COLOR

1. Introduction

Being a perception, it is difficult to give a simple definition of color. We could say that perceived color is the part of perception that is carried to the eye from our surroundings by various wavelengths (or frequencies) of light. First, this involves the nature and spectral power distribution in the light from illuminating light sources. Next, there are several often interrelated processes derived from the interaction of the illumination with matter, including absorption, reflection, refraction, diffraction, scattering, and fluorescence. Finally, there is the perception system, involving the eye and the transmission system from eye to brain, leading to the final interpretation reached in the brain.

Perceived color depends on the spectral distribution of the color stimulus, on the size, shape, strucure, and surround of the stimulus area, on the state of adaptation of the observer's visual system, and on the observer's experience of the prevailing and similar conditions of observation., These last are complex processes, involving psychological as well as physiological factors. As one example, a specific shade of green may have a quite different meaning for a jungle resident than it has for a desert dweller. The color perceived is affected by the shape, size, texture, and gloss of the surface being viewed as well as by adjacent colors, recently seen colors, etc. There are also differences in perception for the different viewing modes discussed below.

As with any other perception, such as pain, one cannot know precisely what color another individual perceives, but the development of an agreed terminology of the stimuli that lead to color perception based on common experience has led to a satisfactory science of color description and measurement.The precise measurement of color is of significance in many branches of science and technology. It serves as a record for archival description, for standardization purposes, and for matching and controlling the many colorful products of commerce. In a field that has changed significantly even in the last decade, six books can be particularly recommended for further details (1–6). Additional books for a well-rounded basic library on color might include References 7–14. The latest Commission Internationale de l′Éclairage (CIE) publications (13) should be consulted for the current definitive word.

2. Color Fundamentals

An immediate complexity is illustrated in the two early and apparently incompatible theories of color vision. Trichromatic theory, first proposed in 1801 by Thomas Young and later refined by Hermann von Helmholtz, postulated three types of color receptors in the eye. This explained many phenomena, such as various forms of color blindness, and was confirmed in 1964, when three types of blue-, green-, and red-sensitive cones were reported to be present in the retina. Yet Ewald Hering's 1878 opponent theory, which used three pairs of opposites, light–dark, red–green, and blue–yellow, also offered much insight, including the explanation of contrast and afterimage effects and the absence of some color combinations such as reddish greens and bluish yellows. In the modern zone theories, it is now recognized that the data from three trichromatic detectors in the eye are processed on their way to the brain into opponent signals, thus removing the apparent inconsistencies.

In color technology and measurement, both types of approaches are used. Color printing, eg, generally employs three colors (usually plus black), and the ever useful CIE system was based on experiments in which colors were matched by mixtures of three primary color light beams, blue, green, and red. Yet transmitted television signals are based on the opponent system, with one intensity and two color-balance signals, as are the modern representations of color, such as the CIELAB and related color spaces based on red–green and yellow–blue opponent axes.

2.1. Light and Color.

Visible light is that part of the electromagnetic spectrum, shown in Figure 1, with wavelengths between the violet limit of 400 nm and the red limit at about 700 nm. Depending on the observer, light intensity, etc, typical values for the spectral colors are blue, 450 nm; green, 500–550; yellow, 580; orange, 600; and red, 650. There are also the nonspectral colors purple, magenta, brown, etc, as well as mixtures of all of these with black and white. It has been estimated that an individual with normal color vision can distinguish a total of 7 million different colors.

In 1666, Sir Isaac Newton first split white light with a prism into its component colors, the spectrum, and he assigned the colors red, orange, yellow, green, blue, indigo, and violet, using just seven colors, possibly by analogy with the seven notes of the musical scale. The eye, however, functions quite differently from the ear, which is able to perceive the sound from individual

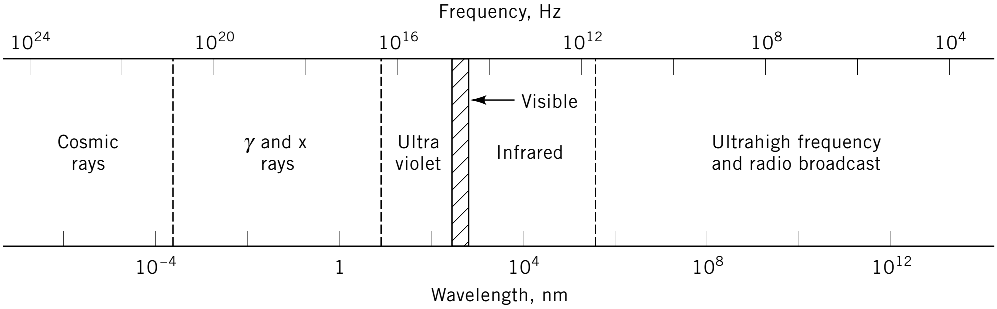


Fig. 1. The electromagnetic spectrum (2).

instruments sounding together, while the eye always perceives only a single color at a given point, whether this be spectrally pure orange, an equivalent mixture of yellow and red, an equivalent mixture of green and red, etc. Newton did recognize that his "rays ... are not coloured. In them there is nothing else than a certain power ... to stir up a sensation of this or that colour." Nevertheless, terms such as "orange light" are commonly used and need not produce any confusion if this qualification is kept in mind.

The spectral color sequence, joined by some nonspectral colors such as purple and magenta, is one of several attributes used in descriptions of color, variously designated hue, chromatic color, dominant wavelength (or simply, but imprecisely and quite unsuitably for the present purposes, color). A second attribute is saturation, chroma, tone, or purity, which gives a measure of how little or much gray (or white or black) is present. Thus a mixture of pure spectral blue with gray gives an unsaturated blue, transforming into gray (or white or black) as the amounts of additive are increased. For any given hue and saturation, there can be different levels of brightness, lightness, luminance, or value, completing the three parameters normally required to specify color.

Color in the full technical sense encompasses a multidimensional space defined at a minimum by the foregoing three parameters with the addition of factors such as the color environment, gloss, reflectancy, and translucency. An example that clarifies this point is that a strong orange becomes, when the brightness is reduced compared to adjacent areas, but with constant hue and saturation, not a weak orange but a brown. Thus to obtain brown one either mixes orange and black paints or one views an orange surface through a hole in a more brightly illuminated screen (so that the orange in appearing to be of low brightness, is then perceived as brown). In the same way, a greenish yellow can be perceived as having an olive color.

The appearance of color clearly depends significantly on the exact viewing circumstances. Normally one thinks of viewing a colored object under some type of illumination, the object mode; then there is the surface mode, eg, when light is perceived to be reflected from an object's surface; viewing a light source there is the illuminant or luminous mode; viewing through a hole in a screen there is the aperture mode, and so on. Perception differs significantly in these modes. In the object mode, the eye–brain has the ability to compensate for a wide range of illuminants (white sun, blue sunless sky, reddish incandescent lamp, or candle) and

Table 1. **Object Mode Perceptions**[a]

Object	Dominant perception	Secondary attributes[b]
opaque metal, polished	specular reflection	reflectivity, gloss, hue
opaque metal, matte	diffuse reflection	hue, saturation, brightness, gloss
opaque nonmetal, glossy	diffuse and specular reflections	hue, saturation, gloss, brightness
opaque nonmetal, matte	diffuse reflection	hue, saturation, brightness
translucent nonmetal	diffuse transmission	translucency, hue, saturation
transparent nonmetal	transmission	hue, saturation, clarity

[a] Ref. 1.

[b] In approximate sequence of importance.

infer something very close to the true color. At the same time, various surface effects enter, as shown in Table 1. Even a nonmetallic object with a deeply colored surface will reflect almost pure illuminant in the glare of a glancing angle if it is glossy. The perceived color is influenced by the presence of adjacent colors in the object mode, and several additional color-appearance phenomena also can influence color perception. One, two, or more additional parameters (1) may be required in addition to the customary three for a full specification of the perceived color, but fortunately this is unusually not necessary.

2.2. Interactions of Matter with Light.

In the most generalized interaction of light with matter the many phenomena of Figure 2 are possible. In absorption, electrons are excited by the absorbed photons and their energy may subsequently appear as heat or as fluorescence, an additional emitted light at a lower energy, ie, longer wavelength. This effect is utilized in fluorescent whitening agents used in detergents, paper, textiles, etc. Scattering may derive from irregularities of the surface, diffuse, or matte as distinguished from glossy

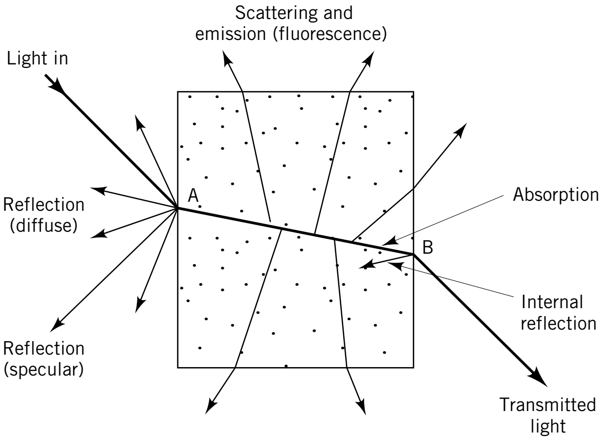


Fig. 2. The adventures of a beam of light passing through a block of partly transparent substance (2).

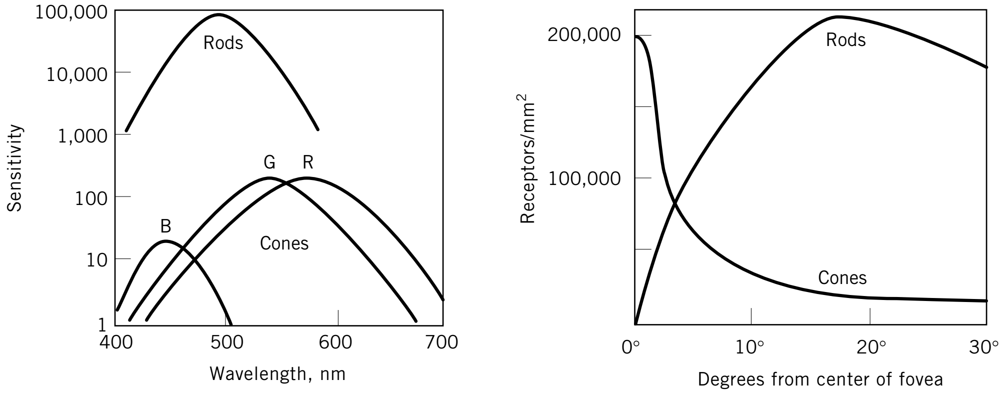
or specular reflection. Interference, eg, the diffraction grating effect, derives from regularly repeated patterns. Irregularities in the interior, depending on the size and geometry, may involve Rayleigh or Mie-type scattering and then lead to translucency or opacity if there is pronounced multiple scattering, as well as color at times.

3. Color Vision

3.1. The Eye.

In vision, light passes through the cornea, the transparent outer layer of the eye, through the lens and the aqueous and vitreous humors, and is focused onto the retina. The iris, forming the pupil, acts as a variable aperture to control the amount of light that enters the eye, varying from ~ *f*/2.5 to *f*/13 with a 30:1 light intensity ratio. The two humors serve merely as neutral transmission media and to keep the eyeball distended. The retina is a layer ~0.1 mm thick that contains the light-sensitive rods and cones. Only the rods function in low levels of illumination of about <1 lux, providing an achromatic, noncolor image. The rod spectral response is shown in Figure 3**a.** The cones are of three types, designated B, G, and R in this figure. Although these are often spoken of as blue-, green-, and red-detecting cones, such designations are incorrect. As can be seen, each set of cones is sensitive to a wide range of wavelengths with extensive overlap. Appropriate designations are short-, medium-, and long-wavelength sensitive cones, but the B, G, and R labels provide a convenient mental picture useful as long as the actual functioning is kept in mind.

The distribution of rods and cones is shown in Figure 3**b** centered about the fovea, the area of the retina that has the highest concentration of cones with essentially no rods and also has the best resolving capability, with a resolution about one minute of arc. The fovea is nominally taken as a 5° zone, with its central 1° zone designated the foveola. There are ~40 R and 20 G cones for each B



(a) (b)

Fig. 3. (**a**) The relative sensitivities of the rods and the three sets of cones in the human eye (2). (**b**) The distribution of rods and cones in the central part of the human retina. The x axis is marked in degrees from the center of the fovea.

cone in the eye as a whole, whereas in the fovea there are almost no B cones. A result of this is that color perception depends on the angle of the cone of light received by the eye. Extremely complex chemistry is involved in the stimulation of opsin molecules, such as the rhodopsin of the rods (2).

The trichromatic theory, subsequently confirmed by the existence of the three sets of cones, must be combined with the opponent theory, which is involved in the signal sent along the retinal pathway from the eye to the brain. A third approach, the appearance theory (4) or the retinex theory, must be added to explain color constancy and other effects. As one example of this last, consider an area in a multicolored object such as a Mondrian painting perceived as red when illuminated with white light. If the illumination is changed so that energy reflected by this same area is greater at shorter wavelengths than the energy reflected at longer wavelengths (as would be the case for green), this area is still perceived as red within the overall visual context. If all other colors are now covered so that only our "red" area is visible, corresponding to the aperture mode, then this area is perceived as green. Clearly, all three approaches must be melded to give a full description of color perception, a process that is not yet fully understood.

In addition to this color constancy phenomenon, there are several other well-known effects that can influence the perception of color. In simultaneous contrast phenomena, there are effects from both luminosity differences and color differences across a boundary. The Bezold-Brücke effect involves a change in hue with luminance, a shift toward the blue end of the spectrum as the luminance is increased. Colors also appear more desaturated at both very high and very low luminances than at intermediate values. In the Helmholtz-Kohlrausch effect there is an increase in the apparent luminance as reflected light increases in spectral purity at constant luminosity. Finally, there is the well-known aftereffect, when prolonged viewing of a color distorts the next-viewed color in the direction of the complementary color of the first.

