}$

in (b) above, then

$$\boldsymbol{[\mathrm{Cl}] = \frac{2k_1\,[\mathrm{M}]\,[\mathrm{ClO}]^2}{k_4\,[\mathrm{O_3}]}}$$

(d) From (b)
$\frac{d\,[\mathrm{O_3}]}{dt} = -k_4\,[\mathrm{Cl}]\,[\mathrm{O_3}]$

$$\boldsymbol{\frac{d\,[\mathrm{O_3}]}{dt} = -2k_1\,[\mathrm{M}]\,[\mathrm{ClO}]^2}$$

(e) If $[\mathrm{ClO}] \propto t$

From (d)

$\frac{d\,[\mathrm{O_3}]}{dt} \propto t^2$

Therefore,

$\boldsymbol{[\mathrm{O_3}] \propto t^3}$

5.30 In the atmosphere at altitudes near and above 30 km the following reactions significantly affect the chemistry of ozone

$$\begin{aligned}
O_3 + hv &\xrightarrow{j_1} O_2 + O^* && \left(j_1 = 1 \times 10^{-4}\ \mathrm{s}^{-1}\right)\\
O^* + M &\xrightarrow{k_1} O + M && \left(k_1 = 1 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}\right)\\
O^* + H_2O &\xrightarrow{k_2} OH + OH && \left(k_2 = 2 \times 10^{-6}\ \mathrm{cm}^3\ \mathrm{s}^{-1}\right)\\
O + O_2 + M &\xrightarrow{k_3} O_3 + M && \left(k_3 = 6 \times 10^{-34}\ \mathrm{cm}^6\ \mathrm{s}^{-1}\right)\\
OH + O_3 &\xrightarrow{k_4} HO_2 + O_2 && \left(k_4 = 2 \times 10^{-14}\ \mathrm{cm}^3\ \mathrm{s}^{-1}\right)\\
HO_2 + O_3 &\xrightarrow{k_5} OH + O_2 + O_2 && \left(k_5 = 3 \times 10^{-16}\ \mathrm{cm}^3\ \mathrm{s}^{-1}\right)\\
OH + HO_2 &\xrightarrow{k_6} H_2O + O_2 && \left(k_6 = 3 \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{s}^{-1}\right)
\end{aligned}$$

where O^* is an electronically excited metastable state of atomic oxygen. The free radical species OH and HO_2 are collectively labeled "odd hydrogen." At 30 km the molecular density of the atmosphere is about 5×10^{17} cm^{-3}, and the molecular fractions of water vapor and O_3 are each about 2×10^{-6} and that of oxygen is 0.2.

(a) What are the approximate steady-state molecular fractions of O^*, HO_2, and OH?

(b) What is the approximate mean residence time of odd hydrogen under steady-state conditions?

(c) For every O_3 molecule that is destroyed under steady-state conditions, how many odd-hydrogen species are produced by the reaction associated with k_2?

(Hint: The steps associated with k_4 and k_5 occur many times for each formation or loss of odd hydrogen.)

Answer (a) 4×10^{-17}, 2×10^{-8} and 3×10^{-10}
(b) 11 sec
(c) $\sim$15

Solution

(a)

$$\frac{d\,[O^*]}{dt} = j_1\,[O_3] - k_1\,[O^*]\,[M] - k_2\,[O^*]\,[H_2O] = 0 \text{ (at steady state)}$$

Therefore,

$$\begin{aligned}
[O^*] &= \frac{j_1\,[O_3]}{k_1\,[M] + k_2\,[H_2O]}\\
&\simeq \frac{j_1\,[O_3]}{k_1\,[M]}
\end{aligned}$$

Hence, the molecular fraction of O*, say $f(\mathrm{O}^*)$, is

$$f(\mathrm{O}^*) \simeq \frac{j_1\ f\,[\mathrm{O}_3]}{k_1\,[\mathrm{M}]} = \frac{10^{-4}\left(2\times10^{-6}\right)}{10^{-11}\left(5\times10^{17}\right)} = \underline{\mathbf{4\times10^{-17}}}$$

Also,

$$[\mathrm{HO}] + [\mathrm{HO}_2] = [\text{odd hydrogen}]$$

Therefore,

$$\frac{d\,[\text{odd hydrogen}]}{dt} = 2k_2\,[\mathrm{O}^*]\,[\mathrm{H_2O}] - 2k_6\,[\mathrm{HO}]\,[\mathrm{HO}_2] \qquad \text{(i)}$$

If the k_4 and k_5 steps occur often compared with the steps associated with k_2 and k_6, they determine the concentrations of HO and HO_2. Therefore, at steady state

$$k_4\,[\mathrm{HO}]\,[\mathrm{O}_3] \simeq k_5\,[\mathrm{HO}_2]\,[\mathrm{O}_3] \qquad \text{(ii)}$$

or,

$$\frac{[\mathrm{HO}_2]}{[\mathrm{HO}]} \simeq \frac{k_4}{k_5} \simeq \frac{2\times10^{-14}}{3\times10^{-16}} \simeq 70 \qquad \text{(iii)}$$

From (i) and (iii), and with $\dfrac{d\,[\text{odd hydrogen}]}{dt} = 0$,

$$k_2\,[\mathrm{O}^*]\,[\mathrm{H_2O}] - k_6\frac{k_5}{k_4}\,[\mathrm{HO}_2]^2 = 0$$

Therefore,

$$[f\,(\mathrm{HO}_2)]^2 = \frac{k_2k_4}{k_5k_6} f\,(\mathrm{O}^*)\,f\,(\mathrm{H_2O})$$

$$f\,(\mathrm{HO}_2) = \left\{\frac{\left(2\times10^{-6}\right)\left(2\times10^{-14}\right)}{\left(3\times10^{-16}\right)\left(3\times10^{-11}\right)}\left(4\times10^{-17}\right)\left(2\times10^{-6}\right)\right\}^{\frac{1}{2}} \simeq \underline{\mathbf{2\times10^{-8}}}$$

Using (iii),

$$f\,(\mathrm{HO}) = \frac{f\,(\mathrm{HO}_2)}{70} \simeq \underline{\mathbf{3\times10^{-10}}}$$

(b) The mean lifetime of odd hydrogen is

$$\tau_{\substack{\text{odd}\\ \text{hyd}}} \simeq \left\{\frac{\text{loss rate of odd hydrogen}}{\text{concentration of odd hydrogen}}\right\}^{-1}$$

Or, since $[\mathrm{HO}_2] \simeq 70\,[\mathrm{HO}]$

$$\tau_{\substack{\text{odd}\\ \text{hyd}}} \simeq \left\{\frac{2k_6\,[\mathrm{HO}]\,[\mathrm{HO}_2]}{[\mathrm{HO}_2]}\right\}^{-1}$$

Therefore,

$$\begin{aligned}\tau_{\substack{\text{odd}\\\text{hyd}}} &= \{2k_6\,[\mathrm{HO}]\}^{-1}\\ &= \{2k_6 f\,(\mathrm{HO})\,[\mathrm{M}]\}^{-1}\\ &= \left\{2\left(3\times10^{-11}\right)\left(3\times10^{-10}\right)\left(5\times10^{17}\right)\right\}^{-1} = \underline{\mathbf{111\ secs}}\end{aligned}$$

(c) Let

$$N = \frac{\text{number of odd hydrogen species produced by } k_2 \text{ per sec}}{\text{number of } \mathrm{O_3} \text{ molecules destroyed per sec}}$$

Since the steps associated with k_4 and k_5 are fast

$$N \simeq \frac{\{[\mathrm{HO}] + [\mathrm{HO_2}]\} \big/ \tau_{\substack{\text{odd}\\\text{hydrogen}}}}{k_4\,[\mathrm{HO}]\,[\mathrm{O_3}] + k_5\,[\mathrm{HO_2}]\,[\mathrm{O_3}]}$$

