

Chapter 2

Discovery of the Physics of Color

Anyone who has shared the company of three-year old children for an afternoon will recognize the conversation. Everything you say is challenged immediately with their favorite word—why? Newly arrived in the world and fascinated by all they see, three-year olds want to know the why of everything. They live in a world of mystery, wonder, and possibility—where magic is real and reality is magic. As we explore the discovery of the physics of color origin and perception, put yourself in the place of the three-year old who always wants to know why. Or put yourself in the place of the discoverers themselves who must have been filled with awe at what they learned and communicated to the world for the first time.

2.1 Theories on the Nature of Light

An inquisitive three-year old could indeed be a model for some of the scientists who people this chapter. First, there is Robert Hooke (1635–1703), described in one of his biographies as a “restless genius.” Hooke was an indispensable assistant to Robert Boyle (1627–1691), having designed and built the air pumps so crucial to Boyle’s development of his laws on gases. However, Hooke was an inventor and theoretician in his own right, being inquisitive on a number of problems that led to formulations of laws (Hooke’s Law), inventions (microscope), paleontological theories (he was the first person to realize the meaning and significance of fossils) and theoretical speculations (gravity). Among these speculations, and developed further by the ideas and work of Christiaan Huygens (1629–1695), was Hooke’s proposal in 1665 on the nature of light: that light has the characteristics of a wave in an invisible medium permeating all space, solids, liquids, gases and vacuum. This medium they called the ‘ether.’ Huygens was able to show mathematically that the fundamental geometric laws of optics could be explained by assuming that a prism or lens slowed the speed of a light wave [1, 2].

Vigorously opposed to Hooke’s and Huygens’ wave theory was an intractable Isaac Newton (1643–1727) who, in his 1704 book, *Opticks or a Treatise on the*

Fig. 2.1 Isaac Newton commemorative stamp issued by Germany in 1993



Reflexions, Refractions, Inflexions and Colours of Light [3] propounded his opinion that light consisted of a flux of imponderable particles based upon his observation of diffraction around a needle and bright bands of colored fringes on thin layers now known as Newton's ring. To explain these colors, Newton said light was a particle that had "fits." Huygens actually offered a more convincing explanation for the phenomena of reflection, refraction, and diffraction based upon wave nature. He suggested that the various colors travel at different velocities in different media, and therefore, each color has a different angle of refraction. Unfortunately, Huygens' theory was overshadowed by Newton's influence in Britain and Newton's idea that eventually came to be known as the particle theory of light dominated scientific thought for the succeeding 200 years.

Theories regarding the nature of light and color go back to the ancient Greeks. Aristotle is credited with making the first important contribution to what is now the modern theory of selective absorption [4]. It was Seneca, a Roman philosopher of the first century CE, who first noted that a prism reproduces the colors of the rainbow. Leonardo da Vinci (1452–1519) noticed that when light struck a water glass placed on a tabletop that it "spread out" as a colored image on the floor, but it remained for Isaac Newton in 1666 to formulate modern color theory on the basis of experiment. After taking his BA degree from Cambridge in 1665, Newton returned to his home at Woolsthorpe near Grantham because the threat of the Great Plague closed down the university. Starting at the age of 22, in a matter of 2 years, he had one of the most remarkable periods of creativity of any person who ever lived. One of these creative ideas that he developed became known as the *experimentum crucis*, the theory of colors based upon experiment. Figure 2.1 commemorates this event as well as the 350th anniversary of Newton's birth.

2.2 Newton's Famous Prismatic Dispersion Experiments

Newton allowed a small beam of sunlight (white, or achromatic, light) to pass through a prism in a darkened room. The light that emerged was no longer white

Fig. 2.2 A schematic diagram of Isaac Newton's famous prismatic dispersion experiment. © 1998, M.V. Orna

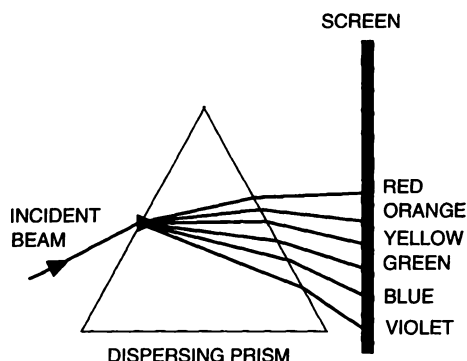
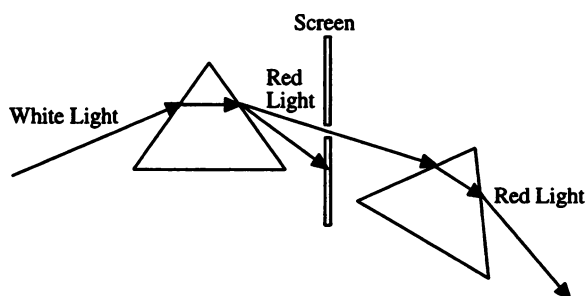


Fig. 2.3 A summary diagram of Newton's "*Experimentum crucis*" © 1998, M.V. Orna



light but exhibited a series of colors ranging from red, through orange, yellow, green, blue to violet (the visible spectrum; see Fig. 2.2).

