

Figure C.4 The electromagnetic spectrum and its classification into regions (the boundaries are not precise).

The functions that describe the oscillating electric field, $\mathcal{E}(x,t)$, and magnetic field, $\mathcal{B}(x,t)$, travelling along the x -direction with wavelength λ and frequency ν are

$$\mathcal{E}(x,t) = \mathcal{E}_0 \cos\left\{\left(\frac{2\pi}{\lambda}\right)x - 2\pi\nu t + \phi\right\} \quad \begin{array}{l} \text{Electro-} \\ \text{magnetic} \\ \text{radiation} \end{array} \quad \begin{array}{l} \text{Electric} \\ \text{field} \end{array} \quad (\text{C.6a})$$

$$\mathcal{B}(x,t) = \mathcal{B}_0 \cos\left\{\left(\frac{2\pi}{\lambda}\right)x - 2\pi\nu t + \phi\right\} \quad \begin{array}{l} \text{Electro-} \\ \text{magnetic} \\ \text{radiation} \end{array} \quad \begin{array}{l} \text{Magnetic} \\ \text{field} \end{array} \quad (\text{C.6b})$$

where \mathcal{E}_0 and \mathcal{B}_0 are the amplitudes of the electric and magnetic fields, respectively, and ϕ is the phase of the wave. In this case the amplitude is a vector quantity, because the electric and magnetic fields have direction as well as amplitude. The magnetic field is

perpendicular to the electric field and both are perpendicular to the propagation direction (Fig. C.5). According to classical electromagnetic theory, the **intensity** of electromagnetic radiation, a measure of the energy associated with the wave, is proportional to the square of the amplitude of the wave.

Equation C.6 describes electromagnetic radiation that is **plane polarized**; it is so called because the electric and magnetic fields each oscillate in a single plane. The plane of polarization may be orientated in any direction around the direction of propagation. An alternative mode of polarization is **circular polarization**, in which the electric and magnetic fields rotate around the direction of propagation in either a clockwise or an anticlockwise sense but remain perpendicular to it and to each other (Fig. C.6).

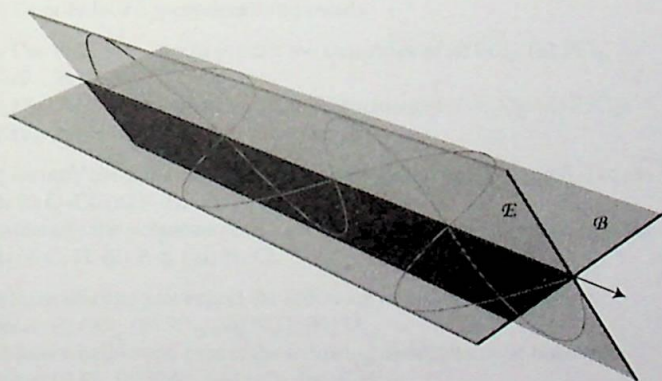


Figure C.5 In a plane polarized wave, the electric and magnetic fields oscillate in orthogonal planes and are perpendicular to the direction of propagation.

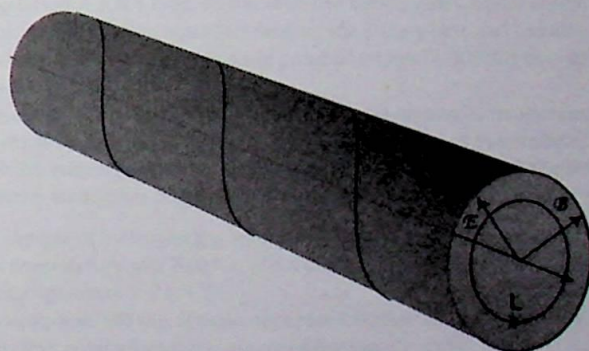


Figure C.6 In a circularly polarized wave, the electric and magnetic fields rotate around the direction of propagation but remain perpendicular to one another. The illustration also defines 'right' and 'left-handed' polarizations ('left-handed' polarization is shown as L).

Checklist of concepts

- 1. A wave is an oscillatory disturbance that travels through space.
- 2. A harmonic wave is a wave with a displacement that can be expressed as a sine or cosine function.

