**Answers to Problems and Exercises**

**Chapter 1**

*Answers to introductory questions*

*What is colour?*

Colour is the sensory perception noted when light of a certain wavelength impinges upon the retina in the eye. For theoretical purposes light can be treated as an electromagnetic wave with a wavelength falling between the approximate ranges of 400 and 700 nm or as a stream of photons each with energy in the range 2.95 × 10-19 J (1.65 eV) – 3.61 × 10-19 J (2.25 eV). When light at the long wavelength end of the visible spectrum, (650 – 700 nm) is seen it is given the name red. Thereafter, as the wavelength stimulating the eye decreases the colour names change in the order orange, yellow, green, blue, indigo until violet is reached at the short wavelength (380 – 400 nm) end of the wavelength range.

*Why do hot objects become red or white hot?*

Hot objects emit a wide range of wavelengths across the electromagnetic spectrum, extending far beyond the sensitivity of the eye for both longer and shorter wavelengths. As the temperature of the body increases the wavelength with maximum intensity shortens. For a body at room temperature the peak wavelength is in the infrared, far beyond the visisble spectrum. When the temperature of the body reaches about 1000 K the range of wavelengths emitted has a short wavelength tail which creeps into the red end of the visible spectrum and the body is seen to be a dull red colour, or red hot. As the temperature increases, the wavelength of maximum intensity moves into the visible. The colour observed changes from dull red to bright red, orange, and then yellow. When the peak wavelength in close to the yellow region of the spectrum, the body looks white to the eye and is said to be white hot. Hot bodies that emit visible radiation are said to be incandescent.

*How does laser light differ from light from the sun?*

The word *laser* is an acronym for the expression *light amplification by stimulated emission of radiation*. Laser light is thus produced by the process of stimulated emission. In this process, atoms in a single excited energy state are triggered to lose energy by passing photons of the same energy. This results in the emission of a virtually monochromatic (single wavelength) beam. Light from the sun is produced by incandescence. The emission from an incandescent solid is due to spontaneous emission, in which a large number of excited atoms with a large range of populated energy levels, emit radiation at random. This gives rise to a continuous emission spectrum, centred on a peak wavelength and extending over a continuous wavelength range. For the sun, this emission peaks in the green region of the visible spectrum, but extends well into the ultraviolet and infrared wavelengths

A further important difference is that light form a laser is usually polarised and coherent – that is, all the waves are in step, and interference effects are readily observed when the light falls on a suitable object. Light from the sun is incoherent, consisting of short bursts of radiation that have a random phase and polarisation compared with those bursts that precede and succeed it, making interference effects difficult to observe unless special efforts are made.

*Quick Quiz*

1 (b); 2 (a); 3 (a); 4 (b); 5 (c); 6 (a); 7 (c); 8 (b); 9 (b); 10 (c)

*Problems and Exercises*

1.1 (a) 4.64 × 10-19 J, 2.90 eV; (b) 3.98 × 10-19 J, 2.48 eV; (c) 3.31 × 10-19 J, 2.07 eV; (d) 2.65 × 10-19 J, 1.65 eV

1.2 = 556 × 10-9 m, *E* = 3.57 × 10-19 J = 2.23 eV

= 407 × 10-9 m, *E* = 4.88 × 10-19 J = 3.05 eV

= 694.3 × 10-9 m, *E* = 2.86 × 10-19 J = 1.79 eV

1.3 (a) 0.002898 m K; (b) (max) = 828 nm in the infrared; the tail moves into the long wavelength (red) end of the spectrum, to give the star a red hue; (c) ~5000 K.

1.4 The temperatures are irrelevant. The colour is due to pigments, notably iron oxide and related minerals. This absorbs in the blue-green part of the spectrum leaving Mars looking red by subtractive coloration.

1.5 These are additive primaries and would look white from a distance. When they are blended together they would appear black (probably nearer to muddy dark brown in practice) as they each absorb complementary parts of the spectrum.

1.6 (a) 1.99 × 10-15 J, 12.40 eV; (b) 3.97 × 10-19 J, 2.48 eV; (c) 3.97 × 10-22 J, 2.48 × 10-3 eV; (d) 3.97 × 10-25 J, 2.48 × 10-6 eV; (e) 1.99 × 10-27 J, 1.24 × 10-8 eV

1.7 (a) orange, 49.6%, cyan 50.4%; (b) violet, 41.7%, yellow 58.3%

1.8 2.19 m-1

1.9 0.023 cm

1.10 1.0 × 10-6 mol litre-1

1.11 2.71 m2 kg-1; 0.49 mm

1.12 350 nm, 7.55 × 1013 W m-3; 500 nm, 9.98 × 1013 W m-3; 650 nm, 0.27 × 1013 W m-3

1.13

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Source | νm / Hz | Δν / Hz | Δ*t*c / s | Δ*s* / m |
| Mercury lamp | 5.49 × 1014 | 1.00 × 1012 | 9.95 × 10-13 | 0.0003 |
| Kr lamp | 4.95 × 1014 | 9.8 × 108 | 1.02 × 10-9 | 0.306 |
| Cd lamp | 4.66 × 1014 | 4.70 × 108 | 2.13 × 10-9 | 0.638 |
| He–Ne laser | 4.74 × 1014 | 7.49 × 105 | 1.34 × 10-6 | 4004 |

**Chapter 2**

*Answers to introductory questions*

*Why are images of objects in water displaced?*

The images of objects in water are perceived by reflected light that is seen by the observer. The velocity of light is different in water than in air, and this causes the ray of light leaving the object to bend in such a way that the object appears to be nearer the surface than it really is. This effect is quantified by the index of refraction of water, which is equal to the ratio of the velocity of light in a vacuum (or, approximately, air) to that in water.

