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THE COLORS OF COLLOIDS. II

BY WILDER D. BANCROFT

Reflection and Refraction

When a beam of light strikes a plane, polished surface, a portion of the light is reflected in such a way that the angle of incidence, measured from the normal to the surface, is equal to the angle of refraction. The remaining portion of the beam is refracted and passes through the surface in such a way that the ratio of the sine of the angle of the incident ray is proportional to the sine of the angle of the refracted ray, or $\sin i/\sin r = \text{constant}$. This is known as Snell's law. It was discovered in 1621 and holds for isotropic media only. The constant in the equation is the relative refractive index between the media, and the equation holds for every value of i, if the second medium is the one in which the light travels at a lesser velocity. While a refracted ray always exists when the light passes from an optically less dense to an optically denser medium, no matter how great the angle of incidence, the converse is not always true. If the relative refractive index is less than one, $\sin r$ should be greater than one when i exceeds a certain angle. No angle has a sine greater than one and therefore there can be no refracted ray and we are dealing with total reflection. The angle at which this occurs is called the critical angle. Tyndall[1] says that "In all cases when the light is incident from air upon the surface of a solid or a liquid, or, more generally still, when the incidence is from a less highly refracting to a more highly refracting medium, the reflection is *partial*. In this case the most powerfully reflecting substances either transmit or absorb a portion of the incident light. At a perpendicular incidence water reflects only 18 rays out of every 1000; glass reflects only 25 rays, while mercury reflects 666. When the rays strike the surface obliquely the reflection is augmented. At an

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[1] "Six Lectures on Light," 17 (1883).

incidence of 40°, for example, water reflects 22 rays, at 60° it reflects 65 rays, at 80° 333 rays; while at an incidence of 89.5° where the light almost grazes the surface, it reflects 721 rays out of every 1000. Thus as the obliquity increases the reflection from water approaches, and finally quite overtakes, the reflection from mercury; but at no incidence, however great, when the incidence is from air, is the reflection from water, mercury, or any other substance, *total.* Still total reflection may occur, and with a view to understanding its subsequent application in the Nicol's prism, it is necessary to state when it occurs......Total reflection never occurs except in the attempted passage of a ray from a more refracting to a less refracting medium; but in this case, when the obliquity is sufficient, it always occurs. Total reflection may be illustrated simply by placing a shilling in a drinking glass and tilting the glass so that the light from the shilling shall fall with the necessary obliquity upon the water surface above it. Look upwards toward that surface and you see the image of the shilling shining as brightly as the shilling itself. Thrust the closed end of a glass test-tube into water, and incline the tube. When the inclination is sufficient, horizontal light falling upon the tube cannot enter the air within it, but is totally reflected upward; when looked down upon such a tube looks quite as bright as burnished silver. Pour a little water into the tube; as the liquid rises, total reflection is abolished, and with it the lustre, leaving a gradually diminishing, shining zone, which disappears wholly when the level of the water within the tube reaches that without it. Any glass tube, with its end stopped water-tight, will produce this effect, which is both beautiful and instructive."

Total reflection will not occur if the medium having the lower index of refraction is present as a thin film.[1] "Bring a convex surface of glass of large radius of curvature into contact with the surface at which total reflection is taking place. The light will be found to enter the lens in an annular region surrounding the point of contact. This is due to the fact

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[1] Wood: "Physical Optics," 373 (1911).

that the two glass surfaces come into optical contact, *i. e.*, we may regard the air film as squeezed out completely. This circular patch over which total reflection fails and complete transmission obtains, is surrounded by a ring which *transmits* light of a reddish and *reflects* light of a bluish tinge. The glass surfaces are not in contact here; but the air film is too thin for total reflection to take place. Transmission will obviously occur for red light first, since the thickness of the film necessary to reflect light is measured in comparison with the wave-length."