He then asked if these colors, in turn, were made up of mixtures of other colors. To find out, he allowed his spectrum to fall upon a screen with hole in it. He then turned his prism until only red light passed through the hole. In back of the screen he placed a second prism and allowed the red light to pass through it. Newton reasoned that if red were a mixture of other colors, the second prism would disperse, or fan out, these colors in the same way that the first prism had dispersed the white light into its constituent colors. No such dispersion into additional colors occurred, nor were any of the other colors dispersed when they were tried in turn. Each color appeared to be the same although, as expected, each was dispersed to a greater degree by the second prism.

A summary of this important experiment is illustrated in Fig. 2.3. Newton concluded that red, orange, yellow, green, blue, violet were the fundamental colors recognized by the human eye and were not themselves mixtures of other colors. (Spectral colors are usually given in order starting with red, perhaps because red light is bent least by a prism.) Newton called this two-prism experiment his "*Experimentum crucis*." By it he conclusively demonstrated that sunlight is a mixture of six (seven, if one includes indigo, as did Newton) colors, that these colors could not be further dispersed into additional colors, and must therefore constitute the fundamental colors. In his own words, he concluded that "Light

itself is a heterogeneous mixture of differently refrangible rays.” Newton summarized the results as:

1. Sunlight consists of a mixture of all the colors observed in the prismatic spectrum (a word that Newton coined).
2. The prism is capable of dispersing the white light into its constituent colors. (Therefore, color was a property of the light not of the prism).

2.3 Consequences of Newton’s Experiment

If Newton’s first conclusion, that sunlight consists of a mixture of all the observed colors dispersed by the prism, then the dispersed colors should also be re-combinable into white light. To clinch this conclusion, therefore, Newton performed his recombination experiment. He placed a second, but inverted, prism in the path of the dispersed light and they did indeed, as predicted, recombine.

The observed variation of angle of refraction with color is due directly to the wave nature of the incident light, though Newton would have vigorously disputed this statement in his time. A series of experiments and theoretical development over a period of about 70 years, carried on by three great English scientists, gradually dismantled the one-sided Newtonian idea that light was corpuscular.

At the beginning of the nineteenth century, Thomas Young (1773–1829) obtained experimental evidence for the principle of interference by passing light through extremely narrow openings and observing the interference patterns. This experiment, along with the newly discovered polarized light by the Frenchman, Etienne Malus (1775–1812), allowed Young to conclude light had a transverse component, or in other words, his experiments could not be interpreted unless light was understood to have wavelike character.

About 165 years after Newton’s experiment, in 1831, Michael Faraday (1791–1867) showed that charged particles produced magnetic fields and that both charges and magnets exerted an influence across space. Then in 1865, James Clerk Maxwell (1831–1879) theorized that light was energy of a special form: a wave in a magnetic and electrical field. He derived equations which described the propagation of light as a wave with an electric field perpendicular to a magnetic field and with both fields perpendicular to the direction of travel. Thus, the idea that light was electromagnetic radiation was conceived. Also, the idea that light was produced by an accelerated charged particle was developed. Light can produce colors by acting on charges in matter. Thus, vibrating ions and moving electrons can interact with light to modify the light.

A characteristic property of all electromagnetic radiation is the frequency of the field of oscillation, ν , which remains invariant as the wave travels through any medium. The frequency is related to the velocity of the wave, c , and the wavelength, λ , by the equation $\nu\lambda = c$. It follows from this relationship that both λ and c

Table 2.1 The fundamental colors of the visible spectrum

Color	Wavelength range (nm) ^a	Band width (nm)	Frequency (s ⁻¹) ^b	Energy (eV)
Red	647.0–700.0	53	4.634–4.283	1.92–1.77
Orange	585.0–647.0	62	5.125–4.634	2.12–1.92
Yellow	575.0–585.0	10	5.214–5.125	2.16–2.12
Green	491.0–575.0	84	6.103–5.214	2.53–2.16
Blue	424.0–491.0	67	7.071–6.103	2.93–2.53
Violet	400.0–424.0	24	7.495–7.071	3.10–2.93

^a A nanometer, nm, is one-billionth of a meter, a very small unit of length
^b These values must be multiplied by 10¹⁴. The unit s⁻¹ is called a reciprocal second; it is essentially 1/s, or time divided into 1. This unit also represents the number of cycles per second in a light wave (cps), and is also known as hertz (hz)

must vary as a wave of a given frequency travels through different media since the frequency remains invariant.

As we examine a series of waves of given frequencies, we see that when the frequency is great, so is the energy of the wave. The equation governing this relationship was worked out by Albert Einstein (1879–1955) and Max Planck (1858–1947) and is thus called the Einstein–Planck relationship, $E = h\nu$, where h is the Planck constant with units of energy times time. A convenient value for h is 4.136×10^{-15} eV s. An electron volt (eV) is defined as the energy an electron gains when moved through a potential of one volt. If, for example, each electron “stored” in an ordinary 12-V automobile battery has a potential of 12 eV, then this amount of energy is expended by each electron as the battery discharges in use. The energies of electromagnetic radiation vary from more than 3×10^6 eV to less than 10^{-5} eV. The visible portion of this spectrum, i.e., the energy response range of the human eye, occupies only the very small region between about 1.7 and 3.1 eV. Each color in the visible spectrum has associated with it a range of frequencies from which can be calculated corresponding wavelength ranges. The fundamental colors of visible light along with their properties can best be summarized in tabular form as in Table 2.1.