Using (ii) and (iii) from (a) above

$$N \simeq \frac{\{[\mathrm{HO_2}] \big/ 70 + [\mathrm{HO_2}]\} \big/ \tau_{\substack{\text{odd}\\\text{hydrogen}}}}{2k_5\,[\mathrm{HO_2}]\,[\mathrm{O_3}]}$$

or,

$$\begin{aligned}N &\simeq \frac{1}{2k_5\,[\mathrm{O_3}]\,\tau_{\substack{\text{odd}\\\text{hydrogen}}}}\\ &\simeq \frac{1}{2k_5 f\,(\mathrm{O_3})\,[\mathrm{M}]\,\tau_{\substack{\text{odd}\\\text{hydrogen}}}}\\ &\simeq \frac{1}{2\,(3\times10^{-16})\,(2\times10^{-6})\,(5\times10^{17})\,111}\\ N &\simeq \mathbf{15}\end{aligned}$$

5.31 Let

$$C = C_o \exp\left(-\frac{t}{\tau}\right)$$

Then τ = e-folding time for removal of chlorine. But for a 1st order reaction (from eqn. 2.9 in Hobbs' "Introduction to Atmospheric Chemistry")

$$\underset{\text{(half-life)}}{t_{1/2}} = -0.69\ \tau$$

Therefore,

$$\begin{aligned}C &= C_o \exp\left(-\frac{t\ 0.69}{t_{1/2}}\right)\\ &= C_o \exp\left(-\frac{0.69}{35}t\right)\end{aligned}$$

where t is in years. For

$$\begin{aligned}
C &= 1.5 \text{ ppbv} \\
C_o &= 5 \text{ ppbv} \\
1.5 &= 5 \exp(-0.0197\, t) \\
\therefore \ln 0.3 &= -0.0197\, t \\
-1.2 &= -0.0197\, t \\
\therefore t &= \underline{60.9 \text{ years} \simeq 61 \text{ years or } \textbf{in year 2057}}
\end{aligned}$$

P. V. Hobbs
1/24/05

Chapter 6

6.12 Show that for a very weak solution droplet ($m \ll \frac{4}{3}\pi r^3 \rho' M_s$), (6.8) can be written as

$$\frac{e'}{e_s} \simeq 1 + \frac{a}{r} - \frac{b}{r^3}$$

where $a = 2\sigma'/n'kT$ and $b = imM_w/\frac{4}{3}M_s\pi\rho^{'}$. What is your interpretation of the second and third terms on the right-hand side of this expression? Show that in this case the peak in the Köhler curve occurs at

$$r \simeq \left(\frac{3b}{a}\right)^{1/2} \quad \text{and} \quad \frac{e'}{e_s} \simeq 1 + \left(\frac{4a^3}{27b}\right)^{1/2}$$

Solution

From eqn. (6.8) in text

$$\frac{e'}{e_s} = \left[\exp\frac{2\sigma'}{n'kTr}\right]\left[1 + \frac{imM_w}{M_s\left(\frac{4}{3}\pi\rho' r^3 - m\right)}\right]^{-1}$$

For a very weak solution $m \ll \frac{4}{3}\pi r^3 \rho'$. Also, since $\frac{2\sigma'}{n'kTr} \ll 1$, we have

$$\begin{aligned} \frac{e'}{e_s} &\simeq \left[1 + \frac{2\sigma'}{n'kTr}\right]\left[1 - \frac{imM_w}{\frac{4}{3}M_s\pi\rho' r^3}\right] \\ &\simeq 1 + \frac{2\sigma'}{n'kTr} - \frac{imM_w}{\frac{4}{3}M_s\pi\rho' r^3} - \underbrace{[\ \ ]\frac{1}{r_4}}_{\text{very small}} \end{aligned}$$

or,

$$\boldsymbol{\frac{e'}{e_s} \simeq 1 + \frac{a}{r} - \frac{b}{r^3}} \qquad (1)$$

where,

$$a = \frac{2\sigma'}{n'kT} \text{ and } b = \frac{imM_w}{\frac{4}{3}M_s\pi\rho'}$$

The second term on the right side of (1) represents the effect of the curvature of the drop in increasing e', and the third term represents the effect of dissolved salt in decreasing e'/e_s. The Köhler curve (i.e., e'/e_s versus r) reaches a peak value when

$$\frac{d}{dr}\left(\frac{e'}{e_s}\right) = 0,$$

that is, when

$$0 \simeq -\frac{a}{r^2} - \frac{3b}{r^4}$$

or, when

$$\boldsymbol{r^2 \simeq \frac{3b}{a}}$$

The maximum value of $\frac{e'}{e_s}$ is

$$\begin{aligned}
\left(\frac{e'}{e_s}\right)_{\max} &\simeq 1 + a\left(\frac{a}{3b}\right)^{1/2} - b\left(\frac{a}{3b}\right)^{3/2} \\
&\simeq 1 + \left(\frac{a^3}{3b}\right)^{1/2} - \left(\frac{b^{2/3}a}{3b}\right)^{3/2} \\
&\simeq 1 + \left(\frac{a^3}{3b}\right)^{1/2} - \left(\frac{a^3}{3^3 b}\right)^{1/2} \\
&\simeq 1 + \left(\frac{a^3}{3b}\right)^{1/2} - \frac{1}{3}\left(\frac{a^3}{3b}\right)^{1/2} \\
&\simeq 1 + \frac{2}{3}\left(\frac{a^3}{3b}\right)^{1/2}
\end{aligned}$$

$$\boldsymbol{\left(\frac{e'}{e_s}\right)_{\max} \simeq 1 + \left(\frac{4a^3}{27b}\right)^{1/2}}$$

6.15 The air at the 500 hPa level in a cumulonimbus cloud has a temperature of 0°C and a liquid water content of 3 g m^{-3}. (a) Assuming the cloud drops are falling at their terminal fall speeds, calculate the downward frictional drag that the cloud drops exert on a unit mass of air. (b) Express this downward force in terms of a (negative) virtual temperature correction. (In other words, find the decrease in temperature the air would have to undergo if it contained no liquid water in order to be as dense as the air in question.) [Hint: At temperatures around 0°C the virtual temperature correction due to the presence of water vapor in the air can be neglected.]

Answer (a) 0.0461 N kg^{-1}. (b) 1.28°C.

Solution

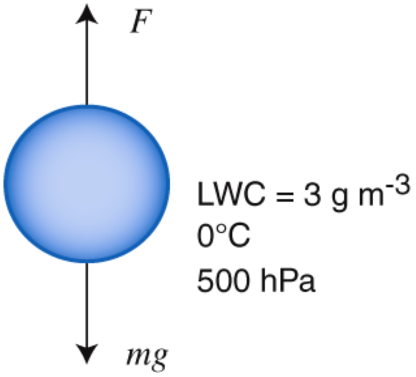


Figure 6.63.