*How do rainbows form?*

Rainbows form when sunlight that originates from behind the observer enters a curtain of raindrops to the front. The light is totally internally reflected by individual raindrops and spread out over the visible spectrum by dispersion so that the light returning to the observer is coloured. A primary bow results from one internal reflection and a secondary bow from two internal reflections. Each colour seen comes from a different arc of raindrops, and each observer sees a different rainbow.

*What is a negative index material (NIM)?*

Normal transparent materials have a refractive index, which is positive and greater than 1.0. This comes about because the electric field of the light wave is slowed by the electrons around the atoms in the material, and is accounted for by a positive value of the dielectric permittivity of the transparent solid. In a negative index material the refractive index is negative and greater than 1.0. This is theoretically feasible, but is difficult to achieve in ordinary materials because ideally both the electric permittivity and the dielectric permittivity of the phase need to be negative. However, under special circumstances, particularly in regions very close to the surface, the noble metals behave as negative index solids. In other cases, metamaterials, composite solids constructed from more than one material, can also be engineered to show negative refractive index for specific frequency ranges.

*Quick Quiz*

1 (c); 2 (a); 3 (c); 4 (c); 5 (b); 6 (a); 7 (c); 8 (b); 9 (b); 10 (c)

*Problems and Exercises*

2.1 (a) 1.579 cm; (b) 15.617 mm

2.2 (a) 36.5; (b) 63.0

2.3 (a) 2.30; (b) 2.32; (c) 2.66

2.4 (a) 1.73; (b) 1.56; (c) 1.61

2.5 2.00

2.6 (a) 4228 kg m-3; (b) 7734 kg m-3

2.7 2.62

2.8 (a) 1.55; (b) 1.575, 1.153; (c) 1.5328, 1.139

2.9 (a) 50%; (b) 1.40; (c) 1.52

2.10 64.2

2.11 The width of the spectrum is 0.3 mm and the red band is at the top.

2.12 (a) *d* = 180 + 2*i* – 4*r*; (b) *d*(min) = 137.6°

2.13 (a) *d* = 360 + 2*i* – 6*r*; (b) *d*(min) = 129.9°

2.14 (a) *d* = 2(*i* – *r*) + *m*(180 – 2*r*); (b) [(*m* + 1)2 – 1] (*IP*)2 = (*m* + 1)2 – (*n*)2

2.15 (a) 3.0 dB km-1; (b) 6 cm

2.16 (a) 22.3 m; (b) 2.2 ns km-1

2.17 200 km

2.18 Δ*n* = 1.71 × 10-4 ; n = 2.22633

**Chapter 3**

*Answers to introductory questions*

*Why are soap bubbles coloured?*

Soap bubbles are coloured because daylight (white light) is reflected from both sides of the thin film that makes up the bubble. The light waves reflected from the two surfaces interfere constructively or destructively depending on the wavelength of the light and the thickness of the film. The colours seen are a result of this process summed over all the wavelengths making up the white light.

*What are antireflection coatings?*

Simple antireflection coatings are produced by the deposition of a layer of a transparent substance with a refractive index lower than that of the glass in the lens. The thickness is chosen to be a quarter of the wavelength of light near to the middle of the visible, approximately 133 nm. To be completely antireflecting at this “design wavelength”, the refractive index of the film should be the square root of the refractive index of the lens. Even if this is achieved, the film will not be perfectly antireflecting for other wavelengths. For the best lenses, multilayers, which give much better antireflection properties, are used.

*How can perfect mirrors be made from transparent materials?*

Perfect mirrors can be made by building up multilayers of transparent materials on a solid substrate. The first of these mirrors were made of alternate high and low refractive index films of thickness equal to one quarter of the wavelength of the light to be reflected, because the calculations could be readily made. Using computer programs, sequences of layers of a variety of thicknesses can be devised which give virtually 100% reflection for the desired wavelength.

*Quick Quiz*

1 (c); 2 (c); 3 (b); 4 (c); 5 (a); 6 (b); 7 (c); 8 (a); 9 (b); 10 (a)

*Problems and Exercises*

3.1 (a) 5.3%; (b) 0.077%; (c) 2.43; (d) 1.47

3.2 indigo, 3.58%; green 3.50%; red, 3.46%; blue-violet cast

3.3 (a) 50 nm; (b) yellow-white to straw yellow; (c) carmine-red to deep violet

3.4 (a) first-order yellow; (b) first-order deep red

3.5 (a) third-order dark blue; (b) second-order violet

3.6 (a) 20.8%; (b) 29.5%

3.7 (a) 2%; (b) 224 nm; (c) 9%; (d) orange (complementary colour)

3.8 1.75

3.9 (a) 1.30%; (b) 4.3%; (c) 4.9%; (d) 44.5%

3.10 No answer is required.

3.11 (a) no variation with depth: *n*h = 1 + 0.58 *l*m / *l*t; (b) *n*h = 1.58 – 0.58 *h* / *h*t; (c) *n*h = 1 + 0.58 (1 – *h* / *h*t)