2.4 The Visible Spectrum Examined

Table 2.1 contains a wealth of information and it would be well to examine it in detail. First of all, one notices that just a very small change in wavelength effects a change in perceived color. Secondly, each color does not consist of a single wavelength, but of a wavelength range. Although the visible spectrum covers the 400–700 nm wavelength range, all of the waves from 400 to 424 nm are seen as violet, all of the waves from 491 to 575 nm are seen as green, and so forth. These individual ranges are called pure spectral colors. It is difficult for the eye to distinguish between waves with wavelengths of 495 and 560 nm. Both waves are perceived as green. The wavelength range accounts for the “smear” effect seen

when white light, or better, achromatic light, is dispersed by a prism. (It should also be noted that the dividing line between spectral colors is difficult to discern; their subdivision into six broad regions is somewhat arbitrary).

A third feature gleaned from the table is that some colors have broader wavelength ranges than others. The term “bandwidth” is used to denote the wavelength range of a given color. For example, the wavelength range of green light is 8.4 times greater than that of yellow light. This fact is also evident when achromatic light is dispersed by a prism. However, if one were to measure the widths of the green and yellow bands with a ruler, it would be found that the green band is not 8.4 times the width of the yellow band. This is because a prism does not disperse each wavelength of light to the same extent.

Another important feature gleaned from this table is the energy values of visible light. The last column gives the energies associated with each color of light. Red light has an energy range of 1.77–1.92 eV, whereas violet light has an energy range of 2.93–3.10 eV. Violet light is considerably more energetic than red light.

The energy differences between colors are exceedingly small because electron volts themselves are very small units. This shows what a very sensitive instrument the eye is. To distinguish between red and orange requires a remarkable ability to discriminate between very small energy differences, yet it is a sensitivity we routinely take for granted. It has been estimated that the human eye is capable of distinguishing between five and eight million different colors.

2.5 The Electromagnetic Spectrum

The large energy range of electromagnetic radiation from more than three million electron volts to less than one ten-thousandth of an electron volt is called the electromagnetic spectrum. The human eye is sensitive to just a very small portion of the spectrum corresponding roughly to the energy-range output of the sun that bathes the earth; sensitivity to other wavelengths would not be useful to the eye. However, other wavelength ranges do exist. This was demonstrated initially by Sir William Herschel (1738–1832), a German-born British astronomer, who dispersed achromatic light and then placed a thermometer covered with an opaque material in the region beyond the red region—and the temperature of the thermometer rose! Herschel had discovered the infrared (IR) region of the spectrum, a region with less energy per wave (photon) than the red region, where there seems to be more heat than light. He reported his findings in a series of articles in 1800 [5–8]. Herschel is most famous for his astronomical discoveries, particularly of the planet Uranus as well as two of their moons. He worked closely with his sister, Caroline Herschel (1750–1848), who was an accomplished astronomer in her own right.

A corresponding experiment on the violet end of the spectrum was performed by Johann Wilhelm Ritter (1776–1810), a German chemist and physicist. Ritter placed silver chloride crystals, that were known to darken on exposure to light, in

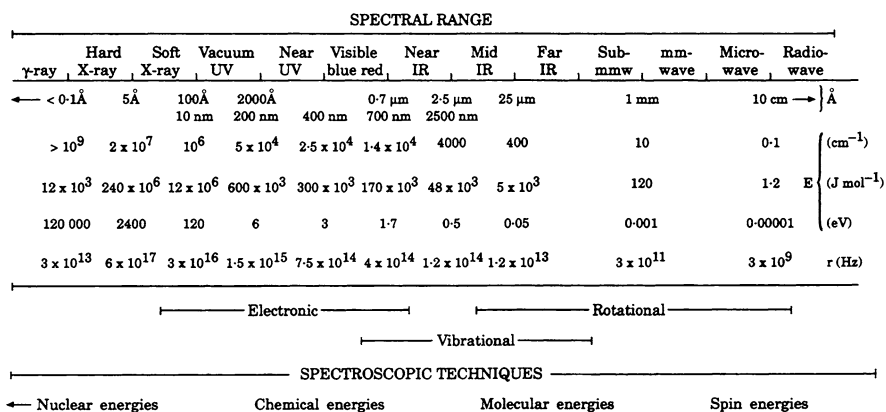


Fig. 2.4 The electromagnetic spectrum (with energy decreasing from left to right). © 1998, M.V. Orna

the region beyond the violet and noticed that they darkened more quickly than when placed in any other region of the visible spectrum. In his own words [9, 10]:

On 22 February, I also encountered rays alongside violet in the colour spectrum of colours—outside it—by means of horn silver. They reduce even more strongly than violet light itself, and the field of these rays is very wide.

Ritter recognized that there are rays beyond the violet end of the visible prismatic spectrum that blacken a chemical substance, but for him, the rays were not themselves an entity, but revealed the inherent polarity in light. Given the fact that he did not realize what he had discovered in terms of modern interpretation, and that his ontological system was one of symmetry, he expected a similar chemical effect on the red end of the spectrum in addition to the heating effect found by Herschel. In addition, his experiments were highly criticized in the decade following his publication, so it took a long time before he realized that there were higher energy waves beyond the violet in what we now call the ultraviolet (UV) region [11]. Although Ritter is best known among chemists for his discovery of the UV, physicists also hail the fact that he constructed the first dry cell battery in 1802 and a storage battery in 1803. His most important contribution to electrochemistry came in 1798: Ritter was the first to establish an explicit connection between galvanism and chemical reactivity. He was so excited by this discovery that he used his own body for many of the tests he conducted on electrical excitation of muscle and sensory organs. It has been speculated that these experiments exacted a very high price from him: he died at the young age of 33.

