

Chapter 2 Thermodynamics

1. Mass of the atmosphere:

From the definitions of pressure and weight,

$$\text{mass} / \text{m}^2 = \frac{p}{g} = \frac{101325}{9.8} = 10340 \text{ kg}$$

$$\text{total mass} = 4\pi R^2 \frac{p}{g} = 5.272 \times 10^{18} \text{ kg}$$

2. Number of molecules per m^3

The mass (in kg) of an average molecule will be

$$m = 29 \times 1.66 \times 10^{-27} = 4.8 \times 10^{-26} \text{ kg}$$

Now determine the air density:

$$\rho = \frac{p}{RT} = \frac{10^5}{287 \times 293} = 1.19 \text{ kg m}^{-3}$$

Hence the number of molecules per unit volume

$$= \frac{\rho}{m} = \frac{1.19}{4.8 \times 10^{-26}} = 2.48 \times 10^{25} \text{ m}^{-3}$$

3. Molecular kinetic energy:

For a diatomic molecule such as O_2 we know that

$$\overline{KE} = 2.5 k_B T = 2.5 \times 1.38 \times 10^{-23} \times 250 = 8.625 \times 10^{-21} \text{ J}$$

Hence the average speed will be

$$\bar{v} = \sqrt{\frac{2\overline{KE}}{m}} = \left(\frac{2 \times 8.625 \times 10^{-21}}{2 \times 16 \times 1.66 \times 10^{-27}} \right)^{1/2} = 570 \text{ ms}^{-1}$$

4. Constant density atmosphere:

$$p = \frac{F}{A} = \frac{mg}{A} = \frac{V\rho g}{A} = \rho g H$$

where H is the height of our atmosphere. Hence

$$H = \frac{p}{\rho g} = \frac{101325}{1.25 \times 9.8} = 8.27 \text{ km}$$

5. Exponential model atmosphere:

$$\rho = \rho_0 e^{-z/H} \quad (\text{by assumption})$$

$$\begin{aligned} \therefore p &= \frac{mg}{A} = g \int_0^\infty \rho dz \\ &= -g \rho_0 H e^{-z/H} \Big|_0^\infty = g \rho_0 H \\ \therefore H &= \frac{p}{g \rho_0} = \frac{101325}{9.8 \times 1.25} = 8.27 \text{ km} \end{aligned}$$

6. Constant lapse rate model atmosphere:

$$T = T_0 - \Gamma z \quad (\text{by assumption})$$

Combining the hydrostatic equation and the gas law gives

$$\frac{dp}{p} = -\frac{g}{RT} dz = -\frac{g}{R(T_0 - \Gamma z)} dz$$

Integrating from p_0 to p (a variable), corresponding to 0 to z , gives

$$\ln \frac{p}{p_0} = -\frac{g}{R} \int_0^z \frac{dz'}{T_0 - \Gamma z'} = \frac{g}{R\Gamma} \ln \left(\frac{T_0 - \Gamma z}{T_0} \right)$$

Hence

$$z = \frac{T_0}{\Gamma} \left\{ 1 - \left(\frac{p}{p_0} \right)^{R\Gamma/g} \right\}$$

7. Mars atmosphere scale height:

We need the gas constant for carbon dioxide, of molecular weight 44:

$$R_{CO_2} = \frac{R^*}{M_{CO_2}} = \frac{8314.3}{44} = 189 \text{ J kg}^{-1} \text{ K}^{-1}$$

Hence

$$H = \frac{RT}{g} = \frac{189 \times 220}{3.8} = 10.9 \text{ km}$$

8. Layer mean temperatures:

$$Z_2 - Z_1 = \frac{R\bar{T}}{g_0} \ln(p_1 / p_2)$$

So, at 30°, where the height is 5500 m,

$$\therefore \bar{T} = \frac{g_0}{R} \frac{Z_2 - Z_1}{\ln(p_1 / p_2)} = \frac{9.8}{287} \times \frac{5900}{\ln(2)} = 291 \text{ K} = 18^\circ \text{C}$$

A similar calculation gives a temperature of 270 K at 70°.