3.2. Color Vision Defects.

Anomalous color vision is present, eg, if one of the three sets of cones is inoperative (dichromacy) or defective (anomalous trichromacy). This affects 2–3% of the population with males more prone because these defects reside on the X chromosome, with only one present in males but two in females. Eye specialists have standard tests for detecting these and other defects. Summaries of this whole field are available (eg, see Ref. 6).

4. Color Order Systems

Many one-, two-, and three-dimensional systems have been developed over the years to order colors in a systematic way and provide specimen colors for visual comparison. Coordination has now been achieved with computer programs between essentially all of these systems, including the CIE systems described below, and conversions can easily be made between them.

4.1. The Munsell System.

The best known and most widely used color order system is the Munsell system (10,14,15), developed by the artist A. H. Munsell in 1905 and modified over the years. This is a three-dimensional space shown in Figures 4 and 5 on the color plate. Munsell value *V* (or lightness)

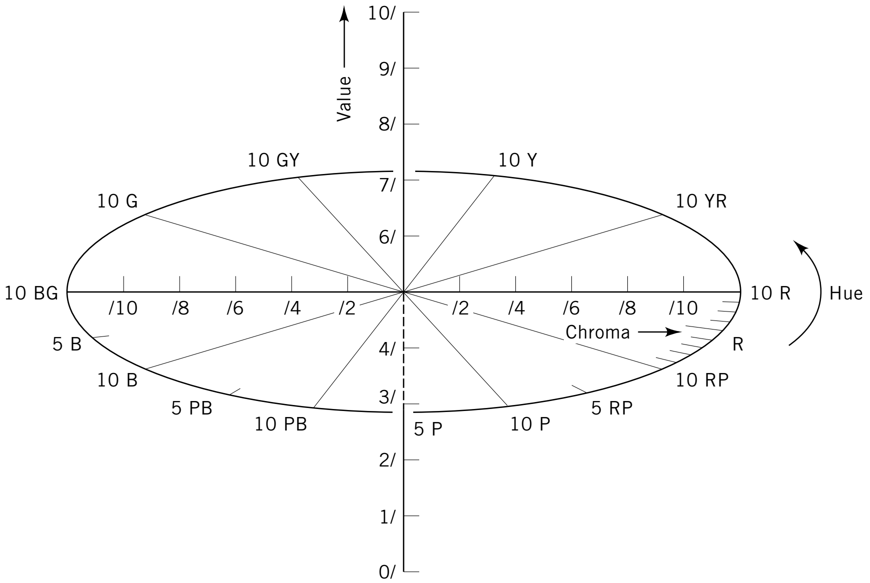


Fig. 4. The coordinate system of the Munsell color order system: R, red; Y, yellow; G, green; B, blue; and P, purple (1).

is used as the vertical axis with 0/ for black at the bottom and 10/ for white at the top. Radially there is the Munsell chroma C with /0 at the center and maximum / 10 or higher at the periphery. The Munsell hue H at the periphery uses the five principal hues: red, yellow, green, blue, and purple and the five adjacent binary combinations such as BG, with 10 steps within each, for a total of 100 hue steps as in Figures 4 and 5. These 100 steps can be further subdivided. A full designation for an orange school bus in the usual HVC sequence and using interpolation might then be 9.5YR 7/9.25. The Munsell system was renotated in 1943 to make it more uniform and consistent with the CIE system. The *Munsell Book of Color* (15) consists of ~1500 painted paper chips available in both glossy and matte versions; there are also textile color collections (15), now discontinued. With interpolations some 100,000 colors can be distinguished within the Munsell system by visual comparison under carefully standardized viewing conditions.

4.2. Other Color Order Systems. The Natural Color System (16), abbreviated NCS, developed in Sweden is an outgrowth of the Hesselgren Color Atlas, and uses the opponent color approach. Here colors are described on the basis of their resemblances to the basic color pairs red-green and blue–yellow, and the amounts of black and white present, all evaluated as percentages. Consider a color that has 10% whiteness, 50% blackness, 20% yellowness, and 20% redness; note that the sum is 100%. The overall NCS designation of this color is 50, 40, Y50R indicating in sequence the blackness, the chromaticness (20 + 20), and the hue (50% on the way from yellow to red; the sequence used is Y, R, G, B, Y).

The Ostwald Color System (17) is a nonequally spaced system and is no longer published, as is also true of the *Maerz and Paul Dictionary of Color*

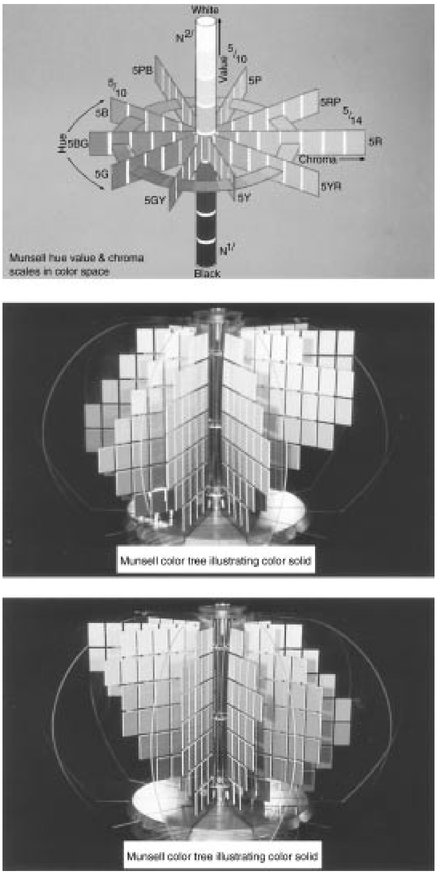


Fig. 5. Munsell hue, value, and chroma scale arrangement. Courtesy of Gretag Macbeth.

(18). There are also the Colorcurve, the Coloroid, and the German DIN systems, among others. The Optical Society of America has published the OSA Uniform Color Scale System (19) with 558 equally spaced color chips. This uses a designation such as 2:5:3, with the first number (ranging from −7 to +5) specifying the lightness, the second (−6 to +15) giving the blue-yellow content, and the third (−10 to +6) for red−green. For many purposes a much simpler set of 267 color regions as provided by the ISCC-NBS Centroid System, a joint project of the Inter-Society Color Council and the USA National Bureau of Standards, now NIST, (20) is convenient. This uses color names with adjectival modifications of the form vivid blue, brilliant yellow-green, light yellowish brown, and so on.

Many systems of limited range or of lower dimensionality are used in industry for the designation and control of color circumstances where a limited scale is suitable. Examples are the systems for describing plant tissues; soils; and skin, hair, and eye colors. There are no <19 color scales for yellow in oil, fat, varnish, etc, under names such as Gardner, Saybolt, Lovibond, and Hellige (5). Then there is the D, E, F... scale used for near-colorless diamonds devised by the Gemological Institute of America. These systems are well known within highly specialized industries and many have been standardized by industry organizations such as ASTM, TAPPI, and Federal Tests. A summary is given in Reference 5.

5. Basic Colorimetry

The International Commission on Illumination (abbreviated CIE from the French name) over the years has recommended a series of methods and standards in the field of color; for a history of this process see Reference 21.

Consider light of a certain spectral energy distribution falling on an object with a given spectral reflectance and perceived by an eye with its own spectral response. To obtain the perceived color stimulus, it is necessary to multiply these factors together as in Figure 6. Standards are clearly required for both the observer and the illuminant.

5.1. The CIE Standard Observer.

The CIE standard observer is a set of curves giving the tristimulus responses of an imaginary observer representing an average population for three primary colors arbitrarily chosen for convenience. The 1931 CIE standard observer was determined for 2° foveal vision, while the later 1964 CIE supplementary standard observer applies to a 10° vision; a subscript 10 is usually used for the latter. The curves for both are given in Figure 7 and the differences between the two observers can be seen in Table 2. The standard observers were defined in such a way that of the three primary responses $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$, the value of $\bar{y}(\lambda)$ corresponds to the spectral photopic luminous efficiency, ie, to the perceived overall lightness of an object.

CIE used the 1931 CIE standard observer to establish a color representation system in which the hue and saturation could be represented on a two-dimensional diagram. Three tristimulus values X, Y, and Z are first obtained, based on the standard observer, so that the hue and saturation of two objects

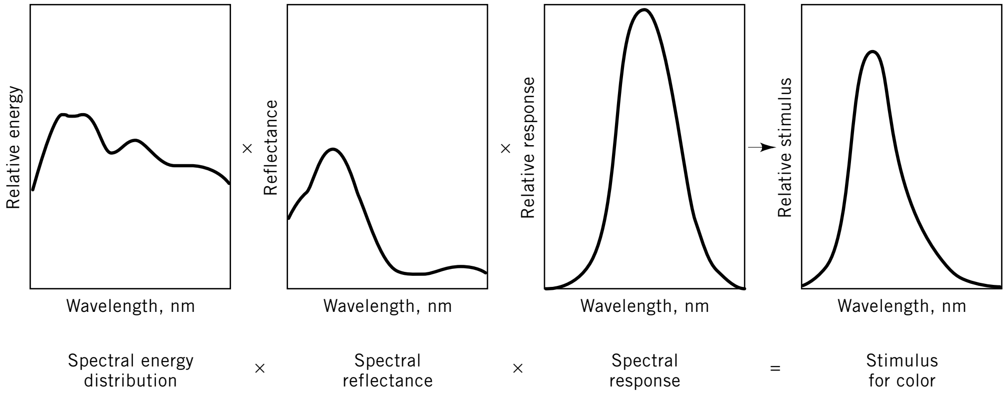


Fig. 6. The stimulus perceived as color is made up of the spectral power (or, as here, energy) curve of a source times the spectral reflectance (or transmittance) curve of an object times the appropriate spectral response curves (one shown here) of the eye (1).

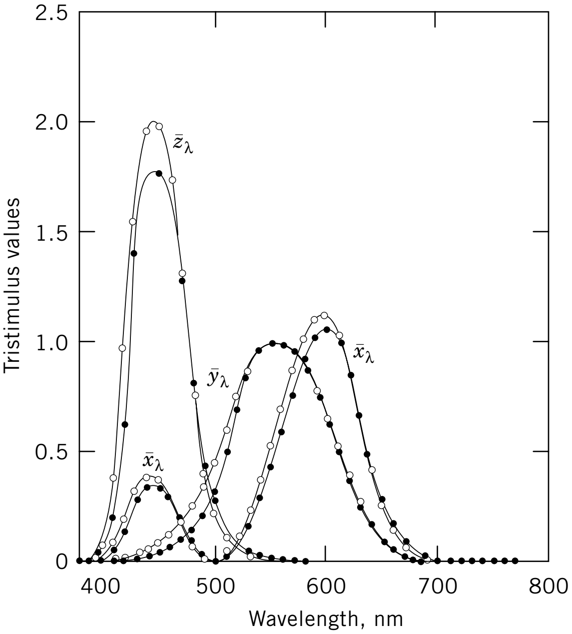


Fig. 7. Color matching functions of the CIE 1931 2° standard colorimetric observer (–●–), and the CIE 1964 10° supplementary standard colorimetric observer (–○–) (1).

match if they have equal values of these three parameters. Each of these is defined, following the concept of Figure 6, in the form:

$$X = k\int S(\lambda)R(\lambda)\bar{x}(\lambda)d\lambda$$

where $S(\lambda)$ is the spectral power distribution of the illuminant, $R(\lambda)$ is the spectral reflectance factor of the object, and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ are the color matching functions of one of the standard observers of Figure 7. The constant k is defined

Table 2. **Spectral Chromaticity Coordinates**[a]

Wavelength, nm	x	y	x_{10}	y_{10}	u'	v'	u'_{10}	v'_{10}
400	0.1733	0.0048	0.1784	0.0187	0.2558	0.0159	0.2488	0.0587
450	0.1566	0.0177	0.1510	0.0364	0.2161	0.0550	0.1926	0.1046
500	0.0082	0.5384	0.0056	0.6745	0.0035	0.5131	0.0020	0.5477
550	0.3016	0.6923	0.3473	0.6501	0.1127	0.5821	0.1375	0.5789
600	0.6270	0.3725	0.6306	0.3694	0.4035	0.5393	0.4088	0.5387
650	0.7260	0.2740	0.7137	0.2863	0.6005	0.5099	0.5700	0.5145
700	0.7347	0.2653	0.7204	0.2796	0.6234	0.5065	0.5863	0.5121

[a] Values for the 2° CIE chromaticity coordinates x, y and the 10° coordinates x_{10}, y_{10}; the 2° and 10° red-green metric chromaticity coordinates u' and u'_{10} and the 2° and 10° yellow-blue metric coordinates v' and v'_{10}.

in terms of $S(\lambda)$, the spectral power distributions of the illuminant as

$$k = 100 \Big/ \int S(\lambda)\bar{y}(\lambda)d\lambda$$

so that Y for a perfectly reflecting diffuser is 100.

5.2. Chromaticity Diagrams. The CIE 1931 chromaticity diagram uses the chromaticity coordinates:

$$x = X/(X+Y+Z); \qquad y = Y/(X+Y+Z); \qquad z = Z/(X+Y+Z)$$

It is not actually necessary to specify z, since $x+y+z=1$. The two-dimensional presentation of x and y is shown in Figure 8 and in Figure 9 on the color plate. Here Newton's pure spectral colors in fully saturated form follow the horseshoe-shaped curve with wavelengths from 400-nm violet to 700-nm red. Coordinates for these spectral colors at 50-nm intervals are given in Table 2 for both 2° and 10° observers. Closing the curves in these figures is the dashed line from red to blue, including the saturated nonspectral purples and magentas.