Other regions of the spectrum were gradually discovered and characterized so that now, in Fig. 2.4, we can see the entire electromagnetic spectrum laid out.

If we can't see the regions of the spectrum beyond the visible, why are they important? As we can see from the diagram, the other regions can be very useful. They include microwaves and radio waves, without which modern life would be inconceivable. They also include the high energy regions, which can be very

dangerous. For example, white snow and bright sunlight can be lethal. Ultraviolet light bouncing off a white surface can be so intense that it burns the cornea of the eye. This can cause the epithelial cell loss seen in cases of photokeratitis or snow-blindness. Severe pain, blurred vision, photophobia, and temporary blindness result. While most people recover within 24 h, prolonged exposure to reflected UV light can lead to some permanent vision loss. In our time, the health risk is exacerbated by ozone depletion in the atmosphere, leading to increased high energy UV radiation, and therefore increased damage to the eyes, the immune system and the skin [12]. Ultraviolet radiation can be harmful to more than the human eye: it can discolor virtually any color of organic origin by destroying the constituent molecules. High energy radiation can also be useful as diagnostic tools when used with caution. What lies beyond the infrared can be useful as well, and we shall see how very useful when we examine some of the major analytical techniques that help us understand and conserve colored artifacts.

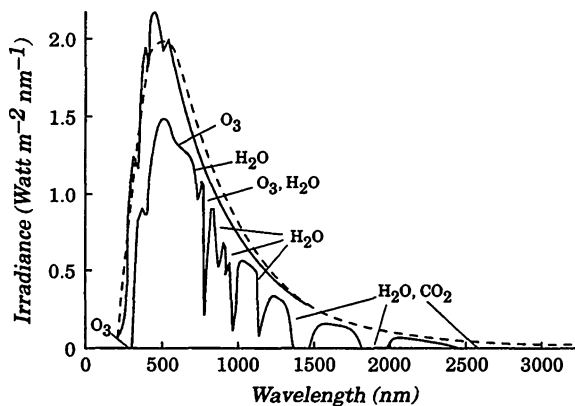
2.6 How We See Color

At this point, we have seen the experimental evidence and the theories that developed around the nature of light and the fact that so-called white, or achromatic, light is anything but! We must now ask: how is it that we see the colors inherent in white light without the use of a modifying prism, and more importantly, how is it that we can see any color at all? To answer these questions, we must look at the three components necessary for the perception of color: the source of light, the object being observed, and the observer.

2.6.1 *The Light Source*

Every source of illumination emits a range of energies which vary across the energy spectrum to yield what is known as a spectral energy distribution curve. Figure 2.5, below, is the complete spectral energy distribution curve of sunlight from 0 to 3,000 nm when the sun is at its zenith (directly overhead). Measurements at other angles generate a family of these curves. Figure 2.5 contains a wealth of information, and some that can be inferred. First of all, we note that the radiation maximum (shown as irradiance measured in $\text{W m}^{-2} \text{nm}^{-1}$) occurs at about 500 nm and falls off sharply on both sides of the maximum. The detection limits of the human eye exactly match the maximum in this curve, indicating an evolutionary link between the development of vision and the environment. Other animal species, e.g., the butterfly, have different sensitivity ranges. Indicated also on this curve are the absorption bands of atmospheric components, ozone (O_3), water (H_2O) and carbon dioxide (CO_2). The fact that ozone absorbs a great deal of the high energy radiation below 400 nm demonstrates its protective nature in the atmosphere and why the so-called

Fig. 2.5 Solar spectral distribution curve. Solar spectral irradiance at ground level (*inner solid curve* showing the absorbance of atmospheric components) and in space (*outer solid curve*), shown together with the spectral irradiance of a black body at 5,760 K (*dashed line curve*). © 1998, ChemSource, Inc



“ozone hole” over the Antarctic is an environmental catastrophe caused mainly by the presence of halocarbon refrigerants in the stratosphere. An extended consideration of this curve also gives us a clue as to why the sky is blue during the day and why many sunsets are brilliant red in color. Light is scattered in direct proportion to its energy, so blue–violet light is scattered by the particles in the atmosphere much more than the lower energy wavelengths of the solar spectrum, so when we look at the sky, we see the scattered blue light, and when we look at the sun, we see the sun’s emitted light minus the blue, and hence blue’s complementary color, yellow [13]. At the end of the day, when the sun is “setting,” the sun’s rays must travel through a greater air mass than at midday. Much of the sunlight is absorbed by the atmosphere, again in proportion to the energy of the waves, so the violet, blue, green and much of the yellow region of the solar spectrum is absorbed, leaving us to feast our eyes on a gorgeous red sunset!

As previously noted, a light source which emits energy with roughly constant radiant power over the limited response range of the human eye, 1.7–3.1 eV, or in terms of wavelength, 700–400 nm (1 nm, nm = 10^{-9} m), is perceived by the eye as “white.”