Wood[1] points out that while "the velocity of light in the free ether of space is independent of the color or wave-length, such is not the case in refracting media. Here the waves not only travel slower than in free space, but waves of different length travel with very different velocities. In all such media as air, water, and glass, the long waves travel faster than the short ones; consequently the deviation of the ray, or the angle through which the wave-front turns when encountering the boundary of the medium, depends on the color of the light as well as on the optical density of the medium."

"When white light enters a transparent medium, the long red waves forge ahead of the green ones, which in their turn get ahead of the blue. If we imagine an instantaneous flash of white light traversing a refracting medium, we must conceive it as drawn out into a sort of linear spectrum in the medium, that is, the red waves lead the train, the orange, yellow, green, blue, and violet following in succession. The length of this train will increase with the length of the medium traversed. On emerging again into free ether the train will move on without further alteration in its length.

"We can form some idea of the actual magnitude involved in the following way: Suppose we have a block of perfectly transparent glass (of refractive index 1.52) twelve miles in thickness. Red light will traverse it in 1/10000 of a second. If white light were to traverse this mass of glass, the time elapsing between the arrival of the first red and the first blue

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[1] "Physical Optics," 91, 101 (1911).

light would be less than 1/6000 of a second. Michelson's determination of the velocity of light in carbon bisulphide showed that the red waves gained on the blue waves during their transit through the tube of liquid. The absence of any change of color in the variable star Algol furnishes direct evidence that the blue and red rays traverse space with the same velocity. In this case the distance is so vast, and the time of transit so long, that the white light coming from the star during one of its periodic increases in brilliancy, would arrive at the earth with its red components so far in advance of the blue that the fact could easily be established by the spectrophotometer or even by the eye.

"Inasmuch as the deviation of a ray of light depends on the change of velocity of a wave on going, say, from a rare into a denser medium, we infer that those rays which are deviated the most, namely the violet, suffer the greatest change of velocity or move the slowest......In addition to the more or less regular gradation in the refractive index of the atmosphere there exist striae, or small regions of sudden change due to the mixing of hot and cold currents, somewhat similar to the conditions existing in a mixture of glycerine and water. When a wave-front of light passes through a region where the refractive index is low, it gains; and it loses while travelling in a region of high refractive index. The result of this is that the striae deform the plane-waves of light coming from the stars into corrugated waves, portions of which are convex in the direction of propagation, while other portions are concave. The concave portions naturally converge, while the convex portions diverge, the result being that the energy concentrates itself in certain areas at the expense of the adjacent areas. This uneven distribution of light produces the familiar phenomenon of scintillation or twinkling of the stars. If the intensity of the light from a star were sufficient, we should find that instead of illuminating a white surface uniformly, as does the sun or the moon, it would illuminate it unevenly, dark and light patches alternating over the surface. This uneven illumination is actually observed during the few moments immediately preceding the total stage of a solar eclipse, the patches of light being arranged in more or less parallel bands."

When a plane wave passes through a glass plate bounded by parallel planes,[1] the emergent wave-front is parallel to the incident wave-front, no matter how great the angle of incidence. The direction of the ray is therefore shifted to one side by its passage through the plate. In the case of a prism, the emerging ray is deviated towards the base of the prism and is therefore not parallel to the incident ray. The amount of deviation depends on the index of refraction and the angle of the prism. Since the index of refraction is ordinarily greater the shorter the wave-length, the violet rays will be deviated the most and the red rays the least. The degree of dispersion or the length of the spectrum depends upon the differences in the refractive indices for the different rays and is therefore not necessarily greater the higher the refractive index of the prism material, though this is often the case.