3.12 *N* = 6 or more

3.13

|  |  |
| --- | --- |
| ***N*** | ***R*** |
| 1 | 0.4369 |
| 2 | 0.7614 |
| 3 | 0.9132 |
| 4 | 0.9702 |
| 5 | 0.9900 |
| 6 | 0.9966 |
| 7 | 0.9989 |
| 8 | 0.9996 |
| 9 | 0.9999 |
| 10 | 1.0000 |



3.14 air, 0.88; TiO2, 0.11; SiO2, 0.11

3.15 365.5 nm

3.16 (a) *n*(anorthite) / *n*(albite) = 1.108; (b) anorthite has the larger refractive index; (c) anorthite, 1.57, (~1.58 experimental), albite, 1.54 (~1.53 experimental)

3.17 (a) 188.4 nm, 1.88 mm; (b) 550.2 nm

3.18 (a) 4.5%; (b) 0.78

3.19 (a) C, 17 nm, Mo, 62 nm; (b) 124 – 276 nm

**Chapter 4**

*Answers to introductory questions*

*Why do some crystals produce double images?*

Uniaxial or biaxial crystals produce double images because the index of refraction is different in different crystallographic directions. Unpolarised light incident upon the crystal is divided into two components, polarised perpendicular to one another, unless the light path is aligned along a particular crystal direction – an optic axis. The refractive indices encountered by these two rays are subjected to different refractive indices, hence the two images are formed by the two polarised light beams. The phenomenon is called double refraction, and holds for all noncubic crystals. However, the effect is small in most crystals and the double image is often difficult to see.

*How can infrared radiation be changed into green light?*

Infrared radiation can be converted into green light by using a nonlinear crystal. These are crystals that are uniaxial or biaxial. The effect is only seen when the power of the input infrared wave is high, as it is when a laser is the source. In the nonlinear crystal the vibration of the electrons in the material, in such an intense field, undergo oscillations at the frequency of the incoming wave and also at double this frequency. These oscillating electrons in turn emit waves of both frequencies. The phenomenon is called second harmonic generation (SHG) and is widely used to turn 1064 nm radiation from Nd3+/YAG lasers into green light of wavelength 532 nm.

*How does a liquid crystal display (LCD) form an image?*

Liquid crystal displays (LCDs) exploit the properties of colourless molecules in a thin liquid crystal film. The molecules can alter the direction of polarisation of a light beam in response to an externally applied electric field. The liquid crystal film is sandwiched between two glass sheets, which are bounded by crossed polars. White unpolarised background lighting provides the illumination. The liquid crystal film is divided into pixels by grids of transparent conducting electrodes imprinted on the glass sheets. When no voltage is applied to the electrodes the molecules in the liquid crystal layer remain in the orientation originally imposed during manufacture. The polarised light beam from the entry polar is not rotated on passing through the liquid crystal layer. In this case, the light is blocked by the exit polariser and the pixel appears dark. Applying voltage to the electrodes causes the liquid crystal molecules to rotate, and in so doing to change the plane of polarisation of the linearly polarised light beam by 90°. The polarised light “follows” the molecules and the plane of polarisation is rotated. It is then passed by the exit polar so the pixel looks bright.

In colour displays each pixel is composed of three *subpixels*, each of which has a colour filter imposed before the final polariser.

*Quick Quiz*

1 (b); 2 (a); 3 (b); 4 (b); 5 (c); 6 (c); 7 (b); 8 (a); 9 (c); 10 (b)

*Problems and Exercises*

4.1 (a) 53; (b) *R*s = 5%, *R*p = 4%

4.2 halite, 0, isotropic; scheelite, 0.016, uniaxial +; corundum, 0.009, uniaxial -; forsterite, 0.035, biaxial; malachite; 0.245, biaxial; stercorite, 0.030, biaxial

4.3 (a) *n*e′ = 1.545; (b) = 45.1°

4.4 θ = 46.3°

4.5 (a) The plate must be cut perpendicular to the **c**-axis. (b) 6.1 m

4.6 *d* = 13 μm or 25.6 μm

4.7 *A* = ½ ε0 χ(2) 02; *B* = ε0 (χ(1) 0 + ¾ χ(3) 03); *C* = ½ (ε0 χ(2) 02); *D* = ¼ (ε0 χ(3) 03)

4.8 (a) 1062 nm; (b) 440 nm

4.9 p = 532 nm, s = 650 nm, i = 2930 nm; p = 532 nm, s = 1060 nm, i = 1068 nm

4.10 (a) 48.9; (b) 30.8; (c) 48.1

4.11 (a) 55.9 m; (b) 15.5 m; (c) 17.2 m

4.12 (a) As crystal thickness increases, more SHG will occur. However, at a certain thickness, intensity will start to be lost due to destructive interference between the input and SH beams. However, as the crystals are distributed at random, some will lie at the birefringent phase matching angle. As the crystal thickness increases, although some intensity will be lost due to interference, enough will lie at or close to the phase-matching angle to compensate and give a steady output, resulting in a plateau at larger particle sizes.

(b) In case (b), no birefringent phase matching is possible, so the intensity increases initially but then diminishes due to destructive interference between the input and SH waves.