- 3. A harmonic wave is characterized by a **wavelength, frequency, phase, and amplitude**.
- 4. **Destructive interference** between two waves of the same wavelength but different phases leads to a resultant wave with diminished amplitude.
- 5. **Constructive interference** between two waves of the same wavelength and phase leads to a resultant wave with enhanced amplitude.
- 6. The **electromagnetic field** is an oscillating electric and magnetic disturbance that spreads as a harmonic wave through space.
- 7. An **electric field** acts on charged particles (whether stationary or moving).
- 8. A **magnetic field** acts only on moving charged particles.
- 9. In **plane polarized** electromagnetic radiation, the electric and magnetic fields each oscillate in a single plane and are mutually perpendicular.
- 10. In **circular polarization**, the electric and magnetic fields rotate around the direction of propagation in either a clockwise or an anticlockwise sense but remain perpendicular to it and each other.

Checklist of equations

Property	Equation	Comment	Equation number
Relation between the frequency and wavelength	$\lambda\nu = v$	For electromagnetic radiation in a vacuum, $v = c$	C.1
Refractive index	$n_r = c/c'$	Definition; $n_r \geq 1$	C.4
Wavenumber	$\tilde{\nu} = \nu/c = 1/\lambda$	Electromagnetic radiation	C.5

FOUNDATIONS

TOPIC A Matter

Discussion questions

A.1 Summarize the features of the nuclear model of the atom. Define the terms atomic number, nucleon number, and mass number.

A.2 Where in the periodic table are metals, non-metals, transition metals, lanthanoids, and actinoids found?

A.3 Summarize what is meant by a single bond and a multiple bond.

A.4 Summarize the principal concepts of the VSEPR theory of molecular shape.

A.5 Compare and contrast the properties of the solid, liquid, and gas states of matter.

Exercises

A.1(a) Express the typical ground-state electron configuration of an atom of an element in (i) Group 2, (ii) Group 7, (iii) Group 15 of the periodic table.

A.1(b) Express the typical ground-state electron configuration of an atom of an element in (i) Group 3, (ii) Group 5, (iii) Group 13 of the periodic table.

A.2(a) Identify the oxidation numbers of the elements in (i) MgCl_2 , (ii) FeO , (iii) Hg_2Cl_2 .

A.2(b) Identify the oxidation numbers of the elements in (i) CaH_2 , (ii) CaC_2 , (iii) LiN_3 .

A.3(a) Identify a molecule with a (i) single, (ii) double, (iii) triple bond between a carbon and a nitrogen atom.

A.3(b) Identify a molecule with (i) one, (ii) two, (iii) three lone pairs on the central atom.

A.4(a) Draw the Lewis (electron dot) structures of (i) SO_3^{2-} , (ii) XeF_4 , (iii) P_4 .

A.4(b) Draw the Lewis (electron dot) structures of (i) O_3 , (ii) ClF_3^+ , (iii) N_3^- .

A.5(a) Identify three compounds with an incomplete octet.

A.5(b) Identify four hypervalent compounds.

A.6(a) Use VSEPR theory to predict the structures of (i) PCl_3 , (ii) PCl_5 , (iii) XeF_2 , (iv) XeF_4 .

A.6(b) Use VSEPR theory to predict the structures of (i) H_2O_2 , (ii) FSO_3^- , (iii) KrF_2 , (iv) PCl_4^+ .

A.7(a) Identify the polarities (by attaching partial charges $\delta+$ and $\delta-$) of the bonds (i) C–Cl, (ii) P–H, (iii) N–O.

A.7(b) Identify the polarities (by attaching partial charges $\delta+$ and $\delta-$) of the bonds (i) C–H, (ii) P–S, (iii) N–Cl.

A.8(a) State whether you expect the following molecules to be polar or nonpolar: (i) CO_2 , (ii) SO_2 , (iii) N_2O , (iv) SF_4 .

A.8(b) State whether you expect the following molecules to be polar or nonpolar: (i) O_3 , (ii) XeF_2 , (iii) NO_2 , (iv) C_6H_{14} .

A.9(a) Arrange the molecules in Exercise A.8(a) by increasing dipole moment.

A.9(b) Arrange the molecules in Exercise A.8(b) by increasing dipole moment.

A.10(a) Classify the following properties as extensive or intensive: (i) mass, (ii) mass density, (iii) temperature, (iv) number density.

A.10(b) Classify the following properties as extensive or intensive: (i) pressure, (ii) specific heat capacity, (iii) weight, (iv) molality.

A.11(a) Calculate (i) the amount of $\text{C}_2\text{H}_5\text{OH}$ (in moles) and (ii) the number of molecules present in 25.0 g of ethanol.