9. Layer thickness:

We start with the same equation as for the previous problem:

$$Z_2 - Z_1 = \frac{R\bar{T}}{g_0} \ln(p_1 / p_2) = \frac{287 \times 278}{9.8} \ln\left(\frac{1000}{900}\right) = 858 \text{ m}$$

10. Average atmospheric temperature:

When $Z_2 - Z_1 = 16000 \text{ m}$, we know that $p_2 / p_1 = 0.1$. Hence

$$\bar{T} = \frac{g_0}{R} \frac{Z_2 - Z_1}{\ln(p_1 / p_2)} = \frac{9.8}{287} \frac{16000}{\ln(10)} = 237 \text{ K}$$

11. 1 kg of air at 17 °C rises from 1000 to 750 hPa:

(a) When the process is isothermal, T is constant, so that

$$W = \int p dV = \int \frac{mRT}{V} dV = mRT \ln\left(\frac{V_f}{V_i}\right)$$

Now, for constant T , the ideal gas equation tells us that $V_f / V_i = p_i / p_f$. Hence

$$W = 1 \times 287 \times 280 \times \ln(0.75) = -23 \text{ kJ}$$

Because the process is isothermal, internal energy is unchanged. Hence, by conservation of energy, the heat added must be 23 kJ.

(b) When the process is adiabatic, $\Delta q = 0$. Hence we may use Equation 2.46:

$$T = T_0 \left(\frac{p}{p_0}\right)^\kappa = 280 \left(\frac{750}{1000}\right)^{0.286} = 258 \text{ K}$$

The work done will equal the decrease in internal energy; that is

$$W = c_p \Delta T = 1004.5 \times (280 - 258) = 22 \text{ kJ}$$

12. Radiative heat loss:

The total heat loss (per square metre) will be

$$\Delta Q = 50 \times 8 \times 60 \times 60 = 1.44 \times 10^6 \text{ J m}^{-2}$$

This heat is drawn from a mass of M which cools (at constant pressure) by ΔT : hence

$$\Delta Q = M c_p \Delta T$$

Now the mass of air (per square metre) in 30 hPa = $3000/9.8 = 306 \text{ kg/m}^2$. Thus

$$\Delta T = \frac{\Delta Q}{M c_p} = \frac{1.44 \times 10^6}{306 \times 1004.5} = 4.7^\circ$$

When some heat is drawn from the ground we now have

$$\Delta Q = \{(M c_p)_{air} + (M' c)_{gr}\} \Delta T$$

$$\text{Hence } \Delta T = \frac{1.44 \times 10^6}{306 \times 1004.5 + 2000 \times 2000 \times 0.2} = 1.3^\circ$$

13. Variations on the Poisson relation:

Using Equation 2.45) plus the ideal gas equation, we see that

$$\frac{T}{T_0} = \left(\frac{p}{p_0} \right)^\kappa = \left(\frac{\rho R T}{\rho_0 R T_0} \right)^\kappa = \left(\frac{T}{T_0} \right)^\kappa \left(\frac{\rho}{\rho_0} \right)^\kappa$$

$$\text{Hence } \frac{T}{T_0} = \left(\frac{\rho}{\rho_0} \right)^{\kappa/1-\kappa} = \left(\frac{\rho}{\rho_0} \right)^{\gamma-1} \quad [\text{using } \kappa = (\gamma - 1)/\gamma]$$

$$\text{Similarly } \left(\frac{p}{p_0} \right)^\kappa = \frac{T}{T_0} = \frac{p/R\rho}{p_0/R\rho_0} = \left(\frac{p}{p_0} \right) \left(\frac{\rho_0}{\rho} \right) \quad \text{etc.}$$

14. Depressurization:

The process will be adiabatic, so we may use Equation 2.45:

$$T = T_0 \left(\frac{p}{p_0} \right)^{0.286} = 295 \left(\frac{350}{850} \right)^{0.286} = 229 \text{ K} = -44^\circ \text{C}$$

15. Chinook:

We may assume that the air warms at the dry adiabatic lapse rate, so

$$\Delta T = 9.8 \times (4.2 - 1.5) = 26.5^\circ \text{C}$$

Hence final temperature = $-10^\circ \text{C} + 26.5^\circ \text{C} = 16.5^\circ \text{C}$.