(a) When drops are falling at terminal fall speed, the frictional drag per unit mass of air is

F_d = Downward force on drops/unit mass of air

$$= \left(\frac{\text{mass of drops}}{\text{mass of air}}\right) \text{g}$$

Since, air density $= \rho = \dfrac{\text{mass of air}}{\text{volume of air}}$

$$\begin{aligned} F_d &= \frac{(\text{mass of drops})}{(\text{volume of air})}\,\frac{g}{\rho} \\ &= \left[3\times10^{-3}\left(\text{kg m}^{-3}\right)\right]\,\frac{g}{\rho} \end{aligned}$$

Also, for air

$$\begin{aligned} p &= R_d\rho T \\ \therefore F_d &= \left(3\times10^{-3}\right)\, g\,\frac{R_dT}{p} \\ &= \frac{\left(3\times10^{-3}\right)(9.81)(287)(273)}{500\times10^2} \\ &= \frac{3\times9.81\times287\times273}{5}\times10^{-7} \\ &= 461174\times10^{-7} \end{aligned}$$

$$\boldsymbol{F_d = 0.0461\ N\ \text{kg}^{-1}}$$

(b) Without drops being present

Downward force acting on a unit mass of air $= g$

When drops are present

$$\begin{aligned}\text{Downward force acting on a unit mass of air} &= (g + 0.0461) \\ &= (9.81 + 0.0461) \\ &= 9.8561\ N\ \text{kg}^{-1}\end{aligned}$$

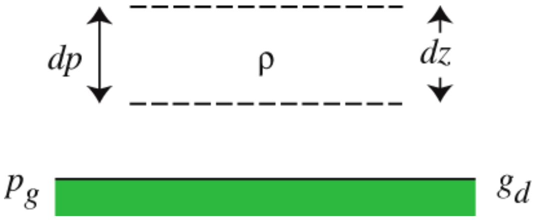


Figure 6.64.

$$\text{Pressure at ground} = p_g = -\int_{p_g}^{o} dp$$

But,

$$\frac{dp}{dz} = -\rho g$$

Therefore,

$$p_g = \int_{o}^{\infty} \rho g dz = g \int_{o}^{\infty} \rho dz \qquad (1)$$

Now the presence of 3 g m^{-3} $\left(= 3 \times 10^{-3}\ \text{kg m}^{-3}\right)$ of water in air, will have negligible effect on the density of air, which is ~ 1.275 kg m^{-3} at surface. Therefore from (1) we can write

$$p_g \propto g$$

Similarly, at cloud height

$$p \propto g$$

Hence,

$$\begin{aligned}\frac{p\,(\text{air alone}))}{p\,(\text{air + cloud water})} &= \frac{g}{g + 0.0461} \\ &= \frac{9.81}{9.8561} \qquad (2)\end{aligned}$$

Since,

$$p = R_d \rho T$$

the air in question (i.e., air containing water vapor) has density

$$\rho = \frac{p\,(\text{air + cloud water})}{R_d T} \qquad (3)$$

If the air had no cloud water, but is required to have density ρ given by (3), then

$$\text{Density} = \frac{p\,(\text{air only})}{R_d T_v}$$

or,

$$\frac{p\,(\text{air + cloud water})}{R_d T} = \frac{p\,(\text{air alone})}{R_d T_v}$$

where T_v is the virtual temperature required if the air alone is to have density ρ. Therefore,

$$T_v = \frac{p\,(\text{air alone})}{p\,(\text{air + cloud water})} T \tag{4}$$

From (2) and (4)

$$\begin{aligned} T_v &= \frac{9.81}{9.8561} T \\ &= 0.9953\,(273) \\ &= 271.72 \text{ K} \end{aligned}$$

Therefore, the (*negative*) virtual temeprature correction is $273 - 271.72 = \mathbf{1.28°C}$.

6.20 Consider a saturated parcel of air that is lifted adiabatically. The rate of change in the supersaturation ratio S ($S = e/e_s$ where e is the vapor pressure of the air and e_s the saturated vapor pressure) of the air parcel may be written as

$$\frac{dS}{dt} = Q_1 \frac{dz}{dt} - Q_2 \frac{d(LWC)}{dt}$$

where dz/dt and LWC are the vertical velocity and the liquid water content of the air parcel, respectively.

a) Assuming that S is close to unity, and neglecting the difference between the actual temperature and the virtual temperature of the air, show that

$$Q_1 \simeq \frac{g}{TR_d} \left(\frac{\varepsilon L_v}{T c_p} - 1 \right)$$

where, T is the temperature of the parcel (in degrees kelvin), L_v the latent heat of condensation, g the acceleration due to gravity, R_d and R_v are the gas constants for 1 kg of dry air and 1 kg of water vapor, respectively, $\varepsilon = R_d/R_v$, and c_p the specific heat at constant pressure of the saturated air. [Hint: Consider ascent with no condensation. Introduce the mixing ratio of the air, which is related to e by Eqn. (3.62).]

b) Derive a corresponding approximate expression for Q_2 in terms of R_d, T, e, e_s, L_v, p, c_p and the density of the moist air (ρ). Assume that $e/e_s \simeq 1$, $T \simeq T_v$ and $\varepsilon >> w$ (the mixing ratio of the air).

Answer $Q_2 = \rho \left[\frac{R_d T}{\varepsilon e_s} + \frac{\epsilon L_v^2}{pTc_p} \right]$

Solution

(a) For ascent with no condensation LWC = 0, therefore:

$$\frac{dS}{dt} = Q_1 \frac{dz}{dt} \tag{1}$$

since,

$$S = \frac{e}{e_s}$$

$$\frac{dS}{dt} = \left(e_s \frac{de}{dt} - e \frac{de_s}{dt} \right) \Big/ e_s^2 \tag{2}$$

We will first evaluate $\frac{de}{dt}$

$$e = \frac{w}{\varepsilon + w} p$$

where, w = mixing ratio, which is constant if there is no condensation.

$$\therefore \frac{de}{dt} = \frac{w}{\varepsilon + w} \frac{dp}{dt}$$

or

$$\frac{de}{dt} = \frac{w}{\varepsilon + w} \frac{dp}{dz} \frac{dz}{dt} \tag{3}$$

But,

$$\frac{dp}{dz} = -g\rho$$

and

$$p = R_d \rho T \qquad (T = T_v) \tag{4}$$

From (3)–(4):

$$\frac{de}{dt} = -\frac{eg}{R_d T} \frac{dz}{dt} \tag{5}$$

We will now evaluate $\frac{de_s}{dt}$. From the Clausius-Clapeyron equation

$$\frac{de_s}{dT} = \frac{L_v}{T(\alpha_2 - \alpha_1)} \simeq \frac{L_v}{T(\alpha_2)}$$

and,

$$e_s = R_v \frac{1}{\alpha_2} T$$

$$\therefore \frac{de_s}{dT} = \frac{L_v e_s}{R_v T^2}$$

$$\therefore \frac{de_s}{dt} = \frac{L_v e_s}{R_v T^2} \frac{dT}{dt}$$

or,

$$\frac{de_s}{dt} = \frac{L_v e_s}{R_v T^2} \frac{dT}{dz} \frac{dz}{dt}$$

But,

$$-\frac{dT}{dz} = +\frac{g}{c_p} = \begin{array}{l}\text{Dry adiabatic lapse rate} \\ \text{(because there is no condensation)}\end{array}$$

Therefore,

$$\frac{de_s}{dt} = -\frac{L_v e_s}{R_v T^2} \frac{g}{c_p} \frac{dz}{dt} \tag{6}$$

From (2), (5) and (6):

$$\frac{dS}{dt} = \frac{1}{T} \frac{e}{e_s} \left(\frac{\varepsilon L_v g}{R_d c_p T} - \frac{g}{R_d} \right) \frac{dz}{dt}$$

Since $\frac{e}{e_s} \simeq 1$

$$\frac{dS}{dt} \simeq \frac{1}{T} \left(\frac{\varepsilon L_v g}{R_d c_p T} - \frac{g}{R_d} \right) \frac{dz}{dt} \tag{7}$$

Comparing (1) and (7):

$$\boldsymbol{Q_1 = \frac{g}{TR_d} \left(\frac{\varepsilon L_v}{c_p T} - 1 \right)}$$