A.11(b) Calculate (i) the amount of $\text{C}_6\text{H}_{12}\text{O}_6$ (in moles) and (ii) the number of molecules present in 5.0 g of glucose.

A.12(a) Calculate (i) the mass, (ii) the weight on the surface of the Earth (where $g = 9.81 \text{ m s}^{-2}$) of 10.0 mol $\text{H}_2\text{O}(\text{l})$.

A.12(b) Calculate (i) the mass, (ii) the weight on the surface of Mars (where $g = 3.72 \text{ m s}^{-2}$) of 10.0 mol $\text{C}_6\text{H}_6(\text{l})$.

A.13(a) Calculate the pressure exerted by a person of mass 65 kg standing (on the surface of the Earth) on shoes with soles of area 150 cm^2 .

A.13(b) Calculate the pressure exerted by a person of mass 60 kg standing (on the surface of the Earth) on shoes with stiletto heels of area 2 cm^2 (assume that the weight is entirely on the heels).

A.14(a) Express the pressure calculated in Exercise A.13(a) in atmospheres.

A.14(b) Express the pressure calculated in Exercise A.13(b) in atmospheres.

A.15(a) Express a pressure of 1.45 atm in (i) pascal, (ii) bar.

A.15(b) Express a pressure of 222 atm in (i) pascal, (ii) bar.

A.16(a) Convert blood temperature, 37.0°C , to the Kelvin scale.

A.16(b) Convert the boiling point of oxygen, 90.18 K , to the Celsius scale.

A.17(a) Equation A.4 is a relation between the Kelvin and Celsius scales.

Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol (78.5°C) in degrees Fahrenheit.

A.17(b) The Rankine scale is a version of the thermodynamic temperature scale in which the degrees ($^\circ\text{R}$) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

A.18(a) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0°C . What can its pressure be expected to be when the temperature is 7.0°C ?

A.18(b) A sample of 325 mg of neon occupies 2.00 dm^3 at 20.0°C . Use the perfect gas law to calculate the pressure of the gas.

A.19(a) At 500°C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m^{-3} . What is the molecular formula of sulfur under these conditions?

A.19(b) At 100°C and 16.0 kPa, the mass density of phosphorus vapour is 0.6388 kg m^{-3} . What is the molecular formula of phosphorus under these conditions?

A.20(a) Calculate the pressure exerted by 22 g of ethane behaving as a perfect gas when confined to 1000 cm^3 at 25.0°C .

A.20(b) Calculate the pressure exerted by 7.05 g of oxygen behaving as a perfect gas when confined to 100 cm^3 at 100.0°C .

A.21(a) A vessel of volume 10.0 dm^3 contains 2.0 mol H_2 and 1.0 mol N_2 at 5.0°C . Calculate the partial pressure of each component and their total pressure.

A.21(b) A vessel of volume 100 cm^3 contains 0.25 mol O_2 and 0.034 mol CO_2 at 10.0°C . Calculate the partial pressure of each component and their total pressure.

TOPIC B Energy

Discussion questions

- B.1** What is energy?
- B.2** Distinguish between kinetic and potential energy.
- B.3** State the Second Law of thermodynamics. Can the entropy of the system that is not isolated from its surroundings decrease during a spontaneous process?