Dispersion of this light by a dispersing instrument such as a prism or a grating yields the spectral colors ranging from red at around 1.7 eV to violet at around 3.1 eV. The light source, usually a luminous body like the sun, emits packets of energy called photons with a range of energies, and the intensity of the radiation may vary with the energy, yielding spectral energy distribution curves such as those shown in Fig. 2.6. The x-axis, as in Fig. 2.5, is wavelength measured in nanometers; the longer the wavelength, the lower the energy of a given photon. The color range is from violet at 400 nm through green at 500 nm to red at about 700 nm. Figure 2.6a shows the curve for typical sunlight restricted to the 400–700 nm range (just a portion of Fig. 2.5), Fig. 2.6b for a 100 W incandescent light bulb, and Fig. 2.6c for a 15 W standard cool fluorescent light bulb.

From these curves, we can see that the intensities of radiation for sunlight vary only a little over the entire wavelength range for visible light. The incandescent light bulb’s radiation intensity increases dramatically toward the red end of the

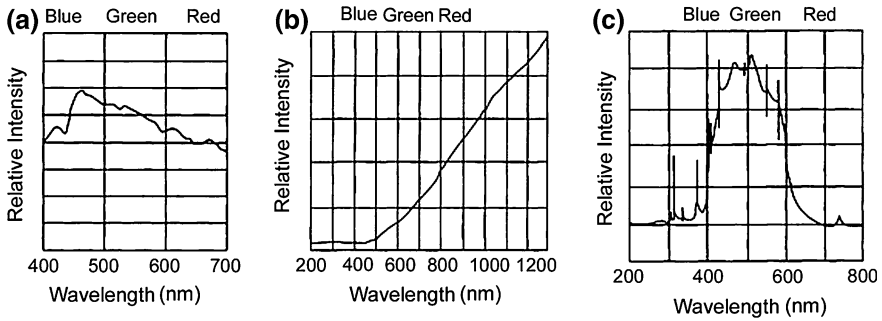


Fig. 2.6 Spectral energy distribution curves of **a** Sunlight, **b** Incandescent light, and **c** Fluorescent light. © 1998, M.V. Orna

spectrum (>700 nm), whereas its intensity is very weak in the violet–blue–green region. Incandescence is a phenomenon observed when objects are heated, and the hotter the object, the closer its radiant incandescent energy approaches white light. The radiation intensity of the fluorescent bulb exhibits a maximum at around 500 nm, but includes appreciable intensities of the entire wavelength range of the visible spectrum. A fluorescent lamp is actually a tube containing a gas at very low pressure that by application of high voltage, produces excited atoms that subsequently excite phosphors coating the inside of the tube; the phosphors convert the high energy UV light to a satisfactory range of visible light. So perhaps it should more properly be called a phosphorescence lamp.

A source which emits energy continuously over the limited response range of the human eye, from about 380 to 720 nm, and with appreciable intensities at all wavelengths, like sunlight, is perceived by the eye–brain complex as white and is therefore described as “white” or achromatic light. A source which emits energy with great intensities in the red region of the spectrum, and very little in the low wavelength region (blue–green region) of the spectrum is perceived as reddish–yellow, like an incandescent light bulb, commonly described as “warm” light. On the other hand, fluorescent lighting is very poor in red and is sometimes described as “cool” light for that reason; few people would appreciate fluorescent lighting in their living rooms. Yet for energy saving compact fluorescent lighting is now recommended, and will soon be mandated.

2.6.2 Interaction of Light with Matter

At this point, it is necessary to ask how light from the sources examined in the previous section might behave when it strikes an object, whether that “object” be the atmosphere, a liquid, solid or gaseous substance, or any other material substance one can think of. We can call any of these substances or objects the light “modifier” since light is indeed changed upon interaction. Some of the more

common changes that light undergoes are: reflection, transmission, refraction, dispersion, scattering, absorption, diffraction, polarization, and interference. Each of these interactions can give rise to a perceived color change, and understanding the mechanism for each of them is important when studying the physics of color. Most important to the chemist are the phenomena of reflection, transmittance, refraction, and absorption, especially when dealing with colored objects.

2.6.3 The Object Observed

We all know that a light beam can be modified with respect to the direction in which it travels by being reflected from the surface of an object. In certain special cases, not only the appearance of an object, but also its color, can be affected by the manner in which it reflects light. In most instances, our experience of reflection involves our observation of reflection from a smooth surface such as a mirror or a pool of water or a polished metal surface. In these cases we always expect to see some sort of reflected image, and the integrity of the image depends upon the smoothness of the reflecting surface. The reason why is that light emitted by an object or a source as parallel rays will be reflected from an object at an angle equal to the angle of incidence, and the reflected rays all remain nearly parallel because each ray has a normal plane parallel to the normal planes of all the other rays. In the case of reflection from a rough surface, on the other hand, normal planes must be constructed perpendicular to the surface which a particular ray is striking, and these are seldom parallel. Since the reflected rays are no longer parallel either, very few rays from the same surface region will reach the observer's eye, so the surface will appear quite dull. This phenomenon explains the difference between a glossy finish and a matte finish. Furthermore, if the surface is very rough, it is possible that hardly any reflected light at all will reach the observer. Such a phenomenon is observed when platinum is precipitated as finely divided particles with such a rough surface that it is incapable of reflecting much light to the observer's eye and the material is called "platinum black," which may be a counter-intuitive term to those who only know platinum as a shiny, almost colorless, metal. Other important interactions of light with bulk matter are refraction, absorption and transmittance. For our purposes, refraction is a most important interaction. Some detailed refractive interactions are shown in Fig. 2.7.