(b) If we assume no vertical air motion $\left(\frac{dz}{dt} \simeq 0 \text{ and } p = \text{constant} \right)$ while condensation occurs, then:

$$\frac{dS}{dt} = -Q_2 \frac{d\,(LWC)}{dt} \tag{8}$$

Equation (2) still holds, and we will now evaluate $\frac{de}{dt}$ for this case.

$$e = \frac{w}{\varepsilon + w} p$$

w now varies, but p is constant. Therefore,

$$\frac{de}{dt} = \frac{\varepsilon}{(\varepsilon + w)^2} \frac{dw}{dt} p$$

But,

$$\frac{dw}{dt} = -\frac{d\,(LWC)}{dt}$$

Therefore,

$$\frac{de}{dt} = -\frac{\varepsilon}{(\varepsilon + w)^2} p \frac{d\,(LWC)}{dt}$$

Since

$$p = R_d \rho T \qquad\qquad (T = T_v)$$

and

$$\varepsilon \gg w$$

$$\frac{de}{dt} \simeq -\frac{1}{\varepsilon} \rho R_d T \frac{d\,(LWC)}{dt} \tag{9}$$

We now evaluate $\frac{de_s}{dt}$ for this case. As before, from the Clausius-Clapeyron eqn. and the gas eqn. for vater vapor, we get:

$$\begin{aligned} \frac{de_s}{dt} &\simeq \frac{L_v e_s}{R_v T^2} \frac{dT}{dt} \\ &= \frac{L_v e_s}{R_v T^2} \frac{dT}{d\,(LWC)} \frac{d\,(LWC)}{dt} \end{aligned} \tag{10}$$

But,

$$d\,(LWC) = -dw$$

and

$$dQ = L_v d\,(LWC) = -L_v dw$$

also,

$$dQ = c_p dT$$

Hence,

$$c_p dT = -L_v dw$$

or,

$$dT = -\frac{L_v dw}{c_p} \tag{11}$$

From (10) and (11):

$$\frac{de_s}{dt} = +\frac{L_v^2 e_s}{R_v T^2 c_p} \frac{d\,(LWC)}{dt} \tag{12}$$

From (2), (9) and (12):

$$\frac{dS}{dt} = \left(e_s \frac{de}{dt} - e \frac{de_s}{dt} \right) \Big/ e_s^2$$

Therefore,

$$\frac{dS}{dt} = -\frac{1}{\varepsilon e_s} \rho R_d T \frac{d\,(LWC)}{dt} - \frac{e}{e_s} \frac{L_v^2}{R_v T^2 c_p} \frac{d\,(LWC)}{dt}$$

Substitute

$$p = \rho R_d T \text{ so that } T = p/\, R_d \rho$$

Therefore,

$$\frac{dS}{dt} = -\frac{1}{\varepsilon e_s} \rho R_d T \frac{d\,(LWC)}{dt} - \frac{e}{e_s} \frac{L_v^2 R_d \rho}{R_v T c_p p} \frac{d\,(LWC)}{dt}$$

Or, since $\dfrac{e}{e_s} \simeq 1$,

$$\frac{dS}{dt} \simeq -\rho \left[\frac{R_d T}{\varepsilon e_s} + \frac{\varepsilon L_v^2}{T p c_p} \right] \frac{d\,(LWC)}{dt} \tag{13}$$

From (8) and (13),

$$\boldsymbol{Q_2 = \rho \left[\frac{R_d T}{\varepsilon e_s} + \frac{\varepsilon L_v^2}{p T c_p} \right]}$$

6.24 If a raindrop has a radius of 1 mm at cloud base, which is located 5 km above the ground, what will be its radius at the ground and how long will it take to reach the ground if the relative humidity between cloud base and ground is constant at 60%? [Hint: Use (6.21) and the relationship between v and r given in Exercise 6.23. If r is in micrometers, the value of G_l in (6.21) is 100 for cloud droplets, but for the large drop sizes considered in this problem the value of G_l should be taken as 700 to allow for ventilation effects.

Answer 0.67 mm and 16.4 min

Solution From the relation between v and r given in Exercise (6.23)

$$V = 6 \times 10^3 r$$

where V is in m s^{-1} and r in meters. Therefore,

$$V = \left(6 \times 10^3\right) 10^{-4} r = 0.6r$$

where V is now in cm s^{-1} and r is in μm. Let x = distance of drop (in cm) below cloud base at time t, then

$$\frac{dx}{dt} = V = 0.6r \tag{1}$$

where r is in μm. Therefore,

$$dx = 0.6r\ dt$$

From (1),

$$r\frac{dr}{dt} = G_\ell S = \left(7 \times 10^2\right)\ S \tag{2}$$

where r is in μm and S is expressed as a fraction. Therefore,

$$rdr = \left(7 \times 10^2 S\right) \frac{dx}{0.6r}$$

or,

$$r^2 dr = \frac{\left(7 \times 10^2 S\right)}{0.6} dx$$

Therefore, integrating from cloud base, where $r = 1000$ μm and $x = 0$, to the ground, where $r = R$ (in μm) and $x = 5 \times 10^5$ cm,

$$\int_{1000\ \mu\text{m}}^{R(\mu\text{m})} r^2 dr = \frac{700S}{0.6} \int_{0\ \text{cm}}^{5\times10^5\ \text{cm}} dx$$

$$\left[\frac{r^3}{3}\right]_{1000}^{R(\mu\text{m})} = \frac{700S}{0.6}\left(5 \times 10^5\right)$$

If $RH = 60\%$ the supersaturation (as a fraction) is

$$\frac{e - e_s}{e_s} = \frac{e}{e_s} - 1 = \underset{\text{(as a fraction)}}{RH} - 1 = 0.6 - 1 = -0.4$$

Therefore,

$$S = -0.4$$

$$\begin{aligned}
\left[\frac{r^3}{3}\right]_{1000}^{R(\mu\text{m})} &= \frac{700\,(-0.4)}{0.6}\left(5 \times 10^5\right) \\
\frac{R^3}{3} - \frac{1000^3}{3} &= \frac{-7\,(0.4)\,(5)\,10^7}{0.6} \\
&= -23.33 \times 10^7 \\
R^3 &= 10^9 - 3\left(23.33 \times 10^7\right) \\
&= 10^9 - 0.7 \times 10^9 \\
&= 0.3 \times 10^9
\end{aligned}$$

Therefore,

$$\begin{aligned}
R &= 3\sqrt{0.3} \times 10^3 \\
&= 0.6694 \times 10^3\ \mu\text{m}
\end{aligned}$$

Radius at cloud base = 0.67 mm

Time taken, from (2) above:

$$dt = \frac{rdr}{700S}$$

Therefore,

$$\int_{1000\ \mu\mathrm{m}}^{r} r dr = 700S \int_{o}^{t} dt$$

$$\begin{aligned}\left[\frac{r^2}{2}\right]_{1000}^{r} &= 700St \\ \frac{r^2}{2} - \frac{1000^2}{2} &= 700St\end{aligned}$$

or,

$$r^2 = 1000^2 + 2\,(700)\,St$$

But, from (1) above,

$$\frac{dx}{dt} = 0.6r$$

Hence,

$$\frac{dx}{dt} = 0.6\left(10^6 + 1400St\right)^{1/2}$$

Therefore,

$$\begin{aligned}\int_{o}^{5\times10^5\ \mathrm{cm}} dx &= 0.6\int_{o}^{T}\left(10^6 + 1400St\right)^{1/2} dt \\ 5\times10^5 &= 0.6\left[\frac{2}{3}\left(10^6 + 1400St\right)^{3/2}\frac{1}{1400S}\right]_{o}^{T} \\ &= 0.6\left[\frac{2}{4200S}\left(10^6 + 1400ST\right)^{3/2} - \frac{2\times10^9}{4200S}\right]\end{aligned}$$