Any straight line passing through the central achromatic point marked W for white (standard daylight D_{65} in this instance) connects complementary colors,

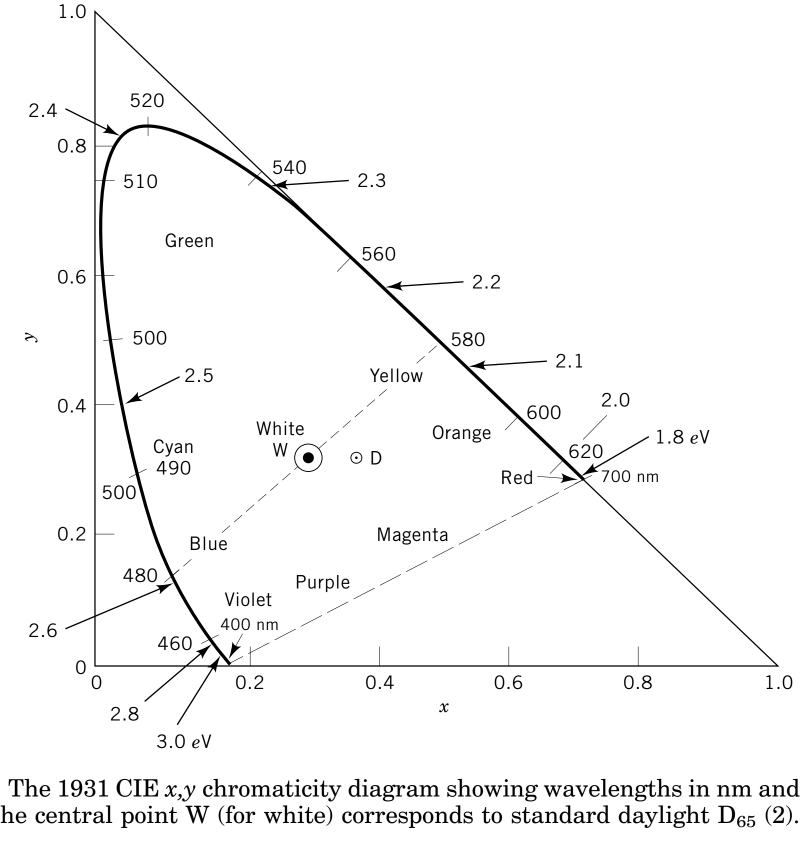


Fig. 8. The 1931 CIE x,y chromaticity diagram showing wavelengths in nm and energies in eV. The central point W (for white) corresponds to standard daylight D_{65} (2).

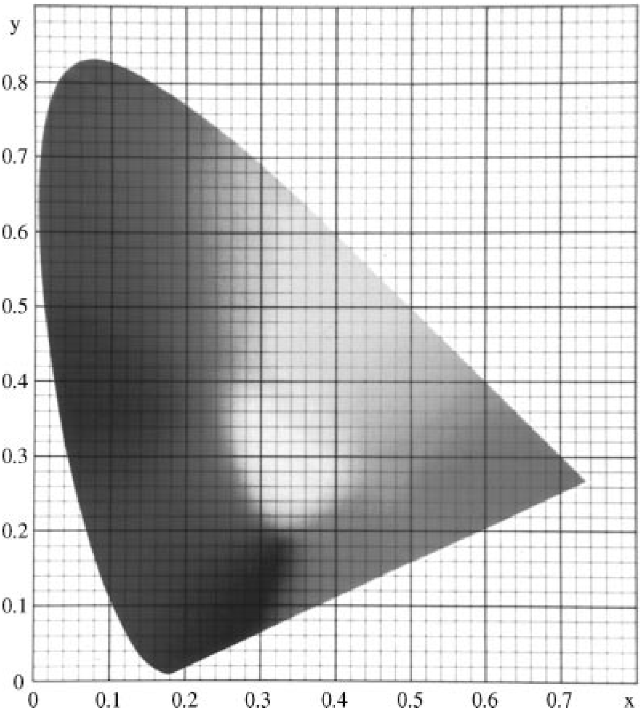


Fig. 9. An artist's representation of where the colors lie on the 1931 CIE *x, y* chromaticity diagram. The CIE does not asociate specific colors with regions on this diagram. Courtesy of Minolta.

such as the line connecting 480-nm blue and 580-nm yellow shown. These two colors will together give white in amounts given by the law of the lever lengths (length WY of the blue and length BW of the yellow). Saturated orange at 620 nm becomes unsaturated when mixed with white as at D. The color of D can be specified by its X, Y, and Z tristimulus values, by the chromaticity coordinates $x = 0.4$, $y = 0.3$ together with the lightness Y in the frequently used x, y, Y designation, or it could be described by Y together with the dominant wavelength of 620 nm, with 25% purity, since D corresponds to three parts of W and one part of 620-nm orange. If a point is in the lower right part of Figure 8, where the dominant hue is on the nonspectral blue to red join, then there is no dominant wavelength; instead the line is extended upward through the W point to reach the spectral curve at the complementary dominant wavelength, such as 510c nm.

One of several defects of the chromaticity diagram of Figures 8 and 9 is that the minimum distinguishable colors are not equally spaced, ie, that equal changes in x, y, and Y do not correspond to equally perceived color differences. Very obviously, the greens occupy a disproportionately large area in these figures. Many transformations have been studied to adjust this, but none is perfect. Probably, the most useful employs L^* (the perceived lightness) and the CIE 1976

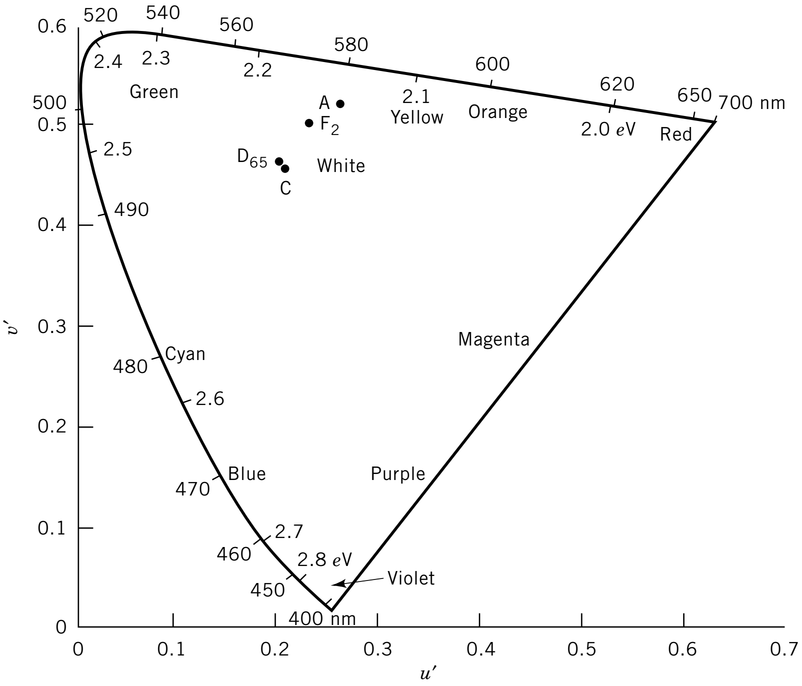


Fig. 10. The currently recommended 1976 CIE uniform u', v' chromaticity diagram showing wavelength in nm and energies in eV; A, C, and D_{65} are standard illuminants and F_2 is a typical fluorescent lamp.

Chromaticity Coordinates u' and v' as shown in Figure 10 obtained from

$$u' = 4X/(X + 15Y + 3Z) = 4x(-2x + 12y + 3)$$

$$v' = 9Y/(X + 15Y + 7Z) = 9y(-2x + 12y + 3)$$

5.3. Standard Illuminants.

Three of many sources with quite different energy distributions, which the eye nevertheless accepts as white, are the daylight, incandescent light, and fluorescent lamp light curves shown in Figure 11. The chromaticity diagram is convenient for representing light sources as in Figure 10. One particular use is to describe ideal black body colors, the sequence black, red, orange, yellow, white, and bluish white exhibited as any object is heated up under idealized conditions as described in Section 8.1 below. For real incandescent objects, ie, nonideal black bodies, that ideal black body temperature is used which gives the closest visual color match.

Standardized light sources are clearly desirable for color matching, particularly in view of the phenomenon of illuminant metamerism described below. Over the years, CIE has defined several standard illuminants, some of which can be closely approximated by practical sources. In 1931, there was Source A, defined as a tungsten filament incandescent lamp at a color temperature of

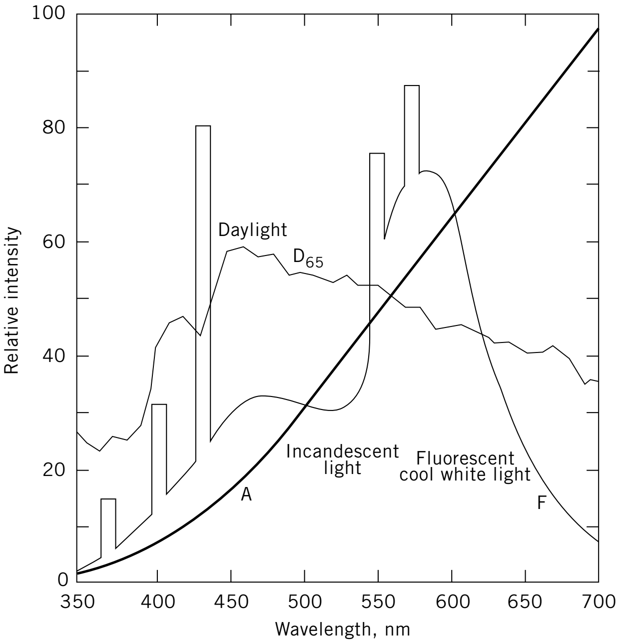


Fig. 11. Energy distributions of CIE standard illuminant A, a tungsten incandescent lamp; a cool white fluorescent lamp F; and CIE standard illuminant D_{65} that approximates average daylight (2).

2854 K. Sources B and C used filtering of source A to simulate noon sunlight and north sky daylight, respectively, but are no longer used. Subsequently a series of D illuminants was established to better represent natural daylight. Of these the most important is Illuminant D_{65}. A series of F illuminants pertain to fluorescent tube lamp sources.

There are ASTM (American Society for Testing and Materials, West Conshohocken, Pa.) standards promulgated for various aspects of color measurement; these are cited in many textbooks (eg, see Ref. 1). Both CIE and ASTM continue to promulgate improved standards and techniques from time to time; this is a field that has not yet reached full maturity.

5.4. Gloss and Opacity. Attributes such as gloss, transparency, translucency, opacity, haze, and luster may apply to some materials (Table 1), and these are relevant in that they may influence the judgment of color differences. As one example, gloss can produce veiling reflections that change the apparent contrast. When present, these attributes can be measured using specialized approaches. Six types of gloss are distinguished (5): specular gloss, sheen, contrast gloss or luster, absence-of-bloom gloss, distinctness-of-image gloss, and surface uniformity gloss. Opacity can be measured by the contrast ratio method, using the reflectance with both a white and a black backing. Standardized procedures for some of these methods have been established by organizations such as ASTM and TAPPI (5).

5.5. Light Mixing. Light or additive mixing applies to light beams, such as stage lighting or on a television screen. A beam of light that appears to match orange at 600 nm when projected onto a white surface may consist of pure 600-nm light or of one of many types of mixtures, eg, of red, orange, yellow, and green, the energy distribution of which has its center of gravity at 600 nm. White results from mixtures of two complementary colors, as discussed in the Section Chromaticity Diagrams, or when any suitable set of three-color beams of the appropriate intensity are mixed, in essence reconstructing the full spectrum in some instances. On the chromaticity diagram of Figures 8 and 9, the condition for equal intensity beams to produce white is that W lies at the center of gravity of the triangle formed by the three sources. A suitable set of primary additive light beams is red, blue, and green, each being near a corner of Figures 8 and 9. Any color within the triangle formed by the three primary colors, designated the gamut, can be reproduced. Red and green by themselves add to give yellow, red and blue give purple and magenta, and blue and green give blue-green and cyan, as can be established by tie lines on Figure 8. It is important to distinguish magenta from red and cyan from blue to avoid confusing the additive from the subtractive system described next.

5.6. Colorant Mixing.

A colorant, whether a dye dissolved in or absorbed by a medium or pigment particles dispersed in a paint, produces color by absorbing and/or scattering part of the transmitted or reflected light. Consider a pigment that when illuminated with white light matches 580-nm yellow. It does so because it absorbs wavelengths complementary to yellow, ie blue; more specifically when the center of gravity of the energy distribution of the absorbed wavelengths falls at the 480-nm blue that is complementary to the 580-nm yellow. If only absorption is present, the Beer-Lambert law applies:

$$A(\lambda) = \log 1/T(\lambda) = \sum_i a_i(\lambda) b c_i$$

where A is the absorbance, T is the transmittance, $a_i(\lambda)$ is the absorptivity or specific absorbance of absorber i at wavelength λ, b is the length of the absorbing path, and c_i the concentration of the absorber. When colorants are mixed, they function by each independently absorbing light and the subtractive mixing rules merely specify this additivity. Here the result of mixing three primary colorants is to absorb all light and produce black if sufficiently concentrated. In actual practice a fourth pigment, usually a white or black opacifier, needs to be added to ensure opacity. The preferred primary colorants are the complementary colors of the corners of Figures 8 and 9, namely, cyan, yellow, and magenta (unfortunately usually designated blue, yellow, and red when taught in elementary school). Combining yellow and cyan colorants then produces green, yellow and magenta give red, and cyan plus magenta give blue. Mixtures of light beams in additive mixing are fully predictable because they give straight lines on the chromaticity diagram. Mixtures of pigments usually give curves on the chromaticity diagram and are therefore not simply predictable. It should also be noted that artists do not in fact mix primary colors on their palette, since this would limit the saturation: no mixture of blue and yellow paints can match the intensity available in the pigment chrome green.

When both absorption and scattering are present, the Beer-Lambert law must be replaced by the Kubelka-Munk equation employing the absorption

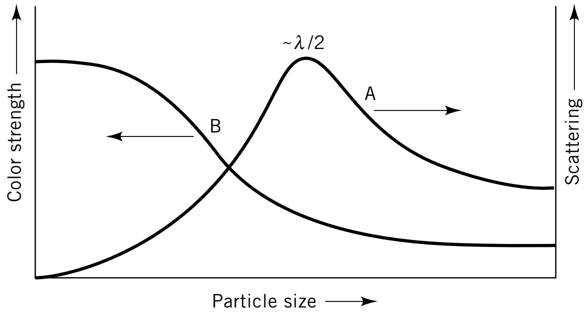


Fig. 12. Curve A, the schematic variation of scattering, and B, color strength for pigment particles of various sizes (2).

and scattering coefficients K and S, respectively. This gives the reflectivity R_∞

$$(1 - R_\infty)^2/2R_\infty = K/S = \sum_i c_i K_i(\lambda) \Big/ \sum_i c_i S_i(\lambda)$$

where c_i is the concentration and $K_i(\lambda)$ and $S_i(\lambda)$ are the specific absorbance and scattering parameters, respectively, of absorber and scatterer i at wavelength λ.