In the seventeenth century, Christiaan Huygens had the insight that the various colors of light travel at different velocities in different media, and therefore, each color has a different angle of refraction. Although he formulated this principle in 1678, his treatise on it was not published until 1690. He proposed that each point in a wave of light can be thought of as an individual source of illumination that produces its own spherical wavelets, which all add together to form an advancing wavefront. This multiple wavelet concept is now known as the Huygens' principle [14]. Besides wave theory, Huygens is known for his eclectic interests in such things as the mechanics of clocks, probability theory, optics and astronomy. His

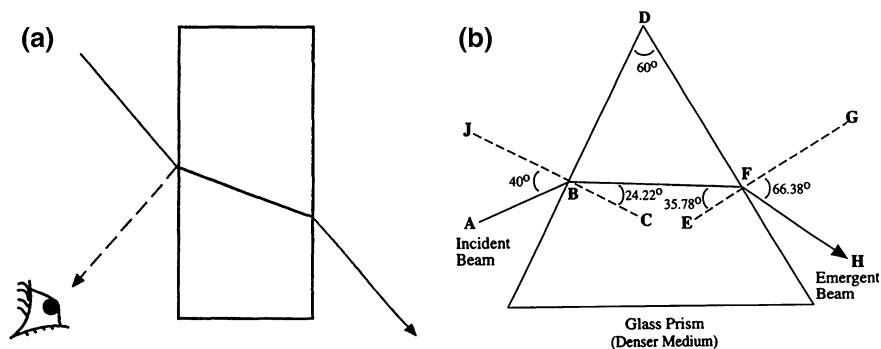


Fig. 2.7 Reflection and refraction at an acute angle to the reflecting surface for a transparent object with parallel sides (a) and detailed mode of interaction of light with a glass prism (non-parallel sides) (b). © 1998, M.V. Orna

rather heady circle of friends and colleagues included Blaise Pascal (1623–1662), René Descartes (1596–1650), and Giovanni Cassini (1625–1712).

Huygens' view is the only one that can help us understand refraction, the bending of light at the interface of two media with different densities. In both Fig. 2.7a and b, the light in air is shown entering and leaving a more dense medium, glass. In Fig. 2.7a, the glass plate has parallel sides. At the entrance surface, the light beam is bent toward the normal plane (an imaginary plane drawn at right angles to the surface) and at the exit surface, it is bent away from the normal plane, and the light beam resumes its original path, but slightly displaced. The reason why this is so is because the beam of light is a wave front and all the waves do not strike the surface at the same time when the angle of incidence is other than 90° , so the velocity of each wave does not change simultaneously, thus bringing about the bending we observe. When the object through which the light travels does not have parallel sides, as in the prism in Fig. 2.7b, then the entrance angle and the exit angle reinforce one another, bringing about the dispersion of each of the wavelengths that Newton observed and described. The shape of the prism is such that the light beam cannot resume its original path.

Two additional important interactions of light with matter are transmittance and absorption. In transmittance, as the word implies, the light passes through an object; the object must be transparent for this phenomenon to occur, but not necessarily colorless. We all know from our experience with stage lighting and colored filters that white light, when passed through a red filter, exits as red light. So, not only has transmittance occurred, but also the process of absorption, i.e., some of the light has been absorbed; only the red light was permitted to pass through the red filter; the rest of the light was held back, absorbed in the filter. So with a colored filter, we have observed transmittance and absorption at the same time. When light strikes an opaque object, this phenomenon of selective absorption can also take place, but what reaches our eye this time is reflected light. Let us see if we can describe this event more exactly. Figure 2.8a is the spectral energy distribution curve of ordinary sunlight. If this light strikes an opaque object that we

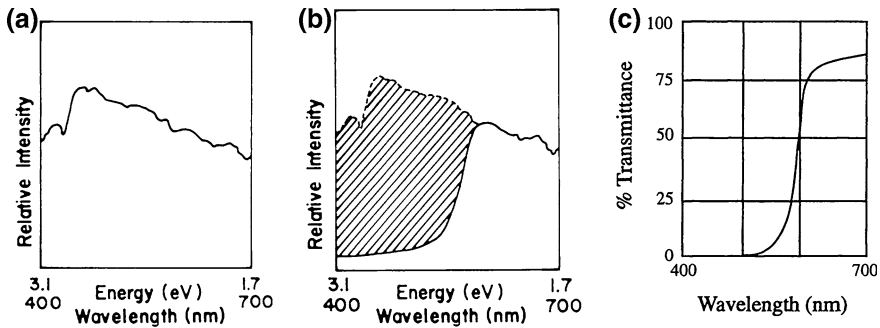


Fig. 2.8 Spectral energy distribution curve of ordinary sunlight (a), absorption spectrum of a red opaque object (b), transmittance spectrum of a transparent red object (c). © 1980, American Chemical Society, Ref. [15]

describe as red, then all the colors of the spectrum except red will be absorbed, and it will be the remaining red wavelengths that reach our eye.