"In the case of transparent substances the dispersion is said to be normal, that is, the refractive index increases as the wave-length decreases, though the rate of change varies according to the nature of the substance. In the case of substances which show selective absorption this is generally not the case, the refractive index for the short waves in the blue side of the absorption band being less than the index for the red light on the other side of the band. This phenomenon has been named anomalous dispersion; but there is nothing anomalous about it, the so-called normal dispersion being nothing more than a special case of the anomalous. Fox Talbot appears to have been the first to notice the peculiar effect, but his discovery was not followed up. In 1860 Le Roux[2] discovered that a prism containing iodine vapor deviated the red rays more than the blue, the indices at a temperature of 700° C for the red and violet being 1.025

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[1] Wood: "Physical Optics," 68 (1911).

[2] Ann. Chim. Phys., [3] 41, 285 (1861).

and 1.019. Christiansen[1] detected anomalous dispersion in the case of an alcoholic solution of fuchsine, which is one of the aniline dyes having a strong absorption band in the green. Of the remaining colors, the red, orange, and yellow occur in the same order as in the case of a glass prism. The violet, however, is less refracted than the red and separated from it by a dark interval. Christiansen's prism was made of two glass plates inclined at an angle of one degree, the solution being held between them by capillarity. The subject was next investigated by Kundt.[2] His observations showed that the phenomenon is to be observed in the case of all bodies which reflect certain wave-lengths selectively. Ordinary pigments do not belong to this class, the color being produced by absorption."

Since the transmission of light through a material medium is always accompanied by absorption, we shall get different degrees of absorption with varying thickness of the absorbing medium.[3] "If the absorbing medium is homogeneous, the quantity of light of a given wave-length which is absorbed will be proportional to the thickness of the medium traversed. If we represent the intensity of the light that enters the front surface of the medium by I, the intensity after transmission through unit thickness can be represented by Ia^{ϵ}, in which a is a fraction depending on the nature of the medium and the wave-length of the light. If the same fraction is absorbed by each successive layer, it is clear that the intensity, after traversing a thickness ϵ of the medium, will be Ia^{ϵ}, the quantity of a being called the coefficient of transmission. The coefficient of transmission varies with the color, and the emergent light is therefore colored. In the case of most absorbing media the color of the transmitted light does not depend to any great degree on the thickness, the depth or saturation merely increasing. In some cases, however, the color depends on the thickness, thin layers, for example, appearing green,

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[1] Pogg. Ann., 41, 479 (1870); 146, 154 (1872).

[2] Ibid., 142, 163; 143, 149, 259; 144, 128 (1871); 145, 67, 164 (1872).

[3] Wood: "Physical Optics," 438 (1911).

and thick layers red. Such substances are said to exhibit dichromatism. Some of the aniline dyes, or mixtures of them, show the phenomenon. Thin layers of a solution of cyanine appear blue, thick layers red. The addition of a little nitrosodimethyl aniline to the solution gives us a green-red dichromatic liquid, as has been shown by Pflüger. The explanation of the change of tint is very simple. Suppose we have a substance which absorbs the yellow and blue. The transmitted light then consists of a mixture of red and green. Let us assume, as is usually the case, that the intensity of the green is greater than that of the red. Writing for these intensities $I_g > I_r$, and assuming that the coefficient of transmission of the green is less than that of the red $a_g < a_r$, it follows that for small thicknesses $I_g a_g^\epsilon$ will be greater than $I_r a_r^\epsilon$, while the reverse will be true for thick layers. This is at once apparent if we call the original intensities of the green and red 100 and 50, and the coefficients of transmission 0.5 and 0.8, and calculated the intensities of the transmitted colors for several different thicknesses. They will be equal for a thickness ϵ given by the equation