But $S = -0.4$, therefore,

$$5\times10^5 = \frac{1.2}{4200\,(-0.4)}\left(10^6 - 560T\right)^{3/2} - \frac{1.2\times10^9}{4200\,(-0.4)}$$

$$\left[\frac{5\times10^5\times4200\,(-0.4)}{1.2} + 10^9\right]^{2/3} = 10^6 = 560T$$

Therefore,

$$T = 985.54 \text{ secs}$$

or,

$$\boldsymbol{T}\mathbf{=16.4\ mins}$$

6.25 A large number of drops, each of volume V, are cooled simultaneously at a steady rate $\beta(= dT/dt)$. Let $p(V,t)$ be the probability of ice nucleation taking place in a volume V of water during a time interval t. (a) Derive a relationship between $p(V,t)$ and $\int_0^{T_t} J_{LS}\, dT$, where J_{LS} is the ice nucleation rate (per unit volume per unit time) and T_t the temperature of the drops at time t. (b) Show that a n-fold increase in the cooling rate produces the same depression in the freezing temperature as an n-fold decrease in drop volume.

Answer $\ln[1-p(V,t)] = -\frac{V}{\beta} \int_0^{T_t} J_{LS}\, dT$

Solution

(a)

$$\begin{aligned} \text{Let } N &= \text{total number of drops} \\ N_t &= \text{number of drops frozen at time } t \end{aligned}$$

Then

$$P(V,t) = \frac{N_t}{N}$$

Number of drops that nucleat between time o and $t+dt$ is

$$N_{t+dt} = N_t + (N - N_t)\, V J_{LS} dt$$

Dividing both sides by N

$$P(V,t+dt) = P(V,t) + [1 - P(V,t)\, V J_{LS} dt]$$

Since

$$P(V,t+dt) = P(V,t) + \frac{d}{dt}[P(V,t)]\, dt$$

it follows that

$$\frac{d}{dt} P(V,t) = [1 - P(V,t)]\, V J_{LS}$$

Hence,

$$\int_o^{P(V,t)} \frac{dP(V,t)}{1-P(V,t)} = \int_o^t V J_{LS} dt$$

$$\therefore \ln[1 - P(V,t)] = -\int_o^t V J_{LS} dt$$

But $\beta = \frac{dT}{dt}$, therefore

$$\boldsymbol{\ln[1 - P(V,t)] = -\frac{V}{\beta} \int_o^{T_t} J_{LS}\, dT}$$

where T_t is temperature at time t.

(b) From the equation following (6.34) in Exercise (6.4):

$$-n = \ln(1-P)$$

Therefore,

$$-\ln(1-P) = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 10^3 \exp a\,(T_1 - T)$$

Since from (a) above

$$\begin{aligned} -\ln(1-P) &\propto \frac{V}{\beta} \\ \frac{V}{\beta} &\propto \exp a\,(T_1 - T) \end{aligned}$$

Therefore,

V and β have inverse effect on the medium freezing temperature T.

6.37 If the velocities of sound in two adjacent thin layers of air are v_1, and v_2, a sound wave will be refracted at the interface between the layers and $\frac{\sin i}{\sin r} = \frac{v_1}{v_2}$ (see Fig. 6.65).

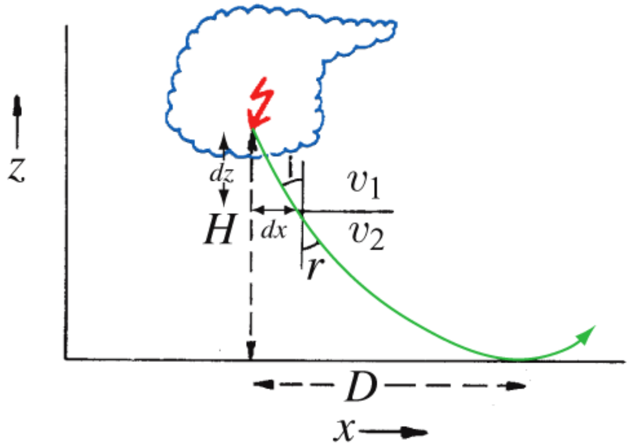


Figure 6.65.

Use this relationship, and the fact that $v \propto (T)^{1/2}$, where T is the air temperature (in degrees kelvin), to show that the equation for the path of a sound wave produced by thunder that is heard at the maximum horizontal distance from the origin of the thunder is

$$dx = -\left(T/\Gamma z\right)^{1/2}\ dz$$

where x and z are the coordinates indicated in Fig. 6.66, Γ the temperature lapse rate in the vertical (assumed constant), and T the temperature at height z.

Solution From Fig. 6.65 and the law of refraction

$$\frac{\sin i}{\sin r} = \frac{v_1}{v_2} \tag{1}$$

Or, in general,

$$\frac{\sin \phi}{v} = \text{constant (along any path of a sound wave)} \tag{2}$$

But,

$$\tan \Phi = \left| \frac{dx}{dz} \right| = -\frac{dx}{dz}$$

Therefore,

$$\frac{\sin \Phi}{\cos \Phi} = \frac{\sin \Phi}{\left(1 - \sin^2 \Phi\right)^{1/2}} = -\frac{dx}{dt} \tag{3}$$

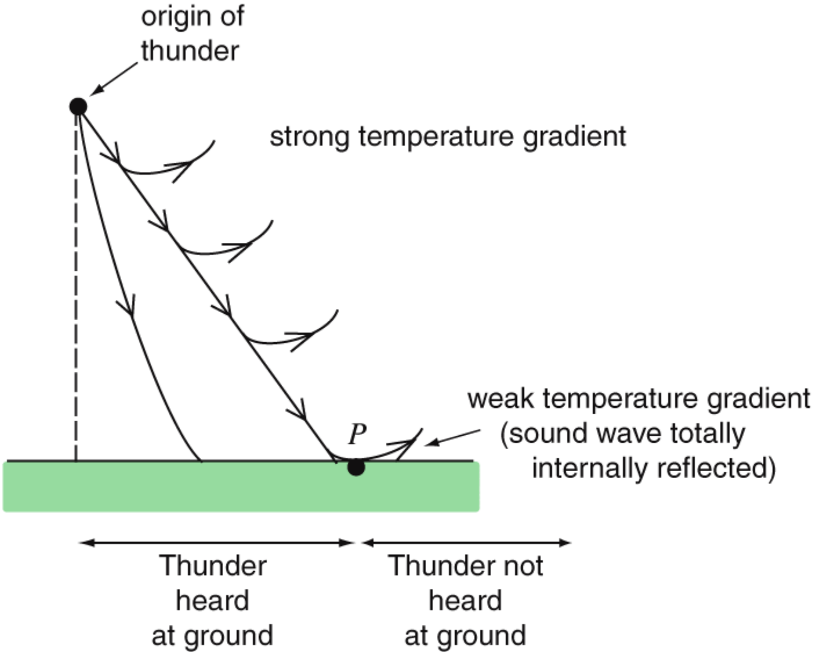


Figure E6.37.