16. Virtual temperature:

Using Equation 2.53 as our definition,

$$T_v = (1 + 0.61r)T = (1 + 0.61 \times 0.015) \times 305 = 307.8 \text{ K} = 34.8^\circ \text{C}$$

17. Energy extracted from the oceans:

Information required: oceans cover $\sim 70\%$ of the Earth's surface; specific heat for liquid water, $c = 4180 \text{ J/kg}$; density of water, $\rho = 1000 \text{ kg/m}^3$; $R_E = 6370 \text{ km}$.

$$\text{Energy} = mc\Delta T = (0.7 \times 4\pi R_E^2 \times h) \times 4180 \times 0.1 \cong 1.5 \times 10^{20} \text{ J}$$

18. Carnot equations:

For an adiabatic expansion we may use the same approach as Exercise 2.11 (a), which will give us both Equations 2.56 and 2.57.

For the two isothermal processes, the ideal gas equation tells us that

$$p_A V_A = p_B V_B \quad \text{and} \quad p_C V_C = p_D V_D$$

And again for the two adiabatic processes we may use the Poisson-like relation

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \quad \text{and} \quad T_D V_D^{\gamma-1} = T_A V_A^{\gamma-1}$$

Now divide the first of these by the second, remembering that

$$T_1 = T_A = T_B \quad \text{and} \quad T_2 = T_C = T_D$$

gives
$$\frac{T_B V_B^{\gamma-1}}{T_A V_A^{\gamma-1}} = \frac{T_C V_C^{\gamma-1}}{T_D V_D^{\gamma-1}} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Combining the results obtained so far immediately gives Equation 2.59

19. Temperature-dependent latent heat:

Picking up the analysis following Equation 2.77 we see that

$$\frac{de_s}{e_s} = \left(\frac{L_1}{R_v T^2} + \frac{L_2}{R_v T} \right) dT$$

Integrating as before, from fixed conditions (0 °C) to a variable T gives

$$\ln\left(\frac{e_s}{6.11}\right) = \frac{L_1}{R_v} \left(\frac{1}{273} - \frac{1}{T} \right) + \frac{L_2}{R_v} \ln\left(\frac{T}{273}\right)$$

Exponentiating both sides then gives

$$e_s = 6.11 \exp \left\{ \frac{L_1}{R_v} \left[\frac{1}{273} - \frac{1}{T} \right] \right\} \left(\frac{T}{273} \right)^{L_2/R_v}$$

Suggested follow-on Exercise.

Use the values for latent heat at 273 K and 373 K to determine L_1 and L_2 ; then use the resulting formula to calculate the s. v. p. at 20 °C and 35 °C, and compare your results with those from Exercise 2.22.

Solution: $L_1 = 3182.5 \text{ kJ kg}^{-1}$, $L_2 = -2.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$: at 35 °C, $e_s = 56.09 \text{ hPa}$.

20. Perspiration cooling:

A reasonable value for the specific heat of the person is 3470 J/kg. Then

$$\text{Heat lost via evaporation} = m_L L$$

$$\text{Heat lost during cooling} = M c \Delta T$$

$$\text{Equating these gives } m_L L = M c \Delta T$$

$$\text{Thus } \frac{m_L}{M} = \frac{c \Delta T}{L} = \frac{3470 \times 5}{2.25 \times 10^6} = 7.7 \times 10^{-3} \sim 1\%$$

In reality our core temperature does not vary this much, and it's mainly our skin which needs to cool, so the ratio would be very much smaller.

21. Isothermal compression of moist air:

From Table 2.1, the s. v. p. at 20 °C is 23.3712 hPa, so at 60% RH the actual vapour pressure will be $0.6 \times 23.3712 = 14.02272$ hPa. Under an isothermal compression this will increase to $5 \times 14.02272 = 70.1136$ hPa. Since this exceeds the s. v. p., the excess will condense: this equates to $70.1136 - 23.3712 = 46.7424$ hPa. Now this is equal to two-thirds of the original amount of water vapour. (This conclusion could, of course, be reached by a more direct, 'ratio' argument.)