4.13 (a) no normal birefringence; (b) 30 mm-1; (c) 1.67 × 10-4

4.14 49.2 mm-1

4.15 red, 51.6, yellow, 86.1, violet, 172.2

4.16 χ(1), no units; χ(2), m V-1; χ(3), m2 V-2

4.17 15.3 × 10-16 C m-2

**Chapter 5**

*Answers to introductory questions*

*Why is skylight polarised?*

The colour of skylight is due to Rayleigh scattering of sunlight from the molecules that make up the atmosphere. The incident light beam can be resolved into two linearly polarised components, one with the electric field vector lying parallel to the plane of observation and one with the electric field vector lying perpendicular to the plane of observation. The wave polarised perpendicular to the plane of observation, is found to be scattered equally in all directions in the plane. The scattering from the component with the electric field vector in the plane of observation has a dumbbell shape. The total scattering curve for skylight is the sum of both of these contributions, as viewed by the observer. The degree of polarisation of skylight is virtually zero in the direction of the sun and strongly polarised in a plane, which includes the observer and is at 90° to the line joining the observer to the sun. In reality, the actual polarisation observed at any point in the sky is a result of multiple scattering, the atmospheric conditions, and the relative positions of the sun and the observer.

*Why are eyes blue at birth?*

The colour of eyes resides in the iris. At birth, the iris is usually unpigmented. The colour observed is caused by outward scattering from the inhomogeneous structures in the iris. As wavelengths at the violet-blue end of the spectrum are scattered preferentially, this dominates light scattered out of the eye. Coupled with the sensitivity of the eye, the colour is perceived as blue. The effect is enhanced because all light passing through the iris and not scattered out again is absorbed within the eye, allowing the scattered colour to appear quite intense.

*How can yellow gold colour glass red?*

The yellow colour of gold is due to its reflectivity over the visible spectrum. In ruby glass the gold exists in the form of minute particles of less than approximately 50 nm diameter. Particles of this size tend to absorb light far more strongly that it is scattered. The absorption peak depends on particle size and wavelength, and ruby glass is manufactured so that particle sizes are just right to absorb mainly in the green-blue region of the visible. The transmitted light is then coloured red. The exact tone is influenced by the sizes of the gold particles, and well-defined heat treatments of the glass are needed to obtain a fine ruby colour.

*Quick Quiz*

1 (c); 2 (a); 3 (b); 4 (b); 5 (a); 6 (c); 7 (c); 8 (a); 9 (c); 10 (b)

*Problems and Exercises*

5.1 (a) 45%; (b) 199.3 m-1; (c) 1.99 × 1017 m-2; (d) 2.05 × 1023

5.2 –0.9

5.3 (a) *I*s / *I*0 = 7.7 × 10-13; (b) *I*s / *I*0 = 8.5 × 10-13

5.4 (a) 1.33; (b) 6.7 km

5.5 (a) *Q* = 3.17313, = 4.09; (b) *Q* = 1.54230, = 7.63

5.6 (a) 0.43 m; (b) 0.8 m

5.7 507 nm

5.8 (a) 0.77; (b) 4.4 × 109 m-3

**Chapter 6**

*Answers to introductory questions*

*What causes the colours reflected from compact discs (CDs) and digital versatile discs (DVDs)*

Data is stored on CDs and DVDs, by making small pits on the reflective recording layer that are darker than the background in reflected light. In a CD the pit size minimum is 0.83 m and the track pitch (the separation between lines of pits), is 1.6 m. The DVD has a pit size of 0.4 m and a track pitch of 0.74 m.

The marks on a CD or DVD are comparable in size to the wavelength of light and the array of surface pits forms a curved line reflection grating. The image of a white light viewed by reflection from the surface will show several orders of diffraction. The zero order “reflection” will show the white light source, but all other orders will appear as continuous spectra, as the disc is tilted. Because of the curvature of the tracks these spectra take a complicated form. The observed colours vary with viewing angle and the degree of distortion of the material.

*Why are opals coloured?*

Gem-quality opals contain small volumes of silica spheres that are packed together in an ordered crystalline array. Both the size and spacing of the spheres are comparable to the wavelength of light. White light incident upon these arrays will be strongly diffracted. The conditions for this to occur are dependent on the sphere size, the packing arrangement and the observation direction, so that only a narrow band of wavelengths are strongly diffracted for a particular viewing direction. These flash out as iridescent colours as the opal is tilted.

*How do liquid crystal thermometers work?*

The “working medium” in liquid crystal thermometers is a line of spots of a chiral nematic liquid crystals that possess a helical structure. The liquid crystals are designed so that the pitch of the helix, the repeat distance along the helix, falls into the range of wavelengths of light, 400–700 nm at a particular temperature in the chosen design range of the thermometer. This allows the liquid crystal dot to strongly diffract light with a wavelength corresponding to the helix pitch at a specific temperature. At an appropriate temperature, only one of the dots will have a pitch that strongly diffracts light, and this spot “lights up”. As the temperature varies, each of the dots in turn will light up in sequence in this way.