The color of an opaque paint depends both on the size of the pigment particles and on refractive index considerations. The scattering is maximum, as shown in Curve A of Figure 12, when the particle size is about one-half of the wavelength of light, ie, in the 200–350-nm range; this is desired for opacity in typical inorganic pigments with refractive index much larger than that of the medium. With organic pigments, where the refractive index is not very different, scattering is replaced by absorption as the principal interaction; here the color strength or absorptive power increases as the particle size is decreased to a much smaller size, as shown in curve B of Figure 12. Unfortunately, too small a particle size may lead to increased chemical reactivity and a reduction of the lightfastness, requiring compromises.

The ready availability of computers has led to the detailed analysis of the colorant formulation problems faced every day by the textile, coatings, ceramics, polymer, and related industries. The resulting computer match prediction has produced improved color matching and reductions in the amounts of colorants required to achieve a specific result with accompanying reductions of cost. Detailed treatments have been given for dyes and for pigments (eg, see 9).

5.7. Metamerism. There are several types of metamerism, the phenomenon in which two objects perceived as having a perfect color match under one set of conditions are found to differ in color under other conditions. Most common is illuminant metamerism that occurs when a change in illuminant is the cause. This originates from the above described situation that a given visually identified hue can be caused by many different stimuli, eg, by an object reflecting, say, only pure spectral orange, or red plus yellow, etc. A change in illuminant to one having more energy in the red, for example, would leave the perceived color of the pure spectral orange unchanged, but would make the red plus yellow combination appear to be a more reddish orange. Another related cause would be the presence of an ultraviolet component in one of the sources (usually actual daylight) causing a fluorescent object to emit light in addition to that reflected compared to a visible-light-only source such as an incandescent lamp. Note that the standard illuminant D_{65} specifies significant intensity at wavelengths less than 400 nm in the uv.

Observer metamerism derives from the significant differences in spectral response found among persons even with normal color vision. The variation in cone concentration and cone-type distribution discussed above results in field size metamerism. Here an example is the difference between the 2° and 10° response curves of the standard observers of Figure 7. Finally, there can also be a change in perceived color with a change in viewing angle, as with some metallic paints and with interference-based color-changing inks.

Quantification of metamerism is difficult and its avoidance is a principal aim in color technology. The car where body color, upholstery, and plastic parts match in the lit showroom should not show clashing colors in daylight. The obvious but rarely applicable solution is to use the same pigments in all parts. Some illuminant metamerism is almost unavoidable; the aim of the color expert is to keep it within acceptable limits, ie, to achieve adequate color consistency.

6. The Measurement of Color Differences

The 1931 CIE system with its x, y, Y chromaticity diagram system is useful for general colorimetry and color matching, but it suffers several drawbacks, including that it is not suitable for color-difference measurements. These problems were partly corrected in the 1976 CIE u', v' chromaticity diagram to achieve a more uniform color space. Both the x, y, and u', v' systems are still basically two-dimensional, with the lightness Y or L^* added. A series of transformations led to modified systems that are fully three-dimensional with the length of any lines, however, oriented within this space, more closely representing perceived color differences. Some of these are opponent related. Two systems were agreed upon, designated the CIELUV and CIELAB color spaces, and have come into widespread use.

6.1. The 1976 CIELUV Color Space.

The CIEUV space, properly designated CIE $L^* u^* v^*$, uses a white object or light source designated by the subscript n as the reference standard and employs the transformations:

$$L^* = (116Y/Y_n)^{1/3}{-}16;\ Y/Y_n > 0.008856$$

$$L^* = (903.3Y/Y_n);\ Y/Y_n \leq 0.008856$$

$$u^* = 13L^*\left(u' - u'_{\mathrm{n}}\right)$$

$$v^* = 13L^*\left(v' - v'_{\mathrm{n}}\right)$$

where L^* is the perceived lightness.

The CIELUV space preserves a property of the CIE 1931 chromaticity space which is important in the field of color reproduction, eg, in the television industry. This is the characteristic that the chromaticities of additive mixtures of color stimuli lie on the straight line connecting the chromaticities of the component stimuli; this is true of the 1976 metric chromaticity diagram but not of the CIELAB space that follows.

6.2. The 1976 Cielab Color Space. Defined at the same time as the CIELUV space, the CIELAB space, properly designated CIE $L^*a^*b^*$, is a nonlinear transformation of the 1931 CIE *x, y* space. It also uses the metric lightness coordinate L^*, together with

$$a^* = 50\left[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}\right]$$

$$b^* = 200\left[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}\right]$$

These equations apply for X/X_n, Y/Y_n, and Z/Z_n all >0.008856. For $X/X_n \leq 0.008856$, the term $(X/X_n)^{1/3}$ is replaced by $[7.787(X/X_n) + 16/116]$ and similarly for Y and for Z in these two equations.

This transformation results in a three-dimensional space that follows the opponent color system with $+a^*$ as red, $-a^*$ as green, $+b^*$ as yellow, and $-b^*$ as blue. CIELAB is closely related to the Munsell system of Figure 4 as well as to the older Adams-Nickerson and other spaces of the *L,a,b* type, which it replaced (1,5).

The CIELAB coordinates $L^*a^*b^*$, either in that form or in the L^* C^*_{ab}, h_{ab} form discussed below, are the most commonly used color descriptors in the field of paints, pigments, textiles, paper, ceramics, polymers, and most other opaque to transparent substances.

6.3. The 1976 CIE Metric Color Spaces. Both the CIELUV and CIELAB spaces can have their Cartesian coordinates converted to cylindrical coordinates, called metric or hue-angle coordinates, with L^* unchanged. These coordinates are designated CIE L^* C^*_{uv} h_{uv} and CIE L^* C^*_{ab} h_{ab}, respectively. The metric hue-angles are given as

$$h_{uv} = \tan^{-1}(v^*/u^*) \qquad h_{ab} = \tan^{-1}(b^*/a^*)$$

and the metric chromas

$$C^*_{uv} = \left[(u^*)^2 + (v^*)^2\right]^{1/2} \qquad C^*_{ab} = \left[(a^*)^2 + (b^*)^2\right]^{1/2}.$$

The close analogy of h_{ab} to the Munsell hue and of C^*_{ab} to the Munsell chroma of Figure 4 is evident; L^* is also closely related to the Munsell value. The set of four opponent (or psychological) primary colors based on CIELAB is red, blue, green, and yellow; these are not the identical colors to those used in the additive and sbtractive primaries of Sections Light Mixing and Colorant Mixing. Closely related are the many types of color wheels, used for pedagogical purposes but never actually used by artist.

In the system derived from CIELUV it is also possible to specify a metric saturation with reference to a standard white designated by subscript *n:*

$$S_{uv} = 13\left[\left(u^* - u^*_n\right)^2 + \left(v^* - v^*_n\right)^2\right]^{1/2}$$

A saturation correlate cannot be given for the CIE L^* C^*_{ab} h_{ab} space.

6.4. Hunter *L,a,b* and Other Color Spaces.

The CIELAB and CIELUV color spaces were the outgrowth of a large and complex group of interrelated early systems and have replaced essentially all of these. An important early system was the 1942 Hunter *L,a,b* group of color spaces (1). This was the earliest practical opponent-based system that is still occasionallyt used. In this system, for illuminant C and the 2° standard observer:

$$L = 10Y^{1/2} \qquad \text{(lightness coordinate)}$$

$$a = 17.5(1.02X - Y)/Y^{1/2} \qquad \text{(red−green coordinate)}$$

$$b = 7.0(Y - 0.847Z)/Y^{1/2} \qquad \text{(yellow−blue coordinate)}$$

There are other equations for other illuminants and other observers (1) and also various modifications for special conditions.

6.5. Color Difference Assessment.

Early color difference scales include those of Judd-Hunter, Macadam, Adams-Nickerson, ANLAB, and ANLAB40. All of these have limitations in some way or another; they are described in most texts (1,3–5). Each applies only to the precise conditions used in their determination and interconversion is not possible; they are falling out of use.

In the CIELAB and CIELUV color spaces, the difference between a batch sample and a reference standard designated with a subscript s, can be designated by its components, eg, $\Delta L^* = L^* - L^*_s$.

The three-dimensional total color differences are given by Euclidian geometry as the 1976 CIE $L^*a^*b^*$ and 1976 CIE $L^*u^*v^*$ color difference formulas:

$$\Delta E^*_{ab} = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2}$$

$$\Delta E^*_{uv} = \left[(\Delta L^*)^2 + (\Delta u^*)^2 + (\Delta v^*)^2\right]^{1/2}$$

In CIE metric coordinates, either for CIELAB or CIELUV, ΔL^* and ΔE^* are the same, $\Delta C^* = C^* - C^*_s$, $\Delta h = h - h_s$, and $\Delta H^* = [(\Delta E^*)^2 - (\Delta L^*)^2 - (\Delta C^*)]^{1/2}$. The last of these, the metric hue difference ΔH^*, is preferred to Δh, since the latter is in degrees rather than in units compatible with ΔL^* and ΔC^*, as in ΔH^*.

An example may clarify this system. Consider a red apple with CIELAB coordinates measured as $L^* = 41.75$, $a^* = 45.49$, $b^* = 9.61$. This converts to metric as $L^* = 41.75$, $C^* = 46.49$, $h = 13.25$ and, incidentally, to Munsell 10RP 4/10 (recall that the sequence is hue, value, chroma). A second apple has $L^* = 49.23$, $a^* = 40.13$, $b^* = 12.20$, $C^* = 41.94$, $h = 18.79$, and Munsell 2.5R 5/9. Taking the differences $\Delta L^* = +7.48$, ie, the second apple is brighter (note Munsell values are 4 and 5, respectively); $\Delta a^* = -5.36$, ie, more green (or less red); $\Delta b^* = +2.59$, ie, more yellow (or less blue); $\Delta C^* = -4.55$, ie, less saturation (note Munsell chromas are 10 and 9, respectively); $\Delta h = +5.54$, ie, larger hue angle that means more yellow in this instance (note Munsell hue 2.5R is $2\frac{1}{2}$ steps from 10RP as in Figure 4 or $2.5 \times 360/100 = 9^\circ$ away). The total three-dimensional color difference $\Delta E^* = 9.56$. The metric hue difference can also now be calculated as $\Delta H^* = 3.84$.

The lightness difference $\Delta L^{*} = +7.48$ is the dominant component in the total color difference $\Delta E^{*} = 9.56$ and the hue difference $\Delta H^{*} = 3.84$ is less important than the chroma difference $\Delta C^{*} = -4.55$.

The color difference magnitudes derived from the CIE as well as from other color-space and color-ordering systems do not agree as well as could be desired with one another or with the visually perceived differences; they cannot be interconverted by a constant factor in general. This is probably the least satisfactory part of colorimetry. Many factors contribute to this. In an ideal three-dimensional color space, the region that is not distinguishably different from a given point would be a sphere. In actual practice this is not achieved fully in any color space; these regions are the so-called MacAdam ellipses (1,3–5) on two-dimensional chromaticity diagrams; they are ellipsoids in the three-dimensional color spaces.

The most recently promulgated improved color-difference equation is CMC(l:c). This quite complex set of equations uses correction factors to reduce the previous deficiencies (1). Work continues on such improvements (eg, see Ref. 1) and the CIEDE2000 color-difference equation set is currently under review but has not yet been promulgated.

$$\Delta E_{\mathrm{CMC}(l:\mathrm{c})} = \left[\left(\frac{\Delta L^{*}}{lS_L}\right)^2 + \left(\frac{\Delta C^{*}_{ab}}{cS_C}\right)^2 + \left(\frac{\Delta H^{*}_{ab}}{S_H}\right)^2\right]^{1/2}$$

where

$$S_L = 0.04097\ L^{*}/(1 + 0.01765\mathrm{L}^{*})$$

unless

$$L^{*} < 16 \quad \text{then}$$

$$S_L = 0.511$$

$$S_C = \{0.0638\ C^{*}_{ab}/(1 + 0.0131\ C^{*}_{ab})\} + 0.638$$

$$S_H = S_C(TF + 1 - F)$$

$$F = \{(C^{*}_{ab})^4/[(C^{*}_{ab})^4 + 1900]\}^{1/2}$$

$$T = 0.38 + [0.4\ \cos\ (h_{ab} + 35)]$$

unless h_{ab} is between 164° and 345°, then

$$T = 0.56 + [0.2\ \cos\ (h_{ab} + 168)]$$

L^{*}, C^{*}_{ab}, and h_{ab} are calculated from the CIELAB L^{*}, a^{*}, and b^{*} values of the standard. Constants l and c are defined by the user and weight the importance of lightness and chroma relative to hue.

A perceived color difference varies with the mode (object, illuminant, aperture); the texture (glossy, rough, metallic, etc); size, flatness, and transparency characteristics of objects; the level, color, and geometry (point-source versus diffuseness) of the illumination; the presence of uv light, fluorescence, and polarized light; and the nature and color of the surroundings and background. Finally, the various metamerisms discussed above are at work as well as observer experience and adaptation to the observing situation. Nevertheless the system does work and color difference measurements can be used successfully in actual practice if all these parameters are controlled.

Finally, it cannot be overemphasized that despite instrumental measurements and data manipulations, it is the perception of the eye that still is the final arbiter as to whether or to what degree two colors match. Instrumental methods do serve well for the typical industrial task of maintaining consistency under sufficiently well-standardized conditions; however, a specific technique may not serve in extreme or unusual conditions for which it was not designed.