If the light described by the curve in Fig. 2.8a were allowed to fall on an opaque object which absorbed some of the light, as shown in Fig. 2.8b, the light reflected to our eyes would no longer consist of significant intensities of all the wavelengths of visible light. The shaded area in the diagram is called the absorption band, and the unshaded area is the resulting reflectance curve of this “red” object. The light in the shaded area, which is largely green and blue light, has been absorbed to a great extent. Our eyes can then be stimulated only by the unabsorbed light at the red end of the spectrum, and so the object that yields this reflectance curve is perceived by the eyes as “red.” The color characteristics of most colored objects can be described partially by reference to the shape, width, intensity and position of their respective absorption bands. The superimposition of the spectral energy distribution curve of Fig. 2.8a on the reflectance curve of Fig. 2.8b yields a composite curve called the “stimulus for color” curve, which stimulates the eye–brain mechanism to see color [8, 16]. Figure 2.8c is the transmittance spectrum of a hypothetical transparent red object—this is the type of spectrum that is usually measured for educational purposes by some simple spectrophotometers.

Color, however, is a very complex phenomenon. Objects can modify light not only by reflectance and selective absorption, as we have seen, but also by transmission, scattering, dispersion, interference, etc.—sometimes all at once. It is the combination of all these possible interactions which ultimately determine the appearance of an object.

2.6.4 The Eye–Brain Detector-Interpreter

After modification the light must strike a detector in order to be evaluated. The most important detector when discussing color is the human eye because perceived

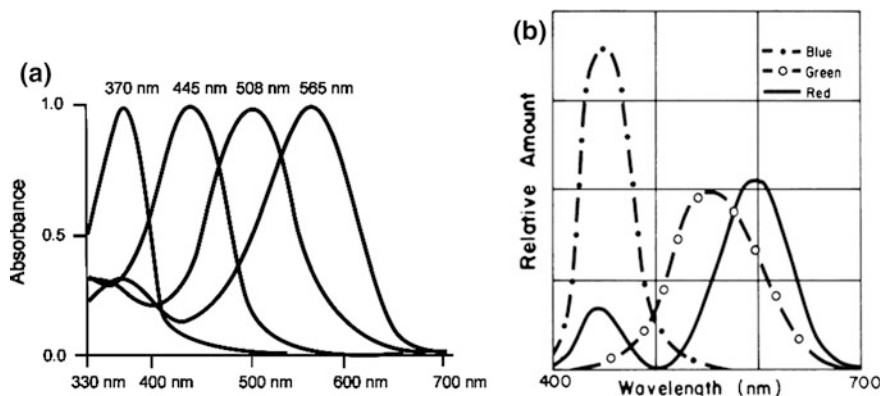


Fig. 2.9 **a** Sensitivity curves for the rods (370 nm curve) and cones (445 nm curve—blue; 508 nm curve—green; 565 nm curve—red, orange, yellow) in the human eye; **b** The 1931 CIE standard observer. © 1980, American Chemical Society, Ref. [15]

color is nothing more than the subjective personal evaluation of the light reflected or transmitted to the eye. A complete description of the color perception process must then involve the stimulus for color curve superimposed on the proper response curve for the human eye. Thomas Young (1773–1829) was the first to correctly recognize that color sensation is due to the presence of structures in the retina which respond to three colors. Young suggested that color blindness is due to the inability of one of these structures to respond to light. Hermann von Helmholtz (1821–1894) and James Clerk Maxwell (1831–1879) elaborated Young’s work into a proper theory. We now know from anatomical studies that the retina of the eye contains cone-like structures that are sensitive to the major regions of the spectrum, roughly divided into red–green–blue, and rod-like structures that are not color-specific. Rods work in dim light and enable the mind to sense brightness. The cones work in normal intensity of light and allow the mind to sense colors. The eye works like a camera with two films, one for black and white, and one for color. A photochemical process selects the proper “film” for the correct lighting conditions [17]. Figure 2.9a shows the sensitivity curves intuited by Young, but in more detail.

The retinal rods are more sensitive in the ultraviolet, and there are specialized cones for the blue, green and red regions respectively. Since these sensitivities are slightly different for each human being, the 1931 Commission Internationale de l’Eclairage (CIE) defined the response curve for a “standard observer” in order to overcome this difficulty. This curve, which is illustrated in Fig. 2.9b is actually three curves, one for each response region of the spectrum, and it is based upon the Young-Helmholtz theory discussed above [18, 19].

For reasons that will be discussed in the following chapter, ultraviolet and visible spectra give rise to characteristic broad bands of radiation. When these broad bands correspond to each of several different regions of the visible spectrum, they are capable of inducing a mental color response interpreted as a single color.