*Quick Quiz*

1 (c); 2 (b); 3 (b); 4 (a); 5 (a); 6 (c); 7 (c); 8 (a); 9 (b); 10 (c)

*Problems and Exercises*

6.1 (a) 9.5 × 10-5 m; (b) 0.05

6.2 (a) 0.014 mm; (b) 0.0024

6.3 No answer is required.

6.4

|  |  |  |
| --- | --- | --- |
| ***m*** | **sin θ*m*** | **θ*m* / °** |
| 0 | –0.258819 | –15.00 |
| 1 | 0.016181 | 0.93 |
| –1 | –0.533819 | –32.26 |
| 2 | 0.2911181 | 16.93 |
| –2 | –0.808819 | –53.98 |

6.5 (a) Some representative values are

|  |  |
| --- | --- |
| ***d* / m** | **θ / °** |
| 1 × 10-3 | 0.032 |
| 1 × 10-4 | 0.315 |
| 1 × 10-5 | 3.15 |
| 1 × 10-6 | 32.37 |
| 5.5 × 10-7 | 90 |
| 1 × 10-7 | invalid |

(b) Some representative values are

|  |  |
| --- | --- |
| **d / mm** | **θ / °** |
| 1 × 10-3 | 1.90 |
| 1 × 10-4 | 6.01 |
| 1 × 10-5 | 19.09 |
| 1 × 10-6 | 63.24 |
| 2.75 × 10-7 | 90 |
| 1 × 10-7 | invalid |

6.6 0.18 mm

6.7 (a) 0.4178 nm; (b) 0.198 nm

6.8 (a) 1.48; (b) 428 nm; (c) no colour visible, 252 nm

6.9 (a) 700 nm, deep red; (b) 52.2

6.10 (a) 396 nm; (b) 1.355 nm; (c0 0.72 (72%)

6.11 (a) 1,25; (b) 457 nm

6.12 (111), 486 nm; (200), 420 nm; (220), 297 nm; (311), 254 nm

6.13 (a) 202 nm; (b) the wavelength diffracted is 496 nm, blue-green

6.14 No answer is required.

6.15 (a) 1.45; (b) 0.09; (c) 161 nm

6.16 *I* (*x*) = ½ 0R2 + ½ 0OB2 + 0R 0OB cos [2 × / (sin R – sin OB )]

**Chapter 7**

*Answers to introductory questions*

*How can the chemical composition of the sun and other stars be determined?*

An incandescent object, like the sun, emits a continuous spectrum – the visible spectrum (Chapter 1). Atoms and ions emit and absorb light in small energy packets called quanta. Thus, when a continuous spectrum from, for example, the sun, passes through a gas of atoms or ions, these will absorb at discrete frequencies, to leave dark lines in the continuous spectral background. These lines are called Fraunhofer lines. The pattern of energy levels and absorption and emission characteristics of each atom or ion is unique, and so the pattern of Fraunhofer lines superimposed upon the spectrum of the sun or any other star gives analytical information about the material in the cooler outer regions of the source. [Note that some Fraunhofer lines are also generated by absorption in the Earth’s atmosphere. These must be subtracted to obtain stellar compositions.]

*How do sodium street lamps produce yellow light?*

Sodium lamps contain a vapour of sodium atoms and ions. These are excited into higher energies by way of collisions with energetic electrons given out within the lamp by the applied electrical potential. The excited atoms and ions all lose energy and return to the lowest energy ground state. In doing so, they pass through a pair of energy levels just above the ground state and emit photons with an energy and wavelength in the yellow region. This closely spaced pair of lines, called the sodium D lines, gives sodium lamps their characteristic yellow colour. In older versions, the lamps contained a low pressure of sodium, and the light given out was totally dominated by this colour. Modern lamps operate with a higher pressure of sodium and contain other gases, so that more lines are emitted and the light appears much whiter.

*Why are transition metal compounds coloured?*

Transition metals are characterised by having electrons in a partially filled *d* orbital. Transition metal ions are not coloured when they are in the gaseous state and the *d* orbitals all have the same energy. However, when these atoms and ions are incorporated into molecules or crystals, the electrons in the *d* orbitals interact with surrounding atoms and their energy splits into groups. This is called crystal-field or ligand-field splitting. Colours arise due to transitions between these new energy levels, which are referred to as *d*–*d* transitions.

*Quick Quiz*

1 (b); 2 (a); 3 (c); 4 (c); 5 (b); 6 (b); 7 (a); 8 (b); 9 (c); 10 (b)

*Problems and Exercises*

7.1 Lyman: *n* = 2, 121.5 nm, *n* = 3, 102.6 nm, *n* = 4, 97.2 nm, *n* = , 91.2nm, far ultraviolet; Paschen: *n* = 4, 1.876 m, *n* = 5, 1.280 m, *n* = , 0.820 m, infrared

7.2 Na, 2S; Mg, 1S, Al, 2P, Si, 3D; P, 4S; S, 3P; Cl, 2P, Ar, 1S

7.3 (a) 3P, 1P; (b) *J* = 3/2, one level

7.4 (a) 3T2g ← 3A2g; 3T1g (from 3F) ← 3A2g; 3T1g (from 3P) ← 3A2g

(b) H2O: 1 176 nm; 741 nm; 397 nm

NH3: 935 nm; 571 nm; 355 nm

(c) Dq H2O = 850 cm-1, 0.10 eV, 1.69 × 10-20 J;

Dq NH3 = 1070 cm-1, 0.13 eV, 2.13 × 10–20 J

7.5 The unit cell of Cr2O3 is larger than that of Al2O3 and so the octahedral sites in Cr2O3 will be larger than in Al2O3. This will reduce the crystal field splitting and the energy levels of the 4T2g and 4T1g excited states will move towards the ground state. The absorption bands in ruby, yellow-red, and violet, move to red and blue, respectively. The transmission window for light not absorbed lies in the green, endowing the material with a green colour.