7. Color Measuring Instruments

There has been a tremendous change in the last two decades as computers have taken over the tedious calculations involved in color measurement. Indeed, microprocessors either are built into or are connected to all modern instruments, so that the operator may merely need to specify, for example, x, y, Y or L^*, a^*, b^* or $L^*, C^*, h,$ either for the 2° or the 10° observer, and for a specific standard illuminant, to obtain the desired color coordinates or color differences, all of which can be stored for later reference or computation. The use of high intensity filtered xenon flash lamps and array detectors combined with computers has resulted in almost instantaneous measurement in most instances.

7.1. Measurement Conditions. In 1968, the CIE recommended the four geometries of Figure 13 for reflectance measurements. In the first 0°/45° or normal/45° geometry, the illumination is normal to the sample and the detector is at 45°. In the second 45°/0° geometry the two conditions are reversed. These techniques usually give the same results except, eg, when polarized light interactswith oriented metallic flakes. In the third 0°/diffuse or normal/diffuse geometry the incident light beam impinges normally onto the sample and the reflected and scattered light is collected by an integrating sphere. In the last diffuse/0° geometry the incident light is first diffused by the integrating sphere before interacting with the sample, with the detector normal to the sample. Integrating sphere instruments in the normal/diffuse geometry are often operated in a "*near-normal*" configuration. Here an offset of 6°–8° is used and a specular port is provided at a symmetrical position By filling this port with a light-absorbing trap instead of the usual sphere material, the effect of specular reflection can be eliminated instead of being included in the measurement.

The illumination used is usually filtered white light to approximate daylight. The detector may respond to all light, may use a monochromator, a diode array, a rotating wedge interference filter, or band pass filters. Often, several photodetectors are covered with filters approximating the CIE color matching functions $\bar{x}$, $\bar{y}$, $\bar{z}$ or a suitable linear combination of these. Problems arise when fluorescence is present. Ideally, one would use a spectrofluorimeter, which contains two monochromators, one before and one after the sample.

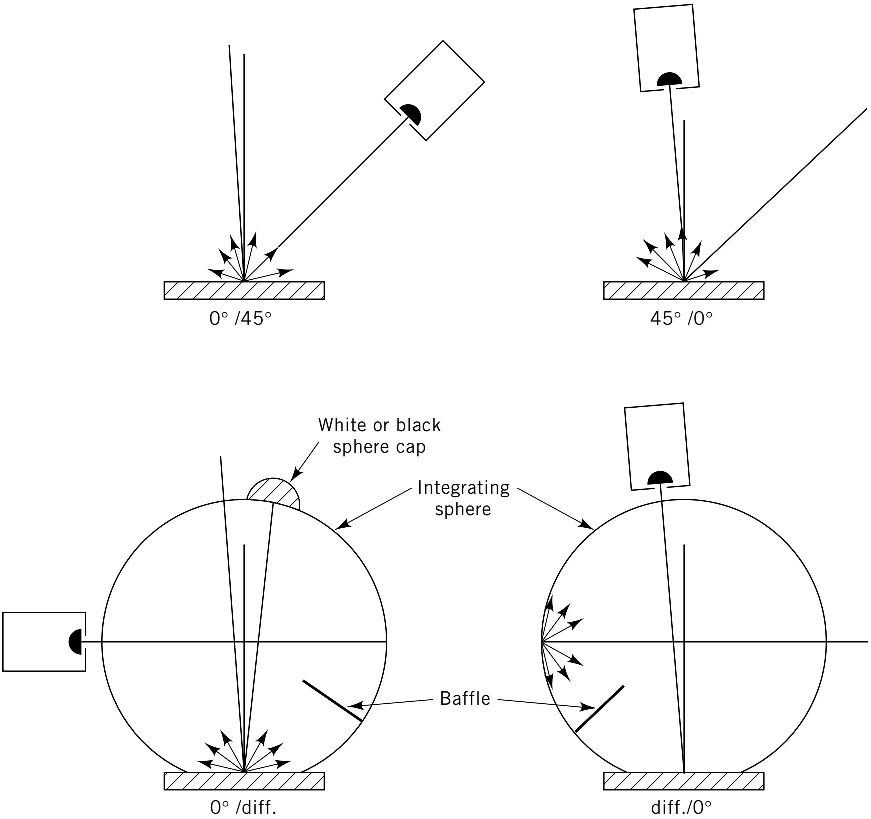


Fig. 13. CIE recommended geometries for illumination and viewing for reflectance-factor measurements (8).

This permits the separation of the fluorescent and nonfluorescent components. More usually D_{65} illumination is used, in which case the detected intensity at the fluorescence wavelength may well be higher than the intensity of that wavelength in the illuminant. Since the fluorescence usually varies strongly with the amount of uv in the illuminant, it may be difficult to obtain meaningful results. Here, as elsewhere there are ASTM standards (eg, see Ref. 1).

For transmittance measurements there are two principal geometries, one with a full collection of all transmitted light by an integrating sphere, the other with both illuminating and detector beams collimated. Translucency can be measured by two reflectance measurements, one with a white background, the other with a black one. Goniophotometric instruments are used to measure specular reflections, important in glossy and metallic objects and coatings, as well as in color-changing paints, containing oriented pigment flakes that show interference.

7.2. Instruments. Spectrophotometers are the most sophisticated color measuring instruments and provide the most detailed and accurate information. They may provide continuous spectral data of reflectance and transmittance against wavelength or use up to 20-nm wavelength steps, with high precision in reflectance (down to 0.01%) and tristimulus values (down to 0.01). There may be dual beams with one for the sample and a second as reference for the most stable and precise operation. Many spectrophotometers use an integrating sphere, although some use other geometries or permit alternative ones. Some of these have additional capabilities such as limited gloss measurements; some are compact, battery-powered, portable units with built-in microprocessors.

High end spectrophotometers may use xenon flash lamps and large diode detector arrays while lower end units may use light emitting diodes and small arrays. Slightly less sophisticated are spectrocolorimeters that determine spectral response curves for the computation of colorimetric values, but from which the spectral curve itself is not available.

Colorimeters, also known as tristimulus colorimeters, are instruments that do not measure spectral data but typically use four broadband filters to approximate the $\bar{y}$, $\bar{z}$ and the two peaks of the $\bar{x}$ color-matching functions of the standard observer curves of Figure 7. They may have lower accuracy and be less expensive, but they can serve adequately for some industrial color control functions.

A goniospectrophotometer measures the angular dependence of the spectral variation of light reflection and scattering. More widely used are abridged goniospectrophotometer or multiangle goniophotometers that may have three-to-five set geometries. Such measurements are important in characterizing metallic and pearlescent finishes, eg. A variety of goniophotometers, reflectometers, gloss meters, haze meters, etc, are available, as are computers and software for acquiring and manipulating data from various instruments and for converting among the various color-order and color-measuring systems. Most modern instruments either have such data manipulating capabilities built in or may connect directly to a computer.

Companies that manufacture color-measuring instruments and other color-related products include (in alphabetical order): BYK-Gardner Instruments (www.byk-gardner.com), Lawrenceville, NJ (subsidiary of BYK-Chemie, Geretsried, Germany); Color-Tec (www.color-tec.com), Clinton, NJ; Datacolor (www.datacolor.com), Lawrenceville, NJ (subsidiary of Eichhof Holding AG, Lucerne, Switzerland); Gretag Macbeth LLC (www.gretagmacbeth.com), New Windsor, NY; Hunter Associates Laboratory (www.hunterlab.com), Reston, Va; Minolta (www.minoltausa.com), Ramsey, NJ (subsidiary of Konica Minolta, Osaka, Japan); Pantone (www.pantone.com), Carlstadt, NJ; X-rite (www.xrite.com) Grandville, MD.

Sample preparation is always critically important. Calibration with standard reflectance and transmittance samples should be routinely used for optimum results in spectrophotometry and colorimetry. Calibration of the wavelength and photometric scales is also advisable. The calibration of a white reflectance standard in terms of the perfect reflecting diffuser is important, as is the use of diagnostic tiles for tristimulus colorimetry. A collaborative reference program is available on instrument performance (22).

Color-order systems, such as the many Munsell collections available from Gretag Macbeth, have been described previously. Essential for visual color matching is a color-matching booth. A typical one, such as the Gretag Macbeth Spectralite, may have available a filtered 7500 K incandescent source equivalent to north-sky daylight, 2300 K incandescent illumination as horizon sunlight, a cool-white fluorescent lamp at 4150 K, and an uv lamp. By using the various illuminants, singly or in combination, the effects of metamerism and fluorescence can readily be demonstrated and measured. Every user should be checked for color vision deficiencies.

8. The Fifteen Causes of Color

No less than 15 distinct chemical and physical mechanisms explain the various causes of color, ordered into five groups as in Table 3. (A detailed book-length treatment may be found in Ref. 2.) In the first group, covered by quantum theory, there are incandescence, simple electronic excitations, and vibrational and rotational excitations. Most chemical compounds contain only paired electrons that

Table 3. **Fifteen Causes of Color**

Cause	Examples
	Vibrations and simple excitations
incandescence	flames, lamps, carbon arc, limelight
gas excitations	vapor lamps, flame tests, lightning, auroras, some lasers
vibrations and rotations	water, ice, iodine, bromine, chlorine, blue gas flame
	Transitions involving ligand field effects
transition-metal compounds	turquoise, chrome green, rhodonite, azurite, copper patina
transition-metal impurities	ruby, emerald, aquamarine, red iron ore, some fluorescence and lasers
	Transitions between molecular orbitals
organic compounds	Most dyes, most biological colorations, some fluorescence and lasers
charge transfer	blue sapphire, magnetite, lapis lazuli, ultramarine, chrome yellow, Prussian blue
	Transitions involving energy bands
metals	copper, silver, gold, iron, brass, pyrite, ruby glass, polychromatic glass, photochromic glass
pure semiconductors	silicon, galena, cinnabar, vermillion, cadmium yellow and orange, diamond
doped semiconductors	blue and yellow diamond, light-emitting diodes, some lasers and phosphors
color centers	amethyst, smoky quartz, desert amethyst glass, some fluorescence and lasers
	Geometrical and physical optics
dispersive refraction	prism spectrum, rainbow, halos, sun dogs, green flash, fire in gemstones
scattering	blue sky, moon, eyes, skin, butterflies, bird feathers, red sunset, Raman scattering
interference	oil slick on water, soap bubbles, coating on camera lenses, some biological colors
diffraction	diffraction gratings, opal, aureole, glory, some biological colors, most liquid crystals

require very high energies to become unpaired and form excited energy levels; this requires uv, hence there is no visible absorption and no color. Absorption color can, however, be derived from the easier excitation of lower energy unpaired electrons in transition-metal compounds and impurities, covered by ligand-field theory in the second group. Absorptions from paired electrons can be shifted into the visible by increasing the size of the region over which the electrons are localized, as in organic compounds, covered by molecular orbital theory in the third group; this also explains various forms of charge transfer. In the fourth group, there is color in metals and alloys as well as in semiconductors such as yellow cadmium sulfide, both pure and doped, covered by band theory; this also covers color centers. In the final group, there are four color-causing mechanisms explained by geometrical and physical optics.

8.1. Color from Incandescence. Any object emits light when heated, with the sequence of blackbody colors, black, red, orange, yellow, white, and bluish-white as the temperature increases. The locus of this sequence is shown on a chromaticity diagram in Figure 14. A blish-white hot is the hottest possible, corresponding to an infinite temperature; terms such as blue-hot and green-hot sometimes seen are spurious.

The distribution of energy under idealized conditions is given by Planck's equation in which the energy E_R radiated into a hemisphere in W/cm^2 in wavelength interval $d\lambda$ at wavelength λ at T in K is

$$E_R = 37415\, d\lambda/\lambda^5 \left[e^{(14338/\lambda T)} - 1\right]$$

The total energy emitted E_T in W/cm^2 is given by Stefan's law as

$$E_T = 5.670 \times 10^{-12}\, T^4$$

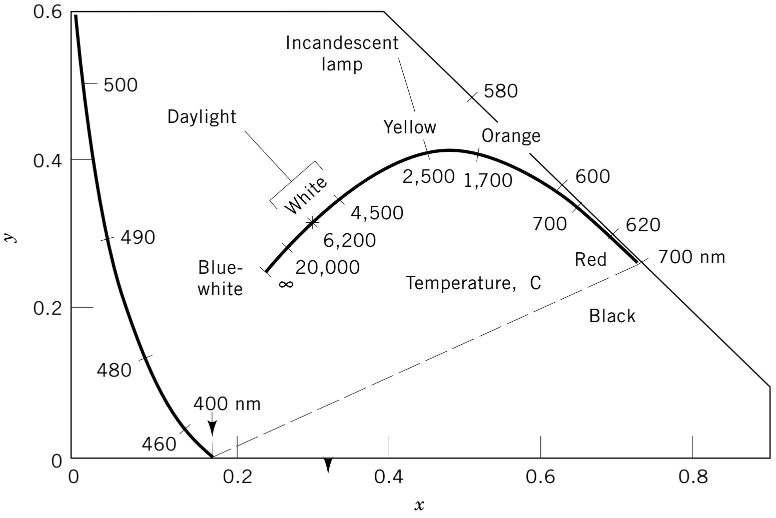


Fig. 14. Blackbody colors shown on the 1931 CIE *x,y* chromaticity diagram of Figures 8 and 9; the asterisk is standard illuminant D_{65} at 650 K (2).

and Wien's law gives the peak wavelength λ_m in nm as

$$\lambda_m = 2,897,000/T$$

Real or gray bodies deviate from these ideal blackbody values by the λ-dependent emissivity, but the color sequence remains essentially the same. This mechanism explains the color of incandescent light sources such as the flame in a candle, tungsten filament light bulb, flash bulb, carbon arc, limelight, lightning in part, and the incandescent part of pyrotechnics (qv).

8.2. Color from Gas Excitation. When the atoms in a gas or vapor are excited, eg, by an electric discharge, electrons on the atoms are elevated to higher energy states. On their way back to the ground state they can emit light, the energies being limited by the quantum states available and by the selection rules that control the probabilities of the various possible transitions. Examples are efficient gas discharge light sources such as sodium and mercury vapor lamps, the latter emission also being present in fluorescent lamps in part; lightning in part; auroras, excited by energetic particles from the sun, in part; the Bunsen-burner flame tests for Na, Li, Sr, etc, where the excitation is thermal; and the electrically excited gas lasers such as the helium–neon laser.