$$I_g a_g^\epsilon = I_r a_r^\epsilon,$$

or taking the logarithms of both sides,

$$\epsilon = \frac{\log I_g - \log I_r}{\log a_r - \log a_g}.$$

For this thickness the intensities of the red and green will be equal, and the color of the transmitted light will appear to be yellow, for a mixture of red and green light produces the sensation of yellow when mixed in proper proportions. An excellent mixture for illustrating this can be formed by dissolving "brilliant green" and "naphthalene yellow" in hot Canada balsam and pressing the mixture between two glass plates in the form of an acute prism. The balsam should be previously boiled down until a drop solidifies on cooling, and the dyes should not be added until the fluid has cooled somewhat, otherwise they are apt to decompose. The thin edge of the wedge will appear green, the thick edge red, and the intermediate portions, where we have equality of transmission, yellow. If some of the same mixture is moulded into a prism of 20 or 30 degrees angle, the mechanism of dichromatism can be beautifully shown by observing a lamp flame through it. The prism will show the red image well separated from the green, and the latter will be found to be extinguished more rapidly than the former as the prism is moved laterally before the eye.

"Our equations for color show us as well that the color of the transmitted light for a given thickness, will vary with the composition of the original light. If the plate of stained balsam is examined by gas-light and then by day-light, it will be found that parts of it will appear red in the former and green in the latter case. A solution of cyanine and nitroso-dimethyl aniline in alcohol appears red by lamp-light and bottle-green by day-light. The same phenomenon is exhibited by the gem Alexandrite, found in the Urals."

Von Bezold[1] says: "If one takes colored films of different thickness, for instance by piling up several strips of colored glass, the color changes. If the color was originally weak, it becomes stronger and stronger as the number of pieces of glass increases, but the transmitted light becomes weaker and weaker, until finally no light comes through and the layer appears black. If the layer is thick enough, even so-called white or, more properly, colorless glass shows a definite color, usually blue or green. With colored solutions, increasing the concentration has the same effect as increasing the thickness of the layer.[2] A drop of ink in water colors this bluish or violet according to the nature of the ink, sometimes even greenish or reddish, while the color of the concentrated solution is quite black. With this change in the brightness there is often a change in the color. A solution made from the beautiful blue crystals of copper sulphate is a pale greenish blue when dilute, and deep blue when concentrated. A few

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[1] "Die Farbenlehre," 54 (1874).

[2] [Not strictly true because increasing the concentration may change the dissociation or the polarization. W. D. B.]

drops of red wine in water colors the water a painful gray and one must add more before one gets the red color of the wine. Similar phenomena are to be noted with plant juices. In thin layers on a white ground madder gives a yellowish Prussian blue to a greenish blue color.

"The red flashed glass colored with cuprous oxide is ordinary glass with a thin superposed film of colored glass; it has a yellowish color when it is put on very thin or when one etches off nearly all of the colored glass. This process is used by people to produce striking chromatic effects on such glasses. The cause of all these variations is that the colored media first absorb certain wave-lengths and then with increasing thickness or concentration gradually absorb others. A series of indigo solutions of varying concentrations has different colors. A very dilute solution appears light blue with a slight touch of green and might easily be mistaken for a solution of Prussian blue. The more concentrated solutions pass through the powerful blue tints to one in which a violet shade cannot be ignored."

It has already been pointed out that we always get both reflection and refraction when a beam of light impinges on a plane, polished surface of an optically denser medium and we have now to consider the factors determining the percentage reflection ignoring for the moment any effect due to actual roughness of the surface. The percentage reflection varies with the angle of incidence, the wave-length, and the polarization of the beam of light, and with the index of refraction and absorptive power of the reflecting medium. Other things being equal, more light is reflected the higher the index of refraction of the reflecting medium and the greater the angle of incidence of the beam. Since the refractive index is usually higher the shorter the wave-length, the percentage reflection will usually increase with decreasing wave-length.