7.6 (a) MgO: blue or white / colourless, ZnO: white / colourless; (b) MgO: Dq = 0.138eV = 1.113 cm-1, ZnO: Dq = 0.093 eV = 750 cm-1; (c) The 4/9 rule is not well obeyed; (d) The two bands indicate that Cu2+ ions occupy both octahedral and tetrahedral sites in MgAl2O4. (e) blue.

7.7 (a) octahedral; (b) t2g2, t2g1 eg1, eg2; (c) Al2O3, 0.27 eV = 2175 cm-1, MgAl2O4, 0.27 eV, 2150 cm-1

7.8 (a) 575 nm, 4A2g 4T2g (F); 418 nm, 4A2g 4T1g (F); 4A2g 4T1g (P); (b) 0.22 eV = 1740 cm-1; (c) 0.92 eV = 7420 cm-1

7.9 (a) 550 cm-1, 0.068 eV;(b) tetrahedral; (c) 3T1 3T2, 3T1 3A2 (F), 3T1 3T1 (P) ; (c) 440 cm-1, 0.55 eV

7.10 (a) M2 is larger; (b) 653 nm, 729 nm; (c) green-blue

7.11 (a) 48 J per pulse; (b)6.7 C

7.12 (a) 624 nm, 4A2g 4T2g, 436 nm, 4A2g 4T1g; (b) 1603 cm-1, 0.20 eV; (c) grey-green

7.13 (a) 556 nm, 218 THz; (b) 400 nm, 291 THz

7.14 (a) 1S0; (b) 1P1; (c) 3D2

7.15 Pr3+, 3H4; Eu3+, 7F0; Tb3+, 7F6; Ho3+, 5I8

**Chapter 8**

*Answers to introductory questions*

Why is deep water tinted blue?

The colour of water bodies in nature depends on reflection, scattering, impurities, the aspect of the sky, and so on. Ignoring these aspects, the colour of pure water in transmission is blue because red light is more strongly absorbed than blue. Passing from the surface to greater depths in clear sea will render the light that penetrates a deeper and deeper blue hue. Absorption is due to transitions between the vibrational energy levels. The water molecule is angular with a bending mode of vibration ν2, which, in the gas phase, absorbs energy in the infrared, at a wavelength of 6273 nm. In addition, two stretching modes, in which the bonds in the molecule lengthen and shorten, also occur. One of these, in which the bonds lengthen and shorten together, the *symmetrical mode*, ν1, absorbs energy at 2730 nm in the gas phase. The other, in which one bond lengthens as the other shortens, the *antisymmetrical mode*, ν3, absorbs energy at 2662 nm in the gas phase. These absorption wavelengths are far from the visible. However, they combine to produce *overtones*, which are harmonics, and *combinatorial tones*, which are sums, of the fundamental frequencies. For example, if we set the frequencies of the absorption maxima as ν1, ν2, and ν3, the overtones are of the form 2ν1 and the combinatorial tones are of the form 2ν2 + ν3. The existence of these terms extends the spectrum of water molecules much closer to the visible – close enough, in fact, to present a sensation of colour to the eye. The weak absorption of light in the red region of the spectrum of both water and ice is most likely to be due to overtones of the fundamental ν1, O-H stretching vibration. This is shifted from the gas phase positions noted above and is found at about 2491 nm in liquid water. The main overtones of importance for colour are the 4th, giving rise to absorption in the infrared at about 735 nm, and the 5th, giving rise to absorption at about 590 nm. Although the absorption due to these transitions is very weak, it is still significant and causes the blue colour of bodies of pure water. At this stage, the strength of the absorption is low, but it is just enough to remove a small fraction of red and orange. This is enough to give sizeable bodies of pure water or ice a pale (watery!) blue colour.

*What colours roses red and cornflowers blue?*

Many of the blues and reds of flowers are derived from a group of flavonoid related compounds called *anthocyanins*. The name derives from cyanin (= blue) as the compound was first isolated from blue cornflowers, *Centaurea cyanus*. All the anthocyanins absorb strongly in the green region of the spectrum, thus allowing the flowers to reflect varying proportions of reds and blues. The colour range of flowers and fruits using anthocyanins spans the range from salmon pink through to blue and violet.

The diversity of this group of plant pigments is considerable. The anthocyanins are composed of an *anthocyanidin* plus one or more sugar molecules. The anthocyanins are glycosides of anthocyanidins and the anthocyanidins themselves are the aglycons of anthocyanins[[1]](#footnote-1). There are about 30 anthocyanidins known, which yield about 1000 anthocyanin pigments when the various substitutions are taken into account. This multiplicity gives rise to the enormous range of colours shown by many of our favourite flowers.

*What is a blueprint?*

A blueprint is a copy of an architectural or engineering drawing made with the cyanotype process. At the end of the nineteenth century architectural and engineering drawing were copied by hand, a process that was very labour intensive, time consuming, and liable to error. The scientist Herschel invented a process of making negative copies of images, which he called cyanotypes. Although these were not suitable for recording ordinary scenes, it was later realised that this technique was perfectly adequate for the copying of drawings. In essence, a blueprint is a negative image made with Prussian blue. A drawing, made on tracing paper, was placed on a sheet of suitably treated paper and exposed to light. Prussian blue was deposited in the areas that were illuminated while the areas under lines were remained white. This forms a negative copy of the drawing in Prussian blue – a blueprint.

Blueprints are now superseded by photocopies of many types.