8.3. Color from Vibrations and Rotations. Vibrational excitation states occur in H_2O molecules in water. The three fundamental frequencies occur in the ir at >2500 nm, but combinations and overtones of these extend with very weak intensities just into the red end of the visible and cause the complementary blue color of water and of ice when viewed in bulk [any green component present derives from algae, etc. The attribution of the blue color to reflection from the sky on water or to the presence of gas bubbles in ice is spurious (2)]. This phenomenon is normally seen only in H_2O, where the lightest atom H and very strong hydrogen bonding combine to move the fundamental vibrations closer to the visible than in any other material.

Electronic energy levels in molecules are often modified by vibrational and rotational excitations. In iodine vapor this mechanism is involved in the intense purple color, as well as in the much weaker colors of bromine and chlorine, both in the condensed and gaseous states. Blue and green emissions from energy levels in the unstable CH and C_2 molecules occur in the premixed region of candle and gas flames. Such emissions also occur in some auroras, particularly in the broad bands from the excited N_2^* molecule. Finally, the slow phosphorescence from triplet states in organic molecules usually involves vibrational states.

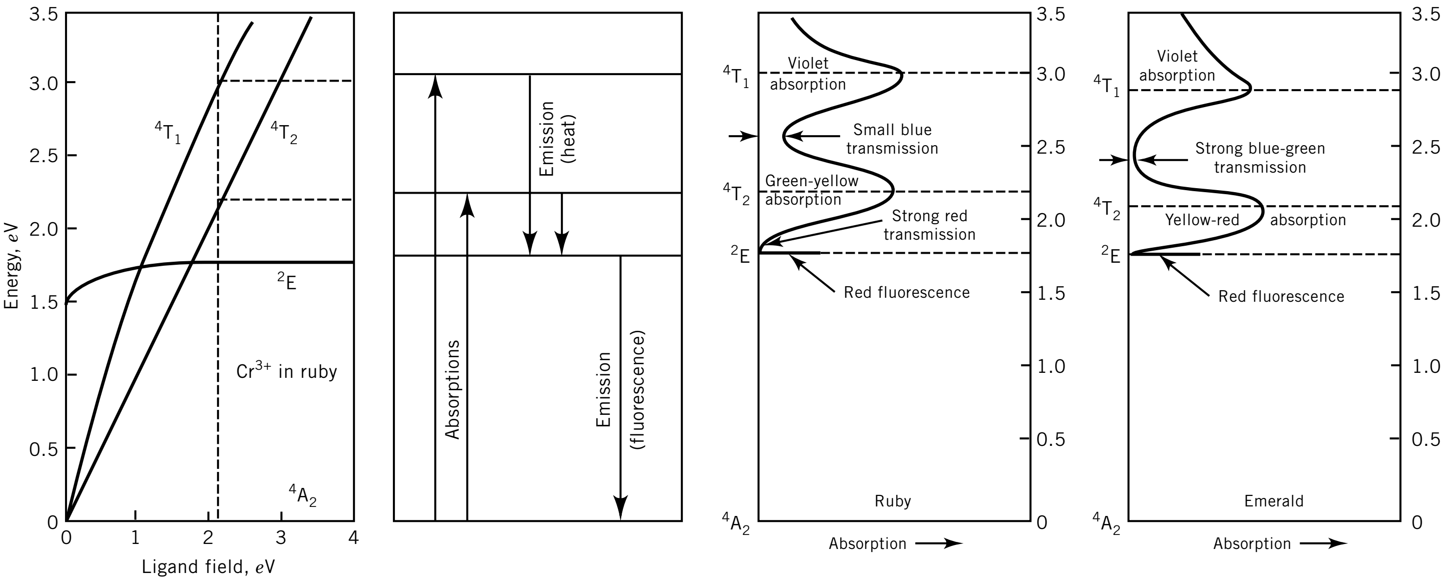
8.4. Color from Transition-Metal Compounds and Impurities. The energy levels of the excited states of the unpaired electrons of transition-metal ions in crystals are controlled by the field of the surrounding cations or cationic groups. From a purely ionic point of view, this is explained by the electrostatic interactions of crystal-field theory; ligand-field theory is a more advanced approach also incorporating molecular orbital concepts.

Consider a crystal of corundum [1302-74-5], pure Al_2O_3. Each Al is surrounded by six O ligands in the form of a slightly distorted octahedron. All electrons are paired and there are no absorptions in the visible region, and hence no color. If a few percent of the aluminum atoms are replaced with chromium, the result is the red mineral, gem, laser, and maser crystal ruby [12174-49-1]. The term diagram, giving the effect of different strength ligand fields on the ^2E, $^4T_1$, and $^4T_2$ excited energy levels with respect to the ground-state $^4\mathrm{A}_2$ level of the three unpaired electrons in the 3*d* orbitals of Cr^{3+}, is shown at (**a**) in Figure 15. The 2.23 eV ligand field in ruby results in the energy level scheme at (**b**) in this figure, with absorption of light in the violet and green as at (**c**), leading to the intense red color with a weak blue component in transmission. There is also the well-known red fluorescence of ruby as the system returns to the ground state after visible light or uv absorption and heat emission, as shown at (**b**) and (**c**). The change in chemistry from $\mathrm{Al_2O_3}$ to the $\mathrm{Be_3Al_2Si_6O_{18}}$ of beryl [1302-52-9] does not change the nature or the symmetry of the Al-surrounding ligands but reduces the ligand field some 8% to 2.05 eV. In Cr^{3+}-containing beryl the result is the scheme at (**d**) in Figure 15, with both ^4T levels shifted to slightly lower energy levels. The result is the intense green color of emerald [12415-33-7], with essentially the same red fluorescence as in ruby.

The unexpected situation intermediate between red ruby and green emerald is chrysoberyl [1304-50-3], $\mathrm{BeAl_2O_4}$, called alexandrite [12252-02-7] when containing Cr^{3+}. Here an intermediate crystal field of 2.17 eV produces evenly balanced red and green transmissions, resulting in the alexandrite effect with a red color perceived when this material is viewed in red-rich incandescent light and a green color when viewed in blue- and green-rich daylight and fluorescent light. This same change occurs as the chromium content of ruby is increased in the solid-solution series $\mathrm{Al_2O_3{:}Cr_2O_3}$, the $\mathrm{Cr_2O_3}$ end member being the pigment chrome green [1308-38-9] with a ligand field near 2.07 eV. At $\sim$25% $\mathrm{Cr_2O_3}$ the color changes from red via gray to green. In the intermediate region, pressure shifts the color to red by shortening the bonds and increasing the ligand field in piezochromism, while temperature has the reverse effect, shifting the color to green in thermochromism (see CHROMOGENIC MATERIALS).

The ligand field decreases in the spectrochemical sequence $\mathrm{CN^-} > \mathrm{NH_3} > \mathrm{O^{2-}} > \mathrm{H_2O} > \mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$ and increases in isoelectronic sequences such as $\mathrm{V(II)} < \mathrm{Cr(III)} < \mathrm{Mn(IV)}$. Whereas in the 3*d* transition elements the color varies strongly with the symmetry and magnitude of the ligand field, in the lanthanides and actinides the unpaired electrons in the 4*f* and 5*f* shells, respectively, are shielded by the outer electrons so that there are only minor energy level changes and, therefore, color changes with the ligand-field. Most ligand-field transitions are formally forbidden by the selection rules, hence transitions have low oscillator strengths and colors tend to be weak. That is why well-colored red ruby and green emerald need to contain several percent of Cr.

Idiochromatic (self-colored) transition-metal compounds occur where the transition-metal ions are an essential part of the structure and contribute to the nature of the ligand field. Examples in addition to the pigment chrome green $\mathrm{Cr_2O_3}$ are purple chrome alum $\mathrm{KCr(SO_4)_2 \cdot 12H_2O}$; pink rhodonite [14567-57-8], $\mathrm{MnSiO_3}$; green vitriol, $\mathrm{FeSO_4 \cdot 7H_2O}$, and yellow goethite [1310-14-1], FeO(OH); blue cobalt oxide CoO [1307-96-6] and pink sphaerocobaltite [14476-13-2], $\mathrm{CoCO_3}$; green bunsenite [1313-99-1], NiO; yellow tenorite [1317-92-6], CuO, blue azurite [1319-45-5], $\mathrm{Cu_3(CO_3)_2(OH)_2}$, turquoise [1319-32-0], $\mathrm{CuAl_6(PO_4)_4(OH)_8 \cdot 5H_2O}$, and the various green salts present in copper patina. Allochromatic impurities may modify these colors.



(a) **(b)** **(c)** **(d)**

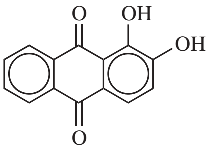
Fig. 15. The term diagram (**a**), energy levels and transitions (**b**) and the resulting absorption and emission of ruby (**c**) and emerald (**d**) (2).

Allochromatic (other-colored) transition-metal compounds, involve small amounts of these same transition elements but in the ligand field of the host lattice. Examples in addition to the above discussed chromium-containing ruby, emerald, and alexandrite are red beryl containing manganese; the iron-containing green or blue beryl aquamarine [1327-51-1] and many brown and red iron-containing minerals such as sandstone and red iron ore; the intense blue cobalt glass; a green vanadium -containing form of emerald; and purple neodymium -containing yttrium aluminum garnet YAG [12005-21-9], $Y_3Al_5O_{12}$. Some of these, such as ruby and Nd:YAG, serve as the active media of optically pumped crystal lasers. The absorptions and fluorescence emissions from ligand field energy levels tend to be relatively narrow in crystals. In glasses, where disorder leads to a range of ligand fields, these absorptions and emissions are much broader, as in the Nd:glass used in lasers such as the NOVA thermonuclear fusion lasers. In the decolorizing of glass, the greenish color caused by iron impurities is removed by adding $Mn^{IV}O_2$ [1313-13-9]. This acts in two ways: it reduces some of the green-producing Fe(II) to the yellow-producing but weaker colorant Fe(III) while forming some Mn(III). This latter also produces a purple color; since this is complementary to the green of Fe(II), it results in an inconspicuous very pale gray.

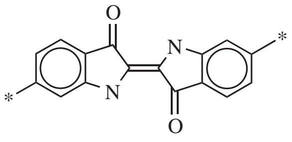
8.5. Color in Organic Compounds. In organic molecules, particularly those containing conjugated chains of alternating single and double bonds, eg, as in the polyenes, $H_3C(-CH{=}CH-)_nCH_3$, the double bonding p_z orbitals have a variety of excited states. For $n = 2$ in 2,4-hexadiene [592-46-1], the transition between the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied MO) is in the uv, hence no color. With $n = 8$ in 2,4,6,8-decatetraene [2423-96-3] this transition has shifted down into the violet end of the visible part of the spectrum, thus producing a complemenmtary yellow color. The electronic energy levels are also modified by vibrational effects, resulting in transitions to triplet states and leading to phosphorescence from the very slow forbidden transition back to the singlet ground state.

Examples of polyene-type colorants are the orange β-carotene pigment [7235-40-7] of carrots, the pink carotenoids of flamingos, and the yellow crocin [42553-65-1] present in saffron, the pollen of the crocus *sativa*. Cyclic but non-benzenoid conjugated colored systems include the green chlorophyll [1406-65-1] of the vegetable kingdom, the red-to-brown hemoglobins and porphyrins of the animal kingdom, and the related blue dye copper phthalocyanin [147-14-8].

The conjugated chromophore (color-causing) system can be extended by electron-donor groups such as $-NH_2$ and $-OH$ and by electron-acceptor groups such as $-NO_2$ and $-COOH$, often used at opposite ends of the molecule. An example is the aromatic compound alizarin [72-48-0], also known since antiquity as the red dye madder.



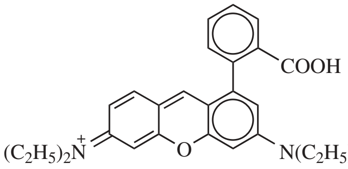
alizarin



indigo

Another ancient dye is the deep blue indigo [482-89-3]; the presence of two bromine atoms at positions marked by an * gives the dye Tyrian purple [19201-53-7] once laboriously extracted from certain sea shells and worn by Roman emperors.

Organic colors caused by this mechanism are present in most biological colorations and in the triumphs of the dye industry (see AZINE DYES; AZO DYES; FLUORESCENT WHITENING AGENTS; CYANINE DYES; DYE CARRIERS; DYES AND DYE INTERMEDIATES; DYES, ANTHRAQUINONE; DYES, APPLICATION AND EVALUATION; DYES, NATURAL; DYES, REACTIVE; POLYMETHINE DYES; STILBENE DYES; and XANTHENE DYES). Both fluorescence and phosphorescence occur widely and many organic compounds are used in tunable dye lasers such as rhodamine B [81-88-9], which operates from 580 to 655 nm.



rhodamine B

8.6. Color from Charge Transfer. This mechanism is best approached from MO theory, although ligand-field theory can also be used. There are several types of color-producing charge-transfer (CT) processes.

Consider corundum, Al_2O_3 containing both Fe^{2+} and Ti^{4+} substituting on adjacent Al sites. The transfer of one electron can occur with the absorption at about 2.2 eV, resulting in the production of Fe^{3+} and Ti^{3+}. This light absorption results in the color of blue sapphire [1317-82-4]. The reverse transition restores the initial state with the production of heat. Since all CT transitions are fully allowed, only a few hundredth of one percent of the impurities involved are required for an intense color. The process can also be termed electron hopping or photochemical redox. Another example of this heteronuclear intervalence CT is the gray to black color of most moon rock, again from the Fe–Ti combination.