To find the condensed mass we need to find the original mass of water vapour. The (mass) mixing ratio is given by

$$r = \frac{m_v}{m_d} = \varepsilon \frac{e}{p} = 0.622 \frac{14.02272}{1013.25} = 8.61 \times 10^{-3} \text{ g/g}$$

To find the dry mass in question we use the ideal gas equation:

$$m_d = \frac{pV}{RT} = \frac{101325 \times 20 \times 10^{-3}}{287.05 \times 293} = 2.41 \times 10^{-2} \text{ kg}$$

So finally, the amount of water which condenses will be

$$m_c = \frac{2}{3} r m_d = \frac{2}{3} \times 8.61 \times 10^{-3} \times 2.41 \times 10^{-2} = 1.38 \times 10^{-4} \text{ kg} = 0.138 \text{ g}$$

22. Using Clausius-Clapeyron:

At 20 °C, where the tabulated value is 23.37 hPa, we calculate a value of

$$e_s = 6.11 \exp \left\{ \frac{L}{R_v} \left[\frac{1}{273} - \frac{1}{T} \right] \right\} = 6.11 \exp \left\{ \frac{2.5 \times 10^6}{461.5} \left[\frac{1}{273} - \frac{1}{293} \right] \right\} = 23.67 \text{ hPa}$$

Similarly, at 35 °C we calculate 58.17 hPa, compared with 56.24 hPa.

Over liquid water at -20 °C we calculate 1.2665 hPa, compared with 1.2539 hPa.

Over ice at -20 °C, we calculate 1.0326 hPa, where the tabulated value is 1.0317 hPa.

23. Boiling point from Clausius-Clapeyron:

At standard pressure, the C-C equation gives

$$1013.25 = 6.11 \exp \left\{ \frac{L}{R_v} \left[\frac{1}{273} - \frac{1}{T} \right] \right\} = 6.11 \exp \left\{ 5417 \left[\frac{1}{273} - \frac{1}{T} \right] \right\}$$

So
$$5417 \left(\frac{1}{273} - \frac{1}{T} \right) = \ln \left(\frac{1013.25}{6.11} \right) = 5.111$$

Solving for T gives $367.7 \text{ K} = 94.7 \text{ }^\circ\text{C}$.

At Denver, assuming $p = 850 \text{ hPa}$, we obtain $90.4 \text{ }^\circ\text{C}$.

On Mt Everest, assuming $p = 310 \text{ hPa}$, we obtain $67.4 \text{ }^\circ\text{C}$.

24. Altitude dependence of boiling point:

We need to combine the stated pressure relation with the C.-C. Equation:

$$1013.25 \exp(-z/H) = 6.11 \exp \left\{ \frac{L}{R_v} \left(\frac{1}{273} - \frac{1}{T_b} \right) \right\}$$

Hence
$$\frac{L}{R_v} \left(\frac{1}{273} - \frac{1}{T_b} \right) + \frac{z}{H} = \ln \left(\frac{1013.25}{6.11} \right) = 5.111$$

Thus
$$\frac{L}{R_v} \frac{1}{T_b} = \frac{L}{273 R_v} - 5.111 + \frac{z}{H} = \frac{5417}{273} - 5.111 + \frac{z}{H}$$

So finally
$$T_b = \frac{L/R_v}{a + z/H}$$

where $a = 19.84 - 5.11 = 14.73$

At sea level $T_b = \frac{5417}{14.73} = 367.75 \text{ K} = 94.75 \text{ }^\circ\text{C}$

For Denver $T_b = \frac{5417}{14.73 + (1.5/8.5)} = \frac{5417}{14.91} = 363.4 \text{ K} = 90.4 \text{ }^\circ\text{C}$

Note that both are in agreement with Exercise 2.23.

25. Neglected term in Equation 2.82:

We need to consider the ratio of the neglected term to the retained term:

$$\frac{\varepsilon e_s p}{p^2 T} \bigg/ \frac{\varepsilon e_s L}{p R_v T^2} = \frac{R_v T}{L} = \frac{T}{5417} \approx \frac{270}{5400} = 0.05$$

where we have taken a typical low to middle tropospheric value of $T = 270 \text{ K}$ for “arithmetical convenience”.