*Quick Quiz*

1 (c); 2 (b); 3 (b); 4 (a); 5 (c); 6 (a); 7 (b); 8 (c); 9 (a); 10 (b)

*Problems and Exercises*

8.1 (a) red, 0.5, violet, 0.93; (b) 9.9 m; (c) 0.61

8.2 CH3(CH=CH)7CH3, absorption maximum ~390 nm, colour yellow-orange; CH3(CH=CH)9CH3 , absorption maximum ~420 nm, colour orange-red

8.3 (a) purple; (b) ligand-to-metal (Fe(III) charge transfer; (c) 1.83 eV, 2.93 × 10-19 J

8.4 (a) yellow, blue, yellow, red, red, yellow, yellow, colourless, red; (b) yellow, blue, blue, yellow, blue, blue, yellow, colourless, red; (c) 5.0 – 7.0; (d) 8.9 – 9.4

8.5 emerald: crystal-field colours, aquamarine, charge-transfer colours; ruby: crystal-field colours, sapphire, charge-transfer colours

8.6 (a) 2.25 eV, 3.61 × 10-19 J; (b) 36480 M-1 cm-1

8.7 The colour cannot be due to crystal-field effects because (a) tetrahedral splitting is smaller than octahedral splitting, (b) Cr6+ has no d electrons. Most likely is charge transfer between Bi3+ and Cr6+.

8.8 Chlorophyll absorbs in the violet and red parts of the spectrum. As the quantity of chlorophyll drops, this absorption falls and the leaf loses its strong green appearance. The carotenoids absorb at about 460 nm, giving orange-red colours. These diminish slowly, so the leaf will appear to become more orange-red.

8.9 *k* = 0.06 min-1.

8.10 (a0 16.3 M; 38 mM

**Chapter 9**

*Answers to introductory questions*

*How do fluorescent tubes produce light?*

Fluorescent tubes are filled with a low pressure of mercury vapour. This is excited by the applied voltage and gives out mostly ultraviolet radiation. The ultraviolet emissions are converted into visible light by a phosphor coating on the inside of the glass lamp tube.

Halophosphate lamps use modified calcium fluorophosphate, Ca5 (PO4)3F, as the host matrix. When doped with Sb3+ ions a blue emission is produced. Manganese ions (Mn2+) doping with Sb3+ ions as sensitiser produces an orange-red emission. Variation in the proportions of Sb to Mn varies the tone of the light.

Trichromatic lamps produce a good spectral balance by using a phosphor mixture which emits equal amounts of the colours red, blue, and green. The favoured red emitter is Eu3+ doped into Y2O3 matrix. The green emission is from Tb3+ coupled with a sensitiser, usually Ce3+, in the host matrices La(Ce)PO4, LaMg(Ce)Al11O19 or La(Ce)MgB5O10. The blue emission is produced by Eu2+ ions in host matrix BaMgAl10O17.

*How do glow-in-the-dark pigments work?*

Glow-in-the-dark pigments display persistent luminescence, characterised by a slow and continuous release of light, for 12 hours or so, after the removal of the exciting radiation, usually sunlight. These are typified by SrAl2O4, doped with Eu2+ as the activator and Dy3+ as a sensitiser, which has a yellow-green luminescence and a persistence time, which can be greater than 30 hours. The general mechanism that produces the luminescence supposes that the exciting radiation interacts with the activator to excite it from the ground state to a higher energy level, as in normal fluorescence or phosphorescence. Instead of fairly rapid decay the excited state is somehow trapped in this high energy condition before the energy is passes to an emitter, whereupon release of a photon allows it to revert to the ground state. Thus, in all cases, there are three types of centres involved: activators, traps, and light emitters, although often the emitting centre and the activating centre are the same. The purpose of the sensitiser dopants in generally to create sufficient traps with a trapping energy that allows slow release of the electrons at normal temperatures.

*How do glow sticks produce colours?*

Glow sticks produce colours by way of chemiluminescence, which is light emitted as a result of a chemical reaction. A glow stick consists of a transparent plastic tube containing one of the active chemicals and a fragile glass ampoule or inner tube containing the other reactant. To activate the glow stick, the outer tube is twisted or bent in order to fracture the inner glass tube, thus allowing the chemicals to mix. The resulting chemical reaction excites incorporated dye molecules, which, in turn, give out light.

The energy providing chemical is hydrogen peroxide, H2O2, contained in the outer part of the stick. The glass tube contains diphenyl oxalate and the chosen dye. Hydrogen peroxide oxidises the diphenyl oxalate to phenol and the very unstable intermediate 1,2-dioxetanedione, which decomposes immediately to carbon dioxide, exciting the dye molecules in the process. A large number of dyes have been used in glow sticks. Two of the commonest are rubrene (5,6,11,12-tetraphenylnaphthacene), which gives a yellow- orange fluorescence and 9.10-diphenylanthracene that gives blue. The concentrations of the chemicals and the temperature influences the length of time over which the glow stick is luminous.