Exercises

- B.1(a)** A particle of mass 1.0 g is released near the surface of the Earth, where the acceleration of free fall is $g = 9.81 \text{ m s}^{-2}$. What will be its speed and kinetic energy after (i) 1.0 s, (ii) 3.0 s. Ignore air resistance.
- B.1(b)** The same particle in Exercise B.1(a) is released near the surface of Mars, where the acceleration of free fall is $g = 3.72 \text{ m s}^{-2}$. What will be its speed and kinetic energy after (i) 1.0 s, (ii) 3.0 s. Ignore air resistance.
- B.2(a)** An ion of charge ze moving through water is subject to an electric field of strength \mathcal{E} which exerts a force $ze\mathcal{E}$, but it also experiences a frictional drag proportional to its speed s and equal to $6\pi\eta Rs$, where R is its radius and η (eta) is the viscosity of the medium. What will be its terminal velocity?
- B.2(b)** A particle descending through a viscous medium experiences a frictional drag proportional to its speed s and equal to $6\pi\eta Rs$, where R is its radius and η (eta) is the viscosity of the medium. If the acceleration of free fall is denoted g , what will be the terminal velocity of a sphere of radius R and mass density ρ ?
- B.3(a)** Confirm that the general solution of the harmonic oscillator equation of motion ($m\text{d}^2x/\text{d}t^2 = -kx$) is $x(t) = A \sin \omega t + B \cos \omega t$ with $\omega = (k/m)^{1/2}$.
- B.3(b)** Consider a harmonic oscillator with $B = 0$ (in the notation of Exercise B.3(a)); relate the total energy at any instant to its maximum displacement amplitude.
- B.4(a)** The force constant of a C–H bond is about 450 N m^{-1} . How much work is needed to stretch the bond by (i) 10 pm, (ii) 20 pm?
- B.4(b)** The force constant of the H–H bond is about 510 N m^{-1} . How much work is needed to stretch the bond by 20 pm?
- B.5(a)** An electron is accelerated in an electron microscope from rest through a potential difference $\Delta\phi = 100 \text{ kV}$ and acquires an energy of $e\Delta\phi$. What is its final speed? What is its energy in electronvolts (eV)?
- B.5(b)** A $\text{C}_6\text{H}_4^{2+}$ ion is accelerated in a mass spectrometer from rest through a potential difference $\Delta\phi = 20 \text{ kV}$ and acquires an energy of $e\Delta\phi$. What is its final speed? What is its energy in electronvolts (eV)?
- B.6(a)** Calculate the work that must be done in order to remove a Na^+ ion from 200 pm away from a Cl^- ion to infinity (in a vacuum). What work would be needed if the separation took place in water?
- B.6(b)** Calculate the work that must be done in order to remove an Mg^{2+} ion from 250 pm away from an O^{2-} ion to infinity (in a vacuum). What work would be needed if the separation took place in water?
- B.7(a)** Calculate the electric potential due to the nuclei at a point in a LiH molecule located at 200 pm from the Li nucleus and 150 pm from the H nucleus.
- B.7(b)** Plot the electric potential due to the nuclei at a point in a Na^+Cl^- ion pair located on a line half way between the nuclei (the internuclear separation is 283 pm) as the point approaches from infinity and ends at the mid-point between the nuclei.
- B.8(a)** An electric heater is immersed in a flask containing 200 g of water, and a current of 2.23 A from a 15.0 V supply is passed for 12.0 minutes. How much energy is supplied to the water? Estimate the rise in temperature (for water, $C = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$).

B.4 What is meant by quantization of energy? In what circumstances are the effects of quantization most important for microscopic systems?

B.5 What are the assumptions of the kinetic molecular theory?

B.6 What are the main features of the Maxwell–Boltzmann distribution of sp

B.8(b) An electric heater is immersed in a flask containing 150 g of ethanol and a current of 1.12 A from a 12.5 V supply is passed for 172 s. How much energy is supplied to the ethanol? Estimate the rise in temperature (for ethanol, $C = 111.5 \text{ J K}^{-1} \text{ mol}^{-1}$).

B.9(a) The heat capacity of a sample of iron was 3.67 J K^{-1} . By how much would its temperature rise if 100 J of energy were transferred to it as heat?

B.9(b) The heat capacity of a sample of water was 5.77 J K^{-1} . By how much would its temperature rise if 50.0 kJ of energy were transferred to it as heat?

B.10(a) The molar heat capacity of lead is $26.44 \text{ J K}^{-1} \text{ mol}^{-1}$. How much energy must be supplied (by heating) to 100 g of lead to increase its temperature by 10.0°C ?

B.10(b) The molar heat capacity of water is $75.2 \text{ J K}^{-1} \text{ mol}^{-1}$. How much energy must be supplied by heating to 10.0 g of water to increase its temperature by 10.0°C ?

B.11(a) The molar heat capacity of ethanol is $111.46 \text{ J K}^{-1} \text{ mol}^{-1}$. What is its specific heat capacity?

B.11(b) The molar heat capacity of sodium is $28.24 \text{ J K}^{-1} \text{ mol}^{-1}$. What is its specific heat capacity?

B.12(a) The specific heat capacity of water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$. What is its molar heat capacity?

B.12(b) The specific heat capacity of copper is $0.384 \text{ J K}^{-1} \text{ g}^{-1}$. What is its molar heat capacity?

B.13(a) By how much does the molar enthalpy of hydrogen gas differ from its molar internal energy at 1000°C ? Assume perfect gas behaviour.