At point P in Fig. E6.37

$$\frac{\sin 90^\circ}{v_o} = \text{constant}$$

or,

$$\frac{1}{v_o} = \text{constant} \tag{4}$$

where, v_o is velocity of sound just above ground level. Hence, in general, from (2)

$$\frac{\sin\Phi}{v} = \frac{1}{v_o}$$

But $v \propto \sqrt{T}$, therefore,

$$\sin\Phi = \frac{v}{v_o} = \left(\frac{T}{T_o}\right)^{1/2} \tag{5}$$

From (3) and (5)

$$-\frac{dx}{dz} = \frac{(T/T_o)^{1/2}}{\left(1 - \dfrac{T}{T_o}\right)^{1/2}} = \left(\frac{T}{T_o - T}\right)^{1/2}$$

But,

$$T = T_o - \Gamma z$$

Therefore,

$$T_o - T = \Gamma z$$

and,

$$\boldsymbol{dx = -\left(\frac{T}{\Gamma z}\right)^{1/2} dz}$$

6.38 Use the expression derived in Exercise (6.37) to show that the maximum distance D at which a sound wave produced by thunder can be heard is given approximately by (see Fig. 6.63 from Exercise 6.37)

$$D = 2\,(T_0 H/\Gamma)^{1/2}$$

where T_0 is the temperature at the ground. Calculate the value of D given that $\Gamma = 7.50$ °C km^{-1}, $T_0 = 300$ K, and $H = 4$ km.

Answer 25.3 km

Solution

From Exercise 6.67:

$$\begin{aligned}
dx &= -\left(\frac{T_o - \Gamma z}{\Gamma z}\right)^{1/2} dz \\
&= -\left(\frac{T_o}{\Gamma z} - 1\right)^{1/2} dz \\
&= -\left(\frac{T_o}{\Gamma z}\right)^{1/2}\left(1 - \frac{\Gamma z}{T_o}\right)^{1/2} dz \\
&= -\left(\frac{T_o}{\Gamma z}\right)^{1/2}\left(1 - \frac{1}{2}\frac{\Gamma z}{T_o} + \begin{array}{c}\text{higher powered}\\ \text{terms in z}\end{array}\right) dz \\
dx &\simeq -\left(\frac{T_o}{\Gamma z}\right)^{1/2}\left(1 - \frac{1}{2}\frac{\Gamma z}{T_o}\right) dz
\end{aligned}$$

Integrating,

$$\begin{aligned}
\int_o^D dx &= -\sqrt{\frac{T_o}{\Gamma}}\int_H^o \left(\frac{1}{\sqrt{z}} - \frac{1}{2}\frac{\Gamma z}{T_o}\right) dz \\
&= -\left(\frac{T_o}{\Gamma}\right)^{1/2}\int_H^o \left(\frac{1}{\sqrt{z}} - \frac{1}{2}\frac{\Gamma z}{T_o}\right) dz \\
&= -\left(\frac{T_o}{\Gamma}\right)^{1/2}\left[2z^{1/2} - \frac{\Gamma}{2T_o}\frac{2}{3}z^{3/2}\right]_H^o \\
&= -\left(\frac{T_o}{\Gamma}\right)^{1/2}\left[2z^{1/2} - \frac{\Gamma}{3T_o}z^{3/2}\right]_H^o \\
&= -\left(\frac{T_o}{\Gamma}\right)^{1/2}\left[-2H^{1/2} + \underbrace{\frac{1}{3}\frac{\Gamma}{T_o}H^{3/2}}_{\substack{\text{small}\\ \text{term}}}\right]
\end{aligned}$$

Therefore, $\boldsymbol{D = 2\left(\frac{T_o H}{\Gamma}\right)^{1/2}}$

With $\Gamma = 7.5^\circ\ \mathrm{km}^{-1}$, $T_o = 300$ K, and $H = 4$ km

$$D = 2\left(\frac{300 \times 4000}{7.5 \times 10^{-3}}\right)^{1/2} = 2\left(1.26 \times 10^4\right)$$

$$\boldsymbol{D = 25.3\ \mathrm{km}}$$

Chapter 7

7.42 The accompanying Fig. 7.31 shows the pressure and horizontal wind fields in an atmospheric Kelvin wave which propagates zonally along the equator. Pressure and zonal wind oscillate sinusoidally with longitude and time, while $v = 0$ everywhere. Such waves are observed in the stratosphere where frictional drag is negligible in comparison with the other terms in the horizontal equations of motion. (a) Prove that the waves propagate eastward. (b) Prove that the zonal wind component is in geostrophic equilibrium with the pressure field.

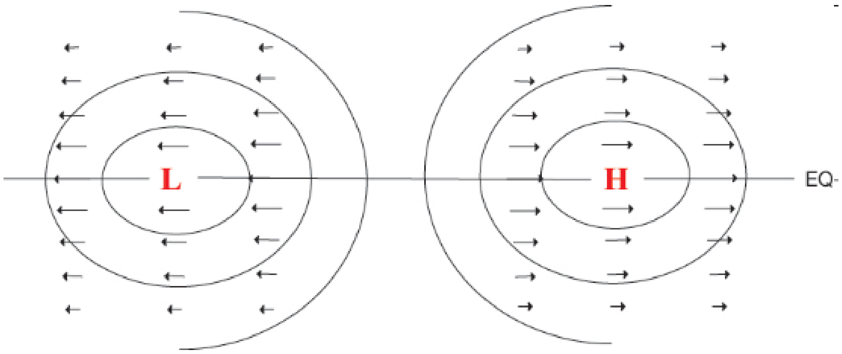


Fig. 7.31 Distribution of wind and geopotential height on a pressure surface, in an equatorial Kelvin wave, as viewed in a coordinate system moving with the wave.

Solution: (a) In the absence of a meridional wind component, for points along the equator the horizontal equation of motion (7.14) reduces to

$$\frac{du}{dt} = -\frac{\partial \Phi}{\partial x}$$

If the wave is sufficiently weak, the distinction between the Lagrangian and Eulerian time derivative can be neglected, provided that we view the wind field in a coordinate system moving with the wave, as in Fig. 7.31. This assumption underlies so called "linear wave theory". Since the Φ and u field are in phase with one another, the horizontal pressure gradient force $-\partial\Phi/\partial x$ is positive to the east of the westerly wind maxima in the waves, imparting an eastward acceleration to equatorial air parcels in that sector of the globe. By similar reasoning it can be inferred that air parcels to the west of the westerly wind maxima in the waves must be experiencing a westward acceleration. Since the motion is purely sinusoidal, it follows that the westerly wind maximum must be propagating eastward, away from the region of easterly acceleration and toward the region of westerly acceleration. Analogous reasoning can be applied to prove that the easterly wind maximum must also be propagating eastward.

Proving that the associated pressure perturbations also propagate eastward requires consideration of the vertical structure of the waves, which is beyond the scope of this problem. However, linear wave theory indicates that similar waves would be observed on a rotating planet covered by a shallow ocean, in which the pressure field is determined by the height of the free surface. In equatorial Kelvin waves in shallow water, the convergence to the east of the westerly wind maximum (Fig. 7.31) has the effect of raising the free surface, thereby causing the pressure to rise in that longitudinal sector, while divergence to the west of the westerly wind maximum has the opposite effect.

(b) The meridional equation of motion is

$$\frac{dv}{dt} = -\frac{\partial \Phi}{\partial y} - fu$$

Since v in equatorial Kelvin waves is identically equal to zero, it follows that the zonal wind component must be in geostrophic balance with the pressure field.

Chapter 9

9.13 If the dissipation length scale is L_ε, what is the e-folding time for the decay of turbulence (i.e., time for TKE/m to equal $1/e$ of its initial value). Assuming you start with finite TKE but there is no production, consumption, transport, or advection?

Answer: $t_{\text{e-fold}} = 0.32\ L_\varepsilon\ (TKE/m)_o^{-1/2}$.

SOLUTION Start with TKE conservation equation with the non-zero terms, namely

$$\frac{d(TKE/m)}{dt} = -\frac{(TKE/m)^{3/2}}{L_\varepsilon}$$

Separate variables and integrate, using $(TKE/m)_o$ at time $t = 0$. The result is

$$TKE/m = \left[(TKE/m)_o^{-1/2} + 2t/L_\varepsilon\right]^{-2}$$

Next, divide both sides by $(TKE/m)_o$, then set $(TKE/TKE_o) = 1/e$, and rearrange to get answer.