Rays of light exist which possess a one-sidedness and which behave differently when differently orientated.[1] "It is possi-

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[1] Wood: "Physical Optics," 288, 289, 335, 369 (1911).

ble to obtain light which a glass or water surface refuses to reflect at a certain angle of incidence. Such light is said to be polarized, and is distinguished from ordinary light in that its vibrations are of a fixed type; that is, the ether particle travels in a fixed orbit. If the motion is back and forth along a line, the light is said to be plane-polarized." Light is said to be polarized elliptically when the ether particles move in an elliptical orbit of fixed eccentricity and orientation in space and is said to be polarized circularly when the orbit is a circle. "The discovery was made by Malus in 1810 that light, which had suffered reflection at a certain angle from a surface of water or glass, exhibited the same peculiarities which had previously been observed only in the case of light after its passage through a crystal of Iceland spar ....In general, as we increase the angle of incidence from normal to grazing, the polarization increases, passes through a maximum, and then decreases. The angle at which the polarization is most complete varies with the nature of the substance and is known as the polarization angle. Jamin found that only a few substances with a refractive index of about 1.46 polarize the reflected light completely. For all other substances the polarizing angle is merely the angle at which the polarization is a maximum.

"The relation between this angle and the refractive index of the substance was investigated by Brewster who discovered the remarkable law that the index of refraction is the tangent of the angle of maximum polarization. When the light is incident at this angle, the refracted ray makes an angle of 90° with the reflected ray for

$$\frac{\sin i}{\sin r} = n = \tan i = \frac{\sin i}{\cos i}.$$

"Therefore $\cos i = \sin r$ and $i + r = 90°$.

"If this law is true, the angle of maximum polarization will be different for the different colors owing to dispersion. In the case of most transparent media the dispersion is too small greatly to affect the angle as can be shown by examining the image of the sun reflected in a glass plate through a Nicol prism so orientated as to cut off most completely the reflected light. The image of the sun appears uncolored; which would not be the case if the angle of polarization was very different for different parts of the spectrum. The Nicol prism takes the place of the second reflector, having the property of cutting off completely light polarized in a certain plane, and transmitting with greater or less facility light polarized in all other planes. In the case of substances having very high dispersion, the variation of the angle with change of wave-length becomes very marked. The organic compound nitroso-dimethyl aniline, which has been found to have the highest dispersion, in the brighter parts of the visible spectrum of any known substance, is adapted admirably for the exhibition of what may be termed the dispersal of the angle of polarization. A little of this substance is fused on a glass or metal plate, or better in a small brass cell heated by steam. A brilliant source of light of small dimensions—nothing is better than a Nernst lamp—is arranged so that its light is reflected from the liquid surface at an angle which can be varied. On examining the light reflected at a fairly large angle with a Nicol prism, it will be found to vary from light blue to deep violet and purple as the angle of incidence is increased, the Nicol being held in such a position as to refuse transmission to the light polarized by reflection."

"When plane-polarized light is twice internally reflected at an angle of 54°, it emerges as circularly polarized light if the original plane of polarization made an angle of 45° with the plane of incidence. Each reflection in this case introduces a phase-difference of $\pi/4$ between the reflected components; consequently a single internal reflection from glass will give us elliptically polarized light. This can be shown with an ordinary right-angle prism. In general, when plane-polarized light is reflected at an azimuth of 45°, *i. e.*, with its plane of vibration inclined at 45° to the plane of incidence, the reflected light will be elliptically polarized to a greater or lesser extent. In the case of glass and other transparent media the eccentricity of the ellipse is very great; in other words the reflected light is very nearly plane-polarized, but the elliptical polarization is very marked in the case of metals. If plane-polarized light is reflected from a silvered mirror, it will be found to be transmitted quite freely by a Nicol prism in all positions if the plane of polarization originally made an angle of 45° with the plane of incidence."

"It was found by Jamin and others that in the majority of the cases the light was not polarized completely by reflection at the Brewsterian angle. Moreover, if the incident light was polarized and reflection occurred in the neighborhood of this angle, the reflected light showed traces of elliptical polarization instead of plane-polarized as the formulas indicate. This means that the phase change enters by degrees instead of occurring abruptly at the polarizing angle. In 1889 Drude observed that the elliptical polarization produced by a freshly split surface of rock salt was very small, but that it increased rapidly on the exposure of the surface to the air. Shortly afterward Lord Rayleigh found that the ellipticity produced by reflection from water could be eliminated completely by removing the surface film of grease which is always present unless special precautions are taken and which naturally has a higher refractive index than water. These experiments indicate that the disagreement with the formulas is caused by surface films having optical properties different from those of the body of the substance....