B.13(b) The mass density of water is 0.997 g cm^{-3} . By how much does the molar enthalpy of water differ from its molar internal energy at 298 K ?

B.14(a) Which do you expect to have the greater entropy at 298 K and 1 bar, liquid water or water vapour?

B.14(b) Which do you expect to have the greater entropy at 0°C and 1 atm, liquid water or ice?

B.15(a) Which do you expect to have the greater entropy, 100 g of iron at 300 K or 3000 K ?

B.15(b) Which do you expect to have the greater entropy, 100 g of water at 0°C or 100°C ?

B.16(a) Give three examples of a system that is in dynamic equilibrium.

B.16(b) Give three examples of a system that is in static equilibrium.

B.17(a) Suppose two states differ in energy by 1.0 eV (electronvolts, see inside the front cover); what is the ratio of their populations at (a) 300 K , (b) 3000 K ?

B.17(b) Suppose two states differ in energy by 2.0 eV (electronvolts, see inside the front cover); what is the ratio of their populations at (a) 200 K , (b) 2000 K ?

B.18(a) Suppose two states differ in energy by 1.0 eV, what can be said about their populations when $T = 0$?

B.18(b) Suppose two states differ in energy by 1.0 eV, what can be said about their populations when the temperature is infinite?

B.19(a) A typical vibrational excitation energy of a molecule corresponds to a wavenumber of 2500 cm^{-1} (convert to an energy separation by multiplying by hc ; see *Foundations C*). Would you expect to find molecules in excited vibrational states at room temperature (20°C)?

B.19(b) A typical rotational excitation energy of a molecule corresponds to a frequency of about 10 GHz (convert to an energy separation by multiplying by h ; see *Foundations C*). Would you expect to find gas-phase molecules in excited rotational states at room temperature (20°C)?

B.20(a) Suggest a reason why most molecules survive for long periods at room temperature.

B.20(b) Suggest a reason why the rates of chemical reactions typically increase with increasing temperature.

B.21(a) Calculate the relative mean speeds of N_2 molecules in air at 0°C and 40°C .

B.21(b) Calculate the relative mean speeds of CO_2 molecules in air at 20°C and 30°C .

B.22(a) Calculate the relative mean speeds of N_2 and CO_2 molecules in air.

B.22(b) Calculate the relative mean speeds of Hg_2 and H_2 molecules in a gaseous mixture.

B.23(a) Use the equipartition theorem to calculate the contribution of translational motion to the internal energy of 5.0 g of argon at 25°C .

B.23(b) Use the equipartition theorem to calculate the contribution of translational motion to the internal energy of 10.0 g of helium at 30°C .

B.24(a) Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of (i) carbon dioxide, (ii) methane at 20°C ; take into account translation and rotation but not vibration.

B.24(b) Use the equipartition theorem to calculate the contribution to the total internal energy of a sample of 10.0 g of lead at 20°C , taking into account the vibrations of the atoms.

B.25(a) Use the equipartition theorem to compute the molar heat capacity of argon.

B.25(b) Use the equipartition theorem to compute the molar heat capacity of helium.

B.26(a) Use the equipartition theorem to estimate the heat capacity of (i) carbon dioxide, (ii) methane.

B.26(b) Use the equipartition theorem to estimate the heat capacity of (i) water vapour, (ii) lead.

TOPIC C Waves

Discussion questions

C.1 How many types of wave motion can you identify?

C.2 What is the wave nature of the sound of a sudden 'bang'?

Exercises

C.1(a) What is the speed of light in water if the refractive index of the latter is 1.33 ?

C.1(b) What is the speed of light in benzene if the refractive index of the latter is 1.52 ?

C.2(a) The wavenumber of a typical vibrational transition of a hydrocarbon is 2500 cm^{-1} . Calculate the corresponding wavelength and frequency.

C.2(b) The wavenumber of a typical vibrational transition of an O-H bond is 3600 cm^{-1} . Calculate the corresponding wavelength and frequency.

Integrated activities

F.1 In Topic 1B we show that for a perfect gas the fraction of molecules that have a speed in the range v to $v + dv$ is $f(v)dv$, where

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

is the Maxwell-Boltzmann distribution (eqn 1B.4). Use this expression and mathematical software, a spreadsheet, or the *Living graphs* on the web site of this book for the following exercises:

(a) Refer to the graph in Fig. B.6. Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K .

(b) Evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K .

F.2 Based on your observations from Problem F.1, provide a molecular interpretation of temperature.