EXPANDED SOLUTION
Separate variables:

$$(TKE/m)^{-3/2}\, d\,(TKE/m) = -\,(1/L_\varepsilon)\, dt$$

Integrate:

$$\begin{aligned}
\int_{\text{start}}^{\text{end}} (TKE/m)^{-3/2}\, d\,(TKE/m) &= -\,(1/L_\varepsilon) \int_{\text{start}}^{\text{end}} dt \\
-2\,(TKE/m)^{-1/2}\, \Big|_{\text{start}}^{\text{end}} &= -\,(1/L_\varepsilon)\, t\, \Big|_{\text{start}}^{\text{end}}
\end{aligned}$$

Use $(TKE/m)_o$ at time $t = 0$ as the initial condition:

$$\begin{aligned}
&(TKE/m)^{-1/2} - (TKE/m)_o^{-1/2} = (2/L_\varepsilon)\cdot(t-0) \\
&(TKE/m)^{-1/2} = (TKE/m)_o^{-1/2} + (2/L_\varepsilon)\cdot t \\
&(TKE/m) = \left[(TKE/m)_o^{-1/2} + (2/L_\varepsilon)\cdot t\right]^{-2}
\end{aligned}$$

Next, divide both sides by $(TKE/m)_o$:

$$\frac{(TKE/m)}{(TKE/m)_o} = \left[1 + (TKE/m)_o^{1/2}\cdot(2/L_\varepsilon)\cdot t\right]^{-2}$$

Set the TKE ratio to: $(TKE/m)\setminus(TKE/m)_o = 1/e$:

$$\begin{aligned}
&e = \left[1 + (TKE/m)_o^{1/2}\cdot(2/L_\varepsilon)\cdot t_{\text{efold}}\right]^2 \\
&\left(e^{1/2} - 1\right)/2 = (TKE/m)_o^{1/2}\cdot(t_{\text{efold}}/L_\varepsilon)
\end{aligned}$$

Solve for t_{efold}:

$$\begin{aligned} t_{\text{efold}} &= \left[\left(e^{1/2}-1\right)/2\right] \cdot L_{\varepsilon} \cdot (TKE/m)_o^{-1/2} \\ t_{\text{efold}} &= 3.2 \cdot L_{\varepsilon} \cdot (TKE/m)_o^{-1/2} \end{aligned}$$

9.15 For the situation shown in Fig. 9.12 in the text (a) derive a relationship for the phase lag Δt between the temperature wave at two depths differing by height Δz, given P the wave period and ν_g. The diffusion equation for heat conduction is $\partial T/\partial t = \nu_g\ \partial^2 T/\partial z^2$, where ν_g is the thermal diffusivity of the soil. (b) Using the annual-cycle data given in Fig. 9.12 in the text, estimate the phase lag between the temperature curves at 1.5 and 6 M, and then use it to find the value of νg.

Answer: (a) $\Delta t = \dfrac{\Delta z}{2}\left[\dfrac{P}{\pi \nu_g}\right]^{1/2}$ (b) ν_g ~1.5 $\times 10^{-6}$ m^2 s^{-1}.

SOLUTION 1
Start with the heat conduction equation in one dimension:

$$\frac{\partial T}{\partial t} = \nu_g \frac{\partial^2 T}{\partial z^2}$$

where $\nu_g = k_T/C_s$ is the thermal diffusivity, k_T is the molecular conductivity of soil, and C_s is the specific heat of soil.

Solve by assuming a sinusoidal wave of period P imposed on the ground surface:

$$T = T_{sa} + a_o \exp\left[-\left(\frac{\pi}{P \cdot \nu_g}\right)^{1/2} \cdot z\right] \cdot \sin\left[\frac{2\pi t}{P} - \left(\frac{\pi}{P \cdot \nu_g}\right)^{1/2} \cdot z + b\right]$$

where T_{sa} is a constant average soil temperature (the base state), a_o is the amplitude of the imposed sine wave at the surface, z is depth, t is time, and b is a phase-shift constant. With increasing depth, the amplitude of the wave is damped and phase shifted relative to the surface wave. This equation can be solved separately for a diurnal wave (P = 24 h) and an annual wave (P=365 days).

SOLUTION 2 (a) From the solution to the diffusion equation, the relationship is derived between phase lag Δt between the temperature wave at two depths differing by Δz

$$\Delta t = \frac{\Delta z}{2}\left[\frac{P}{\pi v_g}\right]^{1/2}$$

where P is the wave period. (b) This last expression can be rearranged to solve for soil diffusivity ν_g. Using data given in Fig. 9.12 in the text, it can be estimated that phase lag $\Delta t = 0.18$ yr and $P = 1$ yr, and $\Delta z = 6 - 1.5$ m $= 4.5$ m.

Uisng these values in $\nu_g = \dfrac{P}{\pi}\left(\dfrac{\Delta z}{2\Delta t}\right)^2 = 1.5 \times 10^{-6}\ \mathrm{m}^2\ \mathrm{s}^{-1}$.

9.18 The flux form of the Richardson number is

$$R_f = \frac{(g/\overline{T}_v)\,\overline{w'\theta_v'}}{\overline{w'u'}\dfrac{\partial \overline{u}}{\partial z} + \overline{w'v'}\dfrac{\partial \overline{v}}{\partial z}}$$

Use gradient transfer theory to show how R_f is related to R_i.

SOLUTION

$$\begin{aligned} R_f &= \frac{(g/\overline{T}_v)\,\overline{w'\theta_v'}}{\overline{w'u'}\dfrac{\partial \overline{U}}{\partial z} + \overline{w'v'}\dfrac{\partial \overline{V}}{\partial z}} = \frac{(g/\overline{T}_v)\,(-K_H)\,\dfrac{\partial \overline{\theta}_v}{\partial z}}{\left(-K_M\dfrac{\partial \overline{U}}{\partial z}\right)\dfrac{\partial \overline{U}}{\partial z} + \left(-K_m\dfrac{\partial \overline{V}}{\partial z}\right)\dfrac{\partial \overline{V}}{\partial z}} \\ &= \frac{(g/\overline{T}_v)\,\dfrac{\partial \overline{\theta}_v}{\partial z}}{\left(\dfrac{\partial \overline{U}}{\partial z}\right)^2 + \left(\dfrac{\partial \overline{V}}{\partial z}\right)^2} = Ri \end{aligned}$$

where it is assumed that $K_M = K_H$. In reality, $K_M > K_H$.]

9.20 (a) Confirm that the following expression is a solution to Eq. (9.26), and (b) that it satisfies the boundary condition that $V = 0$ at $z = z_0$.

$$\frac{V}{u_*} = \frac{1}{k}\left\{\ln\frac{z}{z_0} - 2\ln\left[\frac{1+x}{2}\right] - \ln\left[\frac{1+x^2}{2}\right] + 2\arctan x - \pi/2\right\}$$

where

$$x = \left[1 - 15\frac{(z - z_0)}{L}\right]^{1/4}$$

Solution: (a) Take the derivative with respect to height of the above expression. The result is

$$\Phi_M = 1 - 15\left(\frac{z}{L}\right)^{-1/4}$$

(b) For $z = z_0$, then $x = 1$ and $ln(z/z_0) = 0$, and $\arctan(1) = \pi/4$. Thus, $V = 0$.

9.22 If boundary-layer divergence is constant during fair weather, explain why the mixed layer can stop growing during mid-afternoon even though there are strong sensible heat fluxes into the boundary layer at the ground.