In homonuclear intervalence CT, atoms of the same element but on different sites A and B interact as in

$$Fe_A^{2+} + Fe_B^{3+} \longrightarrow Fe_A^{3+} + Fe_B^{2+}$$

Idiochromatic examples of this are black magnetite [1309-38-2], Fe_3O_4, otherwise written as $Fe(II)O \cdot Fe_2(III)O_3$ and the analogous red Mn_3O_4; and the pigments Prussian blue [14038-43-8] and Turnbull's blue [25869-98-1], both $Fe_4(III)$-$[Fe(II)(CN)_6]_3$. Allochromatic examples are widespread in the mineral field, with $Fe^{2+} + Fe^{3+}$ being involved in blue and green tourmaline [1317-93-7], blue iolite (cordierite) [12182-53-5], etc.

Metal←ligand or cation←anion CT is present in the yellow to orange chromates and dichromates such as $K_2Cr(VI)O_4$ [7789-00-6] and $K_2Cr_2(VI)O_7$ [7778-50-9]; these contain no unpaired electrons but the color derives from transfer of electrons from O^{2-} to the otherwise very highly charged Cr^{6+}. Once again the transitions are fully allowed and intense colors occur as in permanganates such as $KMnO_4$ and the pigments chrome yellow [1344-37-2], $PbCrO_4$, and red ochre (mineral hematite) [1317-60-8], Fe_2O_3. The reverse ligand←metal or anion←cation CT is not common but occurs in the yellow liquid $Fe(CO)_5$ [13463-40-6], where low-energy π-orbitals of CO can accept electrons from the Fe.

Anion←anion CT occurs in the pigment ultramarine [57455-37-5] (mineral lapis lazuli [1302-85-8]), which contains $(S_3)^-$ groups having a total of 19 electrons in molecular orbitals. Among these orbitals there is a strong transition giving an absorption band at 2.1 eV and leading to the deep blue color.

Acceptor←donor CT occurs, eg, in the solution of iodine in benzene, where an electron can transfer from the π-electron system in benzene to the I_2 molecule. Organic dyes containing both donor and acceptor groups can also be approached from this viewpoint.

8.7. Color in Metals and Alloys. This is the first of four mechanisms best approached from an energy-band point of view. The two equivalent equal-energy molecular orbitals of two hydrogen atoms combining to form H_2 split to form a lower energy bonding orbital containing the two electrons and a higher energy empty antibonding orbital, also capable of holding two electrons. In an n-valent metal the $n \times 10^{23}$ or so outermost electrons, n from each atom, are again equivalent and of equal energy, forming an essentially continuous band of energy states. The $n \times 10^{23}$ or so delocalized electrons available fill the band from the bottom up to the Fermi level E_f, (Fig. 16). Electrons in the band can absorb photons at any energy as shown, but the light is so intensely absorbed that it can penetrate to a depth of only a few atoms, typically less than a wavelength. Being an electromagnetic wave, the light induces electrical current on the metal surface, which immediately reemits the light, resulting in metallic

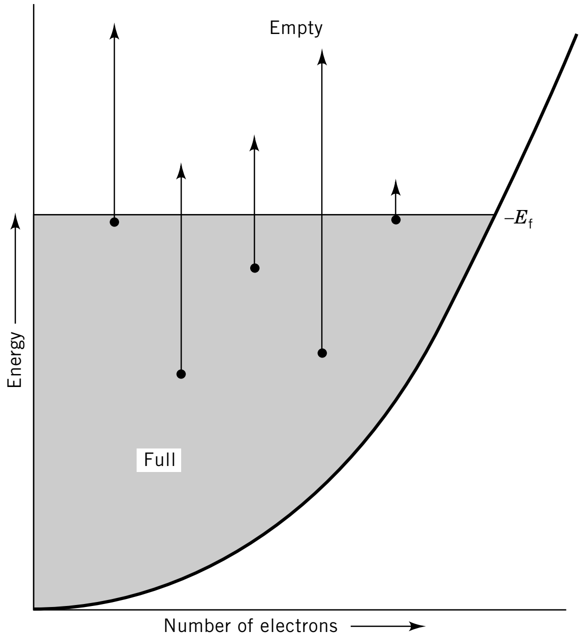


Fig. 16. A metal can absorb some light at any energy, but immediately reemits most of it (2).

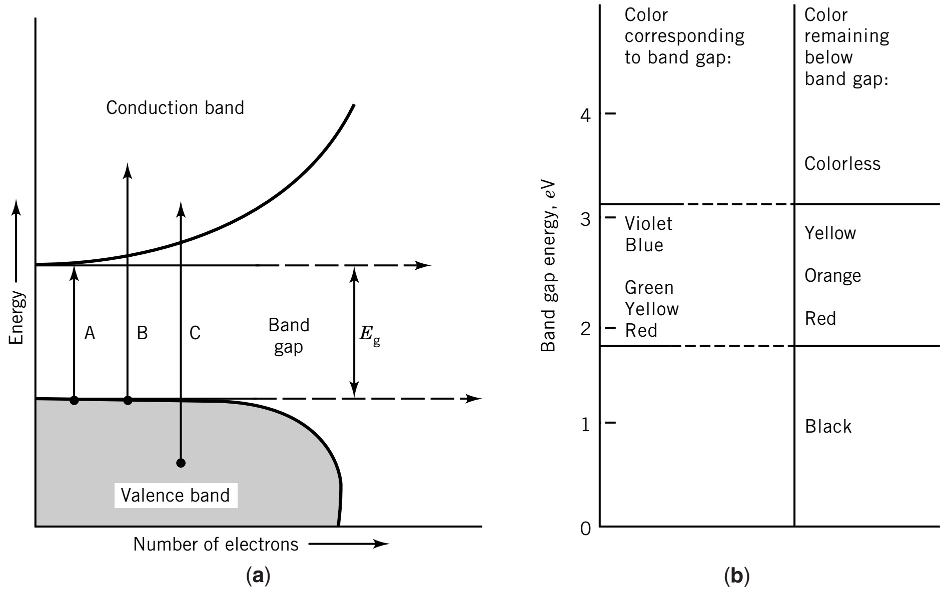
luster and metallic reflection. The same principles apply to alloys and to some metal-like compounds such as the “fool’s gold” pyrite [1309-36-0], FeS_2, which contains both localized and delocalized electrons.

Using the complex refractive index $N = n + iK$, where $i = \sqrt{-1}$ and K is the absorption coefficient, the reflectivity R of metals and alloys is given by

$$R = 100[(n-1)^2 + K^2]/[(n+1)^2 + K^2]$$

where K varies with the wavelength. This variation originates from the nature of the various orbitals that originally combined to form the density of states diagram. Most metals have more complex shapes than the simple parabolic type of Figure 16, which applies to alkali metals; the variation of the efficiency of the reflection process with light energy then controls the color. If all energies are equally efficiently reflected, the almost colorless reflections of clean iron [7439-89-6], mercury [7439-97-6], and silver [7440-22-4] result. However, if the efficiency decreases with increasing energy, there is reduced reflection at the blue end of the spectrum, resulting in the yellow of gold [7440-57-5], brass [12597-71-6], and pyrite, and the reddish color of copper [7440-50-8].

The direct light absorption of a metal in the absence of reflection is observed only rarely. When gold is beaten into gold leaf <100 nm thick, a blue-green color is seen by transmitted light. When in the form of colloidal particles, eg, the 10-nm diameter gold particles in deep red ruby glass, complex Mie scattering theory may be used or the situation can be treated as a bounded plasma resonance. The color produced by such particles also depends on their shape, a characteristic used to produce colored images in polychromatic glass. Here a



(a) (b)

Fig. 17. The absorption of light in a band-gap material (**a**) and the variation of color with the size of the band gap (**b**) (2).

Table 4. **Color of Some Band-Gap Semiconductors**

Substance	CAS Registry number	Mineral name	Pigment name	Band gap, eV	Color
C	[7782-40-3]	diamond		5.4	colorless
ZnO	[1314-13-2]	zincite	zinc white	3.0	colorless
CdS	[1306-23-6]	greenockite	cadmium yellow	2.6	yellow
$CdS_{1-x}Se_x$	[12656-57-4]		cadmium orange	2.3	orange
HgS	[19122-79-3]	cinnabarite	vermilion	2.0	red
HgS	[23333-45-1]	metacinnabar		1.6	black
Si	[7440-21-3]			1.1	black
PbS	[12179-39-4]	galena		0.4	black

glass containing both silver and cerium [7440-45-1] yields on exposure to light the transformation:

$$Ag^+ + Ce^{3+} \longrightarrow Ag + Ce^{4+}$$

with the formation of silver particles; a complex technology causes the aspect ratio of these particles to vary with wavelength and thus produce colored images. Closely related are photochromic sunglasses, where exposure of silver halide particles to intense sunlight produces metallic silver and darkening, with reversal when the intensity of the light is reduced (see CHROMOGENIC MATERIALS, PHOTOCHROMIC).

8.8. Color in Pure Semiconductors. In some materials a gap is present in the band, so that a lower energy valence band is separated from a higher energy conduction band by a band gap of energy E_g as at the left in Figure 17. When there are exactly four valence electrons per atom, the conduction band is exactly full and the energy band is exactly empty. Since most of these materials do not conduct electricity well, the metallic reflection is absent and excitation of electrons by light, as in Figure 17, results in absorption. If the band gap is very small, all light is absorbed and the color is black. If the band gap is very large, then light in the visible region cannot be absorbed and the material is colorless. At a band gap corresponding to 2.2 eV (560 nm) violet, blue, and green are absorbed, leaving a complementary orange transmission color. The full sequence is black, red, orange, yellow, colorless as can be readily deduced from Figure 17. Examples of some band-gap materials are given in Table 4.

8.9. Color in Doped Semiconductors. Consider a diamond crystal [7782-40-3], otherwise colorless because of its large energy band gap, with 10 ppm substitutional nitrogen atoms added. Each N has one more electron than the C it replaces and will donate this electron to a donor level within the band gap that is located 4 eV below the conduction band; this level is broadened by various causes, including thermal vibrations. Absorption of light can now occur, with the excitation of an electron from the donor level into the conduction band from 2.2 eV up, leading to the yellow color of natural and synthetic N-containing diamonds. The analogous presence of boron atoms produces a blue color, as in the famous Hope diamond. In this case, B has one less electron than the C it replaces and each atom forms one hole in an acceptor level within the band gap, located 0.4 eV above the valence band. Light is absorbed by electrons being excited from the valence band into the acceptor level holes, thus producing the blue color as well as electrical conductivity since the excitation energy involved is so small.

Donor and acceptor levels are the active centers in most phosphors, as in zinc sulfide [1314-98-3], ZnS, containing an activator such as Cu and various coactivators. Phosphors are coated onto the inside of fluorescent lamps to convert the intense uv and blue from the mercury emissions into lower energy light to provide a color balance closer to daylight as in Figure 11. Phosphors can also be stimulated directly by electricity as in the Destriau effect in electroluminescent panels and by an electron beam as in the cathodoluminescence used in television and cathode ray display tubes and in (usually blue) vacuum-fluorescence alphanumeric displays.

Some impurities can form trapping levels within the band gap, as shown in Figure 18. Absorption of light can move electrons into the traps, as shown by the arrows. Energy E_b is required to release the electron from the trap into the conduction band and permit it to decay by one of several possible light-emitting paths not shown. If E_b is small so that room temperature thermal excitations can release the electrons slowly, then phosphorescence results. If E_b is a little larger, then ir may permit the escape, as in an ir-detecting phosphor that first has been activated to load up the traps.

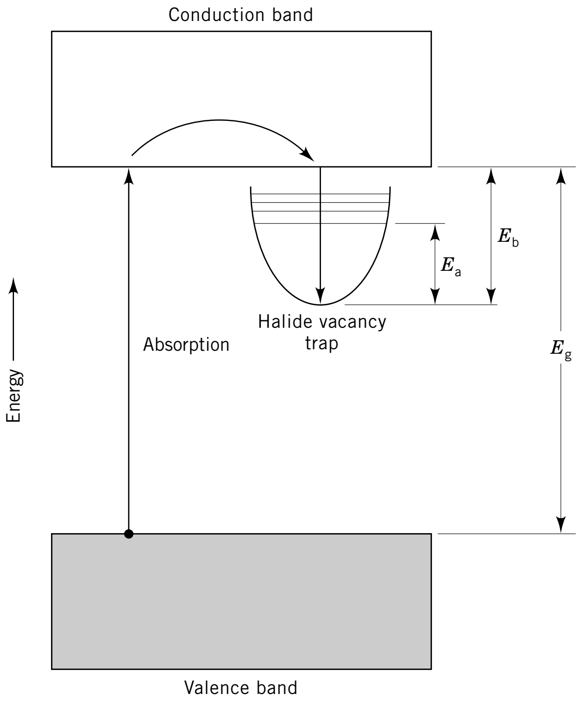


Fig. 18. Trapping energy from absorbed light in a band-gap trap (2).

Finally, an electric current can produce injection luminescence from the recombination of electrons and holes in the contact zone between differently doped semiconductor regions. This is used in light-emitting diodes (LED, usually red), in electronic displays, and in semiconductor lasers.

8.10. Color from Color Centers. Although ligand-field theory can also be used, this mechanism is best approached from band theory. Consider a vacancy, eg, a missing Cl^- ion in a KCl crystal produced by irradiation, designated an F-center (from the German *Farbe* for color). An electron can become trapped at the vacancy and this forms a trapped energy level system inside the band gap just as in Figure 18. The electron can produce color by being excited into an absorption band such as the E_a transition, which is 2.2 eV in KCl and leads to a violet color. In the alkali halides $E_a = 0.257/d^{1.83}$, where E_a is in eV and d is the anion–cation distance in nanometer (nm). In addition to irradiation, F centers in halides can also be produced by solid-state electrolysis, by in-diffusion of metal, or by growth in the presence of excess metal. Many other centers exist in the alkali halides, such as the M center, consisting of two adjacent F centers; the F′, an F center that has trapped two electrons; and the V_K, two adjacent F centers with only one trapped electron between them. All of these are electron color centers, where an electron is present in a location where it is not normally found.