"By carefully cleaning the surface of the water Lord Rayleigh was able to destroy all traces of elliptical polarization almost completely, the value of the amplitude ratio being not more than 0.00035. Quite recently he has found that the positive ellipticity of glass can be changed into negative by repolishing the surface....Lummer and Sorge found, in repeating and extending the work of Rayleigh, that the elliptical polarization of the light reflected from the surface of a glass prism was altered by polishing or rubbing one of the other faces or even by subjecting the prism to pressure applied to the bases. The prism was a right-angled one and they found that by rubbing the two base surfaces the ellipticity was decreased for all three of the other surfaces, that for hypothenuse passing through zero (the condition for the ideal case of sudden transition) and becoming slightly negative. It is impossible to conceive how the refractive index of a surface film could be altered without touching the surface, much less how it could be changed from a value less than that of the medium to one of greater, as we should be obliged to assume for the conditions found in the case of the hypothenuse surface of Lummer's prism. In view of these experiments it appears more probable that the elliptical polarization is caused in some way by surface strains. At all events further work is required before we can feel justified in establishing a theory. Some unpublished experiments by the author have pointed toward a change in the reflecting power resulting from strains. A very thin film of collodion on glass has been found to more than double its reflecting power under certain conditions. The refractive index of collodion is, however, not very different from that of glass, and we should expect but little reflection from the transition surface. A layer of thick glue spread over a glass surface reduces its reflecting power nearly to zero. When the glue dries, the surface is subjected to a strain so great that glass chips are often torn off the surface. The reflecting power of the surface separating the dry glue and the glass was a little higher than that of a surface between glass and damp glue. The change in the refractive index could hardly account for this as it would be in the wrong direction."

Von Bezold[1] has called attention to the fact that "the light reflected from a water surface is polarized and if one looks at such a surface through a Nicol's prism or through a suitably arranged Claude Lorraine glass, one can destroy this reflection and can see into the depths. The light of the blue sky is also polarized, the direction and degree of the polarization varying with the relative position of the portion of the sky under consideration to the sun. If the blue sky is reflected in a smooth water surface, the same phenomena

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[1] "Die Farbenlehre," 84 (1874).

must take place as with a Claude Lorraine glass. Depending upon the relative positions of the sun, the water, and the observer, the light of the sky may be reflected completely, partially, or not at all from the water mirror. In the last case the actual color of the water is seen and this is why a water surface may appear deep blue or blue-green on days when the sky shows quite pale misty tints. Clouds reflect light irregularly and therefore do not polarize it. The reflection of the light from the clouds is therefore never interfered with at a smooth water surface. For this reason on cloudy days the clearest mountain lakes never show that deep color which charms the observer when the sky is clear.

"The elimination of the polarized light from the sky may give rise to quite startling effects. The author remembers one time in a beautiful summer evening when he walked by the side of a body of water with the sun at his back and the trees along a path were reflected in the water. The trees were seen dark against the light horizon but they appeared light on a dark ground in the reflection. The light scattered in all directions from the leaves showed no definite polarization, and the reflected image was therefore nearly as bright as the original, while the light from the sky was polarized so that it was only reflected slightly from the water surface."