SOLUTION (a) As the mixed layer grows, w_i becomes stronger from Eq. (9.28), until $w_i = w_e$, resulting in $dz_i/dt = 0$ from Eq. (9.27) in the text.

(b) The forecast equation for mixed layer depth is $dz_i/dt = w_e - w_i$ from Eq. (9.27). Let $w_e =$ constant, but w_i increases with height according to $w_i = \beta{\cdot}z_i$ from eqn. (9.28). Define an intermediate variable for integration: $y = w_e - \beta{\cdot}z_i$, thus $dy = -\beta{\cdot}dz_i$. The forecast equation for z_i thus becomes

$$dy/dt = -\beta\ y$$

which is easily solved to yield: $\ln(y/y_o) = -\beta\ t$, assuming $y = y_o$ at $t = 0$. Taking the exponential of both sides, and plugging in for y gives:

$$w_i - \beta{\cdot}z_i = \left(w_i - \beta{\cdot}z_i\right)_o \cdot \exp\left(-\beta t\right)$$

Solving for z_i gives:

$$z_i = \frac{w_i}{\beta} - \left(\frac{w_i}{\beta} - z_{io}\right) \cdot \exp\left(-\beta t\right)$$

which approaches the proper limits at zero and infinite times.

9.23 If F^* is known, and if $|F_G| = 0.1|F^*|$, then show how knowledge of the time-averaged temperature at two heights in the surface layer, and of mean humidity at the same two heights, is sufficient to estimate the sensible and latent heat fluxes in the surface layer.

SOLUTION Use K-theory to approximate the heat and moisture fluxes: $\overline{w'\theta'} = -K\Delta\theta/\Delta z$, and $\overline{w'q'} = -K\Delta q/\Delta z$. Thus, the Bowen ratio is $F_{Hs}/F_{Es} = \gamma\Delta\theta/\Delta q$, where γ is the psychometric constant. Combining this with the surface heat budget ($0.9F^* = F_{Hs}+F_{Es}$) gives two equations for two unknowns, that can be solved to yield:

$$F_{Hs} = \frac{0.9F^*}{1 + \dfrac{\Delta q}{\gamma{\cdot}\Delta\theta}} \text{ and } F_{Es} = \frac{0.9F^*}{1 + \dfrac{\gamma\Delta\theta}{\Delta q}}$$

where Δ is the difference operator between the two heights, and γ is the psychometric constant.

9.30 Show that over flat terrain the large scale vertical velocity at the top of the boundary layer is approximately equal to

$$w_i \simeq -z_i \left\{\nabla \cdot \mathbf{V}\right\} \tag{9.28}$$

where

$$\left\{\nabla \cdot \mathbf{V}\right\} \equiv \frac{\int_{p_i}^{p_s} \left(\nabla \cdot \mathbf{V}\right) dp}{\left(p_s - p_i\right)}$$

is the mass-weighted divergence in the boundary layer, and p_s and p_i are the pressures at the earth's surface and at the top of the boundary layer.

SOLUTION From the continuity equation (7.40),

$$\omega_s - \omega_i = \int_{p_i}^{p_s} (\nabla \cdot \mathbf{V})\, dp \tag{9.37}$$

where ω_s and ω_i are the vertical velocities at the earth's surface and at the top of the boundary layer in (x, y, p) coordinates. Noting that $\omega \simeq -\rho g w$, $\omega_s = 0$, and $w_s = 0$, we can write

$$\rho_i g w_i \simeq \int_{p_i}^{p_s} (\nabla \cdot \mathbf{V})\, dp \tag{9.38}$$

where ρ_i is the density of the air at the top of the mixed layer. If we ignore the $\sim$ 10% decrease of density from the bottom to the top of the mixed layer, the hydrostatic pressure difference between the bottom and top of the layer can be written as

$$p_s - p_i \simeq \rho_i g (z_i - z_s)$$

Noting that $z_s = 0$, it follows that

$$\rho_i g \simeq (p_s - p_i) / z_i$$

and substituting into Eq. (9.38) we obtain Eq. (9.28).

Chapter 10

10.25 Using an approach analogous to the one used in Exercise 10.4, estimate the sensitivity of the climate system, comparing global-mean surface air temperature in the year 2000 with conditions at the time of the industrial revolution. Use this value to estimate the rise in surface air temperature that would result from a doubling of the atmospheric carbon dioxide concentration relative to the preindustrial value (280 ppmv), assuming that concentrations of other atmospheric constituents remain fixed at pre-industrial levels and sufficient time has elapsed for the large thermal reservoirs in the Earth system to equilibrate with the forcing.

Solution The analog of the expression used in Exercise 10.4 is

$$\lambda = \frac{T_s(2000) - T_s(1750)}{F(2000) - F(1750)} \tag{1}$$

where (1750) refers to conditions around the time of the industrial revolution. In representing dT_s/dF by the expression on the right-hand side it is assumed that T_s is in equilibrium with the forcing. Because more than half the greenhouse gas forcing since the industrial revolution occurred during the past half century, this expression needs to be modified to account for the transient character of the response. We can represent the transience by deducting from the denominator of Eq. (1) a flux equivalent to the rate of storage of heat in the oceans and the cryosphere; that is to say,

$$\lambda = \frac{T_s(2000) - T_s(1750)}{F(2000) - F(1750) - F(\text{storage})} \tag{2}$$

To estimate $F(\text{storage})$ we will draw upon the following observations and model calculations:

- the rate of warming throughout the depth of the oceans, as inferred from subsurface temperature observations, implies a globally averaged downward energy flux of $\sim$0.3 W m^{-2},
- the rate of melting of glaciers and continental ice sheets, as inferred from the freshening of the oceans, implies an additional downward flux of $\sim$0.3 W m^{-2},
- the rate of sea level rise during the 1990s that is attributable to the expansion of sea water ($\sim$1.5 mm year^{-1}) implies a downward flux of $\sim$0.8 W m^{-2},
- in several coupled climate models the imbalance in the net radiation at the top of the atmosphere due to the storage of heat in the Earth system was found to be $\sim$0.85 W m^{-2}.

On the basis of these data, we will assume that $F(\text{storage}) = 0.7$ W m^{-2}.

The incremental climate forcings F attributable to the various trace gases and aerosols injected into the atmosphere by human activities, as evaluated in the year 2000 [i.e., $F(2000) - F(1750]$ in the above expression, are given in Fig. 10.42. The forcing due to the buildup of greenhouse gases, including the partially cancelling changes in stratospheric and tropospheric ozone concentrations is $\sim$2.7 W m^{-2}. The effects of aerosols are much less certain. As a rough estimate we will use -1.0 W m^{-2}: -0.6 W m^{-2} for direct effects and -0.4 W m^{-2} for indirect effects.

The instrumental record of global-mean surface air temperature does not extend as far back as 1750, but the record shown in Fig. 10.44 provides an indication of the warming that has taken place from 1860 ($\sim$0.7 K).

Substituting these values into Eq. (2) we obtain

$$\lambda = \frac{0.7 \text{ K}}{(2.7 - 1.0) - 0.7 \text{ W m}^{-2}} = 0.70 \text{ K (W m}^{-2})^{-1}$$

On the basis of radiative transfer models it is estimated that a doubling of the atmospheric CO_2 concentration relative to its preindustrial value (280 W m^{-2}) would produce a climate forcing of 3.7 W m^{-2}. Based on the this estimate of the climate sensitivity, a doubling of the atmospheric CO_2 concentration would produce a rise in global mean surface air temperature of $3.7 \times 0.70 = 2.6$ K. This estimate is highly sensitive to choices of values assumed for the various terms in the expression for λ and is therefore subject to large uncertainty, as illustrated in the next exercise.