An example of a hole color center is smoky quartz [14808-60-7]. Here irradiation (either produced by nature or in the laboratory) of SiO_2 containing trace amounts of Al ejects an electron from an oxygen adjacent to the Al or, in customary nomenclature: $[AlO_4]^{5-} \rightarrow [AlO_4]^{4-} + e^-$; the ejected electrons are trapped elsewhere in the crystal, eg, at K^+ or H^+ impurities. The electron-deficient $[AlO_4]^{4-}$ hole color center has excited energy levels and produces light absorption leading to the smoky color. When iron is present in quartz, the result is yellow citrine [14832-92-9], containing $[Fe(III)O_4]^{5-}$; irradiation now analogously produces under certain circumstances the deep purple of amethyst [14832-91-8], which is colored by the $[Fe(III)O_4]^{4-}$ hole color center.

In general, for irradiation-produced color centers, either the hole center or the electron center can be the light-absorbing species, or even both. If the electron is released from the electron center by heat, then bleaching occurs by its recombination with the hole center to restore the preirradiation state. If this bleaching energy, E_b in Figure 18, is small, then the color center will fade either from room-temperature thermal excitation or from light absorption itself; if larger, it then requires higher temperatures as in the 300–500°C required to fade smoky quartz or amethyst. Color center transitions are fully allowed, leading to large oscillator strengths and intense colors even at very low concentration.

Additional examples of color centers are old Mn-containing glass turned purple by irradiation with the mechanism: $Mn^{2+} \longrightarrow Mn^{3+} + e^-$; even uv can produce this change in old sun-exposed bottles then termed desert amethyst glass. In many minerals, the mechanism is unknown, such as the following where F indicates fading at room temperature or in light, and S stands for a light-stable color: purple fluorite, calcium fluoride [7789-75-5] (blue john) (S); two types of yellow sapphire (F and S); blue (S) and two types of brown (F and S) topaz [1302-59-6]; deep blue Maxixe beryl (F); and irradiated yellow, green, blue, and red diamond (all S; these are different from the impurity-caused colors covered in the previous section).

Unusual is some hackmanite [1302-90-5], $Na_4Al_3Si_3O_{12}(Cl,S)$, which can have a deep magenta color as mined but fades in the light; the color can be restored in some material with uv exposure or simply by storing in the dark, where the reaction is $S_2^{2-} \rightarrow S_2^- + e^-$. The hole center S_2^- absorbs at 3.1 eV (400 nm) and the electron combines with a vacancy to form an F center absorbing at 2.35 eV (530 nm); it is the combination of both absorption bands that produces the color. Light absorption while showing the color also reverses this process, as does heat, both causing the color to fade.

8.11. Color from Dispersive Refraction. This mechanism involves the variation of the refractive index n with wavelength λ, given by the Sellmeier dispersion formula:

$$n^2 - 1 = a\lambda^2/\left(\lambda^2 - A^2\right) + b\lambda^2\left(\lambda^2 - B^2\right) + \cdots$$

where $A, B, \ldots$ are the wavelengths of individual ir, vis, and uv absorptions and $a, b, \ldots$ are constants representing the strength of these absorptions. Three terms are normally sufficient for an excellent fit in the visible region.

Even a transparent colorless material has uv absorptions (from electronic excitations) and ir absorptions (from atomic and molecular vibrations), which result in the decrease of n with wavelength in the visible region as seen in Figure 19. Only a vacuum has no absorption and no dispersion; neither of these is fundamental since each can be viewed as producing the other, with the Kramers-Kronig relationships as the connection. As a result Newton's prism produces the spectrum, crystal glassware and faceted gemstones show fire, raindrops produce the primary and secondary rainbows (higher orders can be seen only in the laboratory), and ice crystals produce various colored halos around the sun and moon, as well as sundogs. The green flash, rarely seen

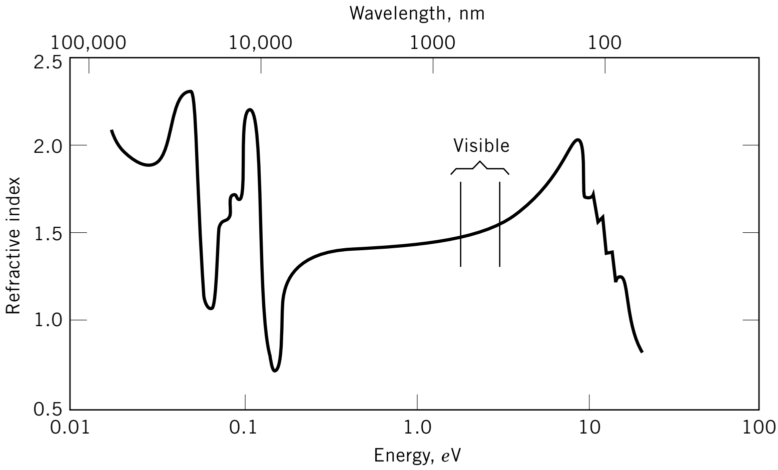


Fig. 19. The dispersion curve of a colorless soda-lime–silicate crown glass where the wt% of $Na_2O = 21.3$; $CaO = 5.2$; and $SiO_2 = 73.5$ (2).

when the sun sets, results when the density gradient of the atmosphere acts as a prism, separating the spectral colors; since violet and blue are strongly scattered from the following mechanism, green is the last spectral color seen. Anomalous dispersion, where n varies anomalously in the vicinity of an absorption band in the visible, can be classified in this section.

8.12. Color from Scattering.

Particles that are small compared to the wavelength of light produce scattering, the intensity of which is proportional to λ^{-4}, as shown by Lord Rayleigh. This happens not only from particles but even from refractive index variations from density fluctuation in gases, thermal vibrations in crystals, and chemical composition variations in glasses and polymers. As a result, violet at the 400-nm limit of visibility is scattered 9.38 times as much as red at the 700-nm limit. Scattered light therefore appears violet to blue, as in the blue of the clear sky, while the remaining light is usually orange to red, as in the setting sun where the effects of dust add to the atmosphere's density fluctuations. The exact color also depends on the shape of the scattering particles. One speaks of Rayleigh scattering and of Tyndall blues after an early investigator. The scattered light is polarized with an intensity variation of $(1+\cos^2\theta)$ with angle θ from the light beam. When the particle size becomes equal to or a little larger than the wavelength, the complex Mie scattering theory must be used; this type of scattering can produce almost any color. At even larger sizes scattering becomes noncolor-selective and produces only white, as in fogs and clouds.

Rayleigh scattering produces, in addition to the blue sky and red sunset, most blue colors in bird feathers and butterfly wings, the blue iris in eyes, cold blue skin, blue cigarette smoke, blue moonstone, and the rare blue moon from forest fire oil-droplet haze. (The supposed blue moon explanation based on calendric occurences is spurious.) A dark background is necessary for intense blues, as in the black of outer space for the blue sky and the melanin backing for the blue iris of the eye (additional yellow-to-brown melanin at the front of the iris leads to green and brown colors). Also included in this group are colors produced by effects such as second harmonic generation and parametric oscillation in nonlinear materials and various inelastic processes such as the Raman, Brillouin, polariton, magnon, Thompson, and Compton scatterings. Mie scattering from metallic particles in glass, such as in ruby glass, can be considered here or under the metals of Section Color of Metals.

8.13. Color from Interference.

Under this heading is considered only that color produced by interference that does not involve any diffraction; the combination of these two processes is considered in the following section.

When two light waves of the same frequency interfere, anything from constructive reinforcement to destructive cancellation can occur, depending on the phase relationship. This is present in a wedge-shaped film, eg, where the light reflected from the front surface interferes with that reflected from the back surface, the phase difference depending on the refractive index and the thickness of the film. With monochromatic light this usually produces light and dark fringes as in interferometers, while with white light the color sequence of Newton's colors is produced. Starting with the thinnest film, this sequence is black, gray, white, yellow, red (end of the first order), violet, blue, green, yellow, orange-red, violet (end of the second order), blue, green, yellow, red, etc.

Newton's colors are seen in the tapered air gap between touching nonflat sheets of glass; cracks in a transparent medium such as glass or a crystal; soap bubbles; oil slicks on water; thin tarnish coatings on substances such as the mineral bornite and on ancient buried glass; supernumerary rainbow fringes; antireflection coatings on camera lenses, etc; the wings of house and dragon flies; and in some beetle wing cases as in Japanese beetles. When intense colors occur, they appear metalliclike in nature and are usually termed iridescent; these effects are intensified by a dark backing. They also can be intense in some multiple layer structures that are present in interference filters; the naturally occurring multilayered mineral labradorite and layer-structured pearls; fish scales and imitation pearls based on fish scale essence, both involving guanidine flakes; peacock, hummingbird, and some other bird feather colors; the luster of hair and nails; and in the metalliclike reflections from the eyes of cats and many other nocturnal animals.

Other interference-produced colors falling into this section include doubly refracting materials such as anisotropic crystals and strained isotropic media between polarizers, as in photoelastic stress analysis and in the petrological microscope.

8.14. Color from Diffraction. Diffraction refers to the nonrectilinear propagation of light, eg, when the edge of an object produces an interrupted wavefront and light bends around the edge; interference can then occur between the bent and the undisturbed parts of the light. Light and dark fringes are formed from monochromatic light and colored fringes from white light in Fresnel diffraction from a collimated beam of light passing through a small slit, as well as in Fraunhofer diffraction when the image of such a slit is focused with a lens. This produces the corona, a set of colored rings around bright lights; the corona aureole, a disk of bluish light seen around the sun behind a thin cloud (the corona of the sun is a different phenomenon); and fog- and cloud-related effects such as the glory and Bishop's ring.

Diffraction from two-dimensional diffraction gratings follows a variant of Bragg's law (2) and produces spectral displays as in diffraction grating spectroscopes; some beetles and snakes; phonograph records and compact disks; a distant street lamp seen through a cloth umbrella; and in the play of color seen in the natural three-dimensional diffraction grating opal. Liquid crystals (qv) of the cholesteric or chiral nematic type also function to diffract light as in liquid crystal thermometers, thermography, and in mood jewelry, where a change in temperature alters the grating spacing and hence the color of a cholesteric mesophase supported between pieces of glass or plastic.

BIBLIOGRAPHY

See "Color Measurement" in the Kirk-Othmer *Encyclopedia of Chemical Technology ("ECT")* 1st ed., Vol. 4, pp. 242–251, by G. W. Ingle, Monsanto Chemical Co.; "Color" in *ECT* 2nd ed., Vol. 5, pp. 801–812, by G. W. Ingle, Monsanto Chemical Co.; in *ECT* 3rd ed., Vol. 6, pp. 523–548, by F. W. Billmeyer, Jr., Rensselaer Polytechnic Institute; in *ECT* 4th ed., Vol. 6, pp. 841–876, by K. Nassau, AT&T Bell Laboratories; "Color" in *ECT* (online), posting date: December 4, 2000, by K. Nassau, AT&T Bell Laboratories.

CITED PUBLICATIONS

1. R. S. Berns, *Billmeyer and Saltzman's Principles of Color Technology*, 3rd ed., John Wiley & Sons, Inc., New York, 2000.
2. K. Nassau, *The Physics and Chemistry of Color*, 2nd ed., John Wiley & Sons, Inc., New York, 2001.
3. R. G. Kuehni, *Color*, John Wiley & Sons, Inc., New York, 1997.
4. R. W. G. Hunt, *Measuring Color*, 3rd ed., Newpro, U.K., Ltd., 1996.
5. R. S. Hunter and R. W. Harold, *The Measurement of Appearance*, 2nd ed., John Wiley & Sons, Inc., New York, 1987; Table A7.
6. P. K. Kaiser and R. M. Boynton, *Human Color Vision*, 2nd ed., Optical Society of America, Washington, D.C., 1996.
7. M. S. Cayless and A. M. Marsden, *Lamps and Lighting*, Edward Arnold, London, 1983.
8. K. L. Kelly and D. B. Judd, *Color: Universal Language and Dictionary of Names*, NBS Special Publication 440, U.S. Government Printing Office, Washington D. C., 1976.
9. R. G. Kuehni, *Computer Colorant Formulation*, D. C. Heath & Co., Lexington, Mass., 1975.
10. A. H. Munsell, *A Color Notation*, 14th ed., Macbeth Division of Kollmorgen Instruments Corp., Newbaugh, N.Y., 1990.
11. W. N. Sproson, *Colour Science in Television and Display Systems*, Hilger, Bristol, U.K., 1983.
12. G. Wyszecki and W. S. Stiles, *Color Science*, 2nd ed., John Wiley & Sons, Inc., New York, 2000.
13. *CIE Publication 15.2 Colorimetry*, 2nd ed., Central Bureau of CIE, Vienna, Austria, 1986; Available from U.S. National Committee CIE, c/o National Institute of Standards and Technology, Washington, D.C.
14. J. Long and J. T. Luke, *The New Munsell Student Color Set*, 2nd ed., Fairchild Books, 2001.
15. *Munsell Book of Color*, glossy or matte finishes, and other collections, Macbeth Division of Kollmorgen Instruments Corp., Baltimore, Md., 1929 on, long discontnued.
16. A. Hård and L. Sivik, *Color Res. Appl.* **6**, 129 (1981).
17. E. Jacobson, *Basic Color: An Interpretation of the Ostwald Color System*, P. Theobald, Chicago, Ill., 1948.
18. A. Maerz and M. R. Paul, *A Dictionary of Color*, McGraw-Hill Book Co., New York, 1930.
19. D. L. MacAdam, *J. Opt. Soc. Am.* **64**, 1691 (1974); *Uniform Color Scales Committee Samples*, Optical Society of America, Washington, D.C., 1977.
20. *ISCC-NBS Centroid Color Charts, NBS Standard Reference Material No. 2106*, National Institute of Standards and Technology, Washington, D.C., 1965.
21. W. D. Wright, *The Measurement of Color*, 4th ed., Adam Hilger, London, 1969.
22. *Color and Appearance Collaborative Reference Program*, Collaborative Testing Services, Inc., Herndon, Va., previously *MCCA-NBS Collaborative Reference Program on Color and Color Differences*, National Institute of Standards and Technology, Washington, D.C., 1991.

GENERAL REFERENCE

K. Nassau, "Colour" in, *Encyclopedia Britannica*, 15th ed., Macropedia Vol. 4, pp. 595–604, 1988 on.

KURT NASSAU
Consultant