*Quick Quiz*

1 (b); 2 (a); 3 (b); 4 (c); 5 (c); 6 (c); 7 (a); 8 (a); 9 (b); 10 (c)

*Problems and Exercises*

9.1 3.3 × 10-19 J; 33,5%

9.2 slope = 1.7; 2-photon process

9.3 532 nm, green, slope = 1.77, two-photon upconversion; 656 nm red, curved plot, probably energy transfer

9.4 0.97 ms

9.5 (a) 3.1 M-1; (b) 7.8 × 108 M-1 s-1

9.6 (a) 9.2 × 1011 M-1 s-1; (b) 2.8 × 10-4 M

9.7 (a) 1.17 s; (b) 0.3

9.8 5.5 nm

9.9 1.25 eV

**Chapter 10**

*Answers to introductory questions*

*How can colourless boron impurities tint diamond blue?*

In blue diamonds, each boron impurity atom occupies a carbon position, forming a substitutional defect, BC. Boron, with an electron configuration 1s2 2s2 2p1 has only three outer bonding electrons instead of the four found on carbon. These three are used in fulfilling the bonding requirements of the structure, but one bond of the four is incomplete and lacks an electron, giving the defect an effective positive charge. In semiconductor physics terms, each boron atom dopant has an accompanying hole in proximity to the occupied site and is an acceptor impurity. This is represented by the creation of a set of new acceptor energy levels approximately 0.4 eV above the valence band. The transition of an electron from the valence band to this acceptor level has an absorption peak in the infrared, but atomic vibrations and other imperfections broaden this into a narrow band of energies allowing the high energy tail of the absorption band to encroach into the red at 700 nm. The boron-doped diamonds therefore absorb some red light and leave the gemstone with an overall blue colour.

*What produces light in a light-emitting diode (LED)?*

An LED is formed (in principle) by the juxtaposition of a region of *n*-type and *p*-type semiconductor, grown into a single crystal. In the *p*-type region the semiconductor has been doped with acceptors to become a hole conductor. In the *n*-type region the semiconductor has been doped with donors to become an electron conductor. When a *p*-type region abuts an *n*-type region, electrons move into the *p*-type region from the *n*-type side and holes move into the *n*-type region from the *p*-type region, by diffusion. The result of the changes is to create a *depletion region* with few charge carriers.

At equilibrium (thermal and electrical) there will still be an exchange of carriers at the junction, but the current in each direction will be the same. Dynamic equilibrium holds. This changes when a forward bias voltage is applied across the junction. This causes a rapid increase in the current flowing across the junction. Electrons and holes now enter the junction and recombine. The energy released, which is approximately equal to the band gap, appears as light. Electrons are continuously pumped into the conduction band and holes into the valence band by the power source, so that recombination occurs continuously, giving a steady light output.

*Why are copper and gold coloured whereas most metals resemble silver?*

The reflectivity of a metal is described in terms of the refractive index *n* and the extinction coefficient *k*, the optical constants of the metal. For a metal, the extinction coefficient *k* and the refractive index, *n*, are both strongly wavelength dependent. The reflectivity of a metal depends on *n*, *k* and the polarisation of the light. For most metals, typified by silver, nickel, aluminium and so on, the combination of *n* and *k* gives a reflectivity over the range of the visible spectrum that is fairly constant. This means that all wavelengths of light are reflected evenly and the surface looks silver. The colours of copper and gold are due to the fact that the absorption and emission of photons are noticeably dependent on wavelength across the visible. Both gold and copper have rather low reflectivity at the short wavelength end of the spectrum and so yellow and red will consequently be reflected to a greater degree. This leads to the colours observed.

*Quick Quiz*

1 (c); 2 (a); 3 (b); 4 (c); 5 (b); 6 (a); 7 (b); 8 (b); 9 (a); 10 (c).

*Problems and Exercises*

10.1 (a) wavelengths absorbed, 400 – ~514 nm, wavelengths reflected, ~5124 nm – 700 nm; (b) 3.28 eV, 521 nm; (c) *x* = 0.1 phase.

10.2 (a) 2.77 eV; (b) wavelengths are from violet to blue, leaving green to red as unabsorbed, which gives the appearance of pale yellow; (c) 2.16 eV; (d) orange-red.

10.3 (a) Na0.25K0.75Br; (b) the absorption peak will move to shorter wavelengths, colour becomes more orange or yellow.

10.4 (a) The large band gap of C means that no light is absorbed, the lower bandgap of Si means that all of the visible is absorbed; (b) As temperature falls, bandgap increases. In the case of tin, this causes the metal to become a semiconductor; (c) higher temperatures.

10.5 (a) Ga0.86In0.14N; (b) 1107 nm

10.6 (a) –0.26; (b) 1.48 eV

10.7 (a) ZnS, white; ZnSe, yellow-orange; ZnTe, orange-red; (b) x = 0.837

10.8 (a) Cr, 0.656; Hg, 0.780; Ti, 0.509; (b) 689 nm, 0.907; 564 m, 0.920; 459 nm, 0.924; (c) although clean silver has a higher reflectivity, it tarnishes rapidly in air and loses reflectivity, while Al maintains its reflectivity.

10.9 (a) 700 nm, 0.91, 34%; (b) 550 nm, 0.73, 37%; 400 nm, 0.009, 48%

10.10 (a) 138 nm; (b) 195 nm; (c) 239 nm

10.11 (a) 1.29 × 1028 m-3; (b) 5.898 × 1028 m-3

10.12 (a) 3.6 × 1015 s-1; (b) 2.4 eV; (c) 28 nm

10.13 (a) yellow-green; (b) 1.83 nm

10.14 309 nm

10.15 p = 6.50 × 1015 rads s-1 , λp = 290 nm

1. An aglycon is the non-sugar compound remaining after replacement of the glycosyl group from a glycoside by an H atom. [↑](#footnote-ref-1)