Table 2.2 Colors of absorbed light and corresponding complementary colors

Wavelength (nm)	Energy (eV)	Color of absorbed light	Color seen
400–420	3.10–2.95	Violet	Green–yellow
420–450	2.95–2.76	Violet–blue	Yellow
445–490	2.76–2.53	Blue	Orange
490–510	2.53–2.43	Cyan	Red
510–530	2.43–2.34	Green	Magenta
530–545	2.34–2.28	Green–yellow	Violet
545–580	2.28–2.14	Yellow	Violet–blue
580–630	2.14–1.97	Orange	Blue
630–720	1.97–1.72	Red	Cyan

For example, if red, green and blue lights are mixed in the proper proportions, the mental color response of the human eye is “white.” If blue light is subtracted from this mixture, and only the red–green combination remains, the human eye interprets this combination as “yellow.” Together, blue and yellow “complete” the visible spectrum; thus they are termed complementary colors. When a chemical substance absorbs the wavelengths of blue light from a “white” light source, the remaining wavelengths will be reflected to the eye and interpreted as the color yellow [20]. Newton himself first recognized these relationships and organized the spectral colors into a color circle. When two colors directly opposite one another in the circle were mixed in equal proportions the result was white (considered to be the center of the circle). This view leads to an infinite number of complementary colors, and a number of variations on Newton’s original color circle are in use today [2, 21]. Table 2.2 is a rough rendition of Newton’s original color circle in tabular form.

2.6.5 Primary Colors

As we have seen in Fig. 2.9, the human eye has three types of receptor cones, a long wavelength red, a medium wavelength green, and a short wavelength blue. Because of the sensitivity of these cones over a broad wavelength range, most of the other colors perceived can be created by adding the wavelengths of these three colors. Thus, adding together red light, green light and blue light produces white light—each of the three regions of the visible spectrum taken together complete it, and each ranges over approximately one-third of the spectrum. These three colors, because of these characteristics, are called the additive primary colors. They are not mixtures of any other colors. Yellow, however, is a mixture of red and green lights; cyan is a mixture of blue and green lights; magenta is a mixture of red and blue lights. The three mixed colors, yellow, magenta, and cyan are called the subtractive primary colors and are mainly useful when dealing with opaque substances such as pigments that selectively absorb broad bands of visible light. Since

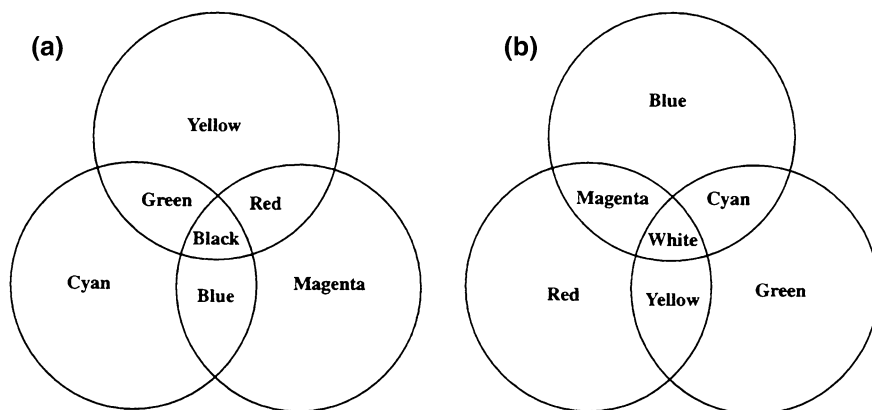


Fig. 2.10 Color circles of the subtractive primaries (a) and the additive primaries (b). © 1998, M.V. Orna

one diagram is worth a thousand words, let us take a look at Fig. 2.10 which are color circles that distinguish easily between the two types of primaries. The circles of Fig. 2.10a apply to the mixing of opaque colors such as paints. If yellow and cyan are mixed together, the yellow subtracts out the blue region of the spectrum, reflecting only red and green; the cyan subtracts out the red region of the spectrum, reflecting only blue and green. Since the only color that is reflected by both pigments is green, then the eye perceives the mixed color as green. Mixing all three subtractive primaries together produces black (or really in practice a muddy brown). The color directly across from each primary is its complement. Thus adding together yellow and blue pigments completes the subtractive process—all regions of the spectrum are absorbed [21].

The circles of Fig. 2.10b apply to the mixing of colored lights, such as one sees in stage settings—producing lights of different colors by using different filters. Mixing together red and blue lights produces magenta. Magenta is the complement to green. By adding green to magenta (actually red and blue) completes the spectrum and one sees a near facsimile of white light. So whenever primary colors are discussed, it must be made clear which ones: additive or subtractive?

One very practical application of these color circles is explaining why water appears blue when viewed in bulk. Due to hydrogen bonding, water absorbs very strongly in the infrared region and very weakly in the red–orange region of the spectrum. This slight red–orange absorption is enough to give water the bluish tint of the red–orange complement which is blue. Bulk ice in glaciers and icebergs also exhibits this blue color due to hydrogen bonding [22]. I was once standing on a glacier when someone asked our guide, “Why is the ice so blue?” The guide replied, “That is due to the ice reflecting the blue sky.” I promptly made a mental note to verify anything else that the guide told us after that incident.

Figure 2.11 is a photograph of a freshly calved iceberg from the South Sawyer Glacier in Tracy Arm, Alaska. I leave it to the viewer to judge if the intense blue of

Fig. 2.11 Freshly calved iceberg. Photograph: M. V. Orna



this ice arises merely from reflecting the blue sky, which incidentally, was quite cloudy on the day the photograph was taken. An understanding of the physical basis of color production and the conditions needed to perceive color will be helpful as we move into the next phase of understanding color: what types of substances are colored, why are they colored, and how can we control color production?

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