The relation between absorption and reflection is not absolutely clear.[1] "At the beginning of the subject we shall find it convenient to distinguish between two types of absorption: general, in which the absorbing power is very nearly the same for all wave-lengths, at least over a fairly wide range; and selective, when the absorbed region is more or less limited in extent. The absorption of metal films and lampblack represents the first type fairly well. The light transmitted through thin layers differs but slightly in its composition from the original light, and exhibits therefore but little color. Of course there are exceptions, for, as is well known, thin films of gold transmit an excess of green light, while silver is fairly transparent to the ultra-violet. Aniline dyes,

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[1] Wood: "Physical Optics," 437, 456 (1911).

and, in fact, all colored media, represent the second type, certain colors being freely transmitted, while others are strongly absorbed. When we come to consider the theory of the phenomena, we shall see that the causes of the absorption are radically different in the two cases, though in many cases both conditions may occur simultaneously in one and the same medium."

The light corresponding to certain absorption bands, usually the intense ones, appears for some reason not to enter the substance to any appreciable extent. This light is therefore not absorbed, but is reflected selectively. Stokes[1] says: "Certain substances, many of them of vegetable origin, have the property of reflecting (not scattering) light which is colored and has a metallic aspect. The substances here referred to are observed to possess an exceedingly intense absorbing action with respect to rays of the refrangibilities of these which constitute the light thus reflected, so that for these rays the opacity of the substances is comparable with that of metals. Contrary, however, to what takes place in the case of metals, this intense absorbing action does not usually extend to all the colors of the spectrum, but is subject to chromatic variations, in some cases very rapid. The aspect of the reflected light, which itself alone would form but an uncertain indication, is not the only nor the principal character which distinguishes these substances. In the case of transparent substances, or those of which the absorbing power is not extremely intense (for example, colored glasses, solutions, etc.), the reflected light vanishes, or almost entirely vanishes, at a certain angle of incidence, when it is analyzed so as to retain only light polarized perpendicularly to the plane of incidence, which is not the case with metals. In the case of the substances at present considered, the reflected light does not vanish, but at a considerable angle of incidence the pencil polarized perpendicularly to the plane of incidence becomes usually of a richer color, in consequence of the removal, in a great measure, of that portion of the reflected light which

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[1] "Mathematical and Physical Papers," 4, 42, 260 (1909).

is independent of the metallic properties of the medium; it commonly becomes, also, more strictly related to that light which is absorbed with such great intensity. The reflexion from a transparent medium is weakened or destroyed by bringing the medium into optical contact with another having nearly or exactly the same refractive index. Accordingly, in the case of these optically metallic substances, the colors which they reflect by virtue of their metallicity[1] are brought out by putting the medium in optical contact with glass or water. A remarkable character of metallic reflexion consists in the circumstance, that as the angle of incidence increases from 0°, the phase of vibration of light polarized in the plane of incidence is accelerated relatively to that of light polarized in the perpendicular plane. Accordingly, the same change takes place, with the same sign, in the case of these optically metallic substances; but the amount of the change is subject to most material chromatic variations, being considerable for those colors which are absorbed with great energy, but insensible for those colors for which the medium is comparatively transparent, so that the absorption may be neglected which is produced by a stratum of the medium having a thickness amounting to a small multiple of the length of a wave of light. If the medium be crystallized, it may happen that one only of the oppositely polarized pencils which it transmits suffers, with respect to certain colors, an exceedingly intense absorption; or, if that is the case with both pencils, that the colors so absorbed are different. It may happen, likewise, that the absorption varies with the direction of the ray within the crystal. In such cases the light reflected by virtue of the metallicity of the medium will be subject to corresponding variations, so that the medium is to be regarded as not only doubly refracting and doubly absorbing, but doubly metallic....

"To illustrate the effect of bringing a transparent medium

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[1] I use this word to signify the assemblage of optical properties by which a metal differs from a transparent medium, or one moderately colored, such as a colored glass.

into optical contact with an optically metallic substance, I may refer to safflower-red. If a portion of this substance be deposited on a glass by means of water, and the water be allowed to evaporate, a film is obtained which reflects on the upper surface a yellowish green light, but on the surface of contact with the glass a very fine green inclining to blue. A green of the latter tint appears to be more truly related to the colors absorbed with greatest energy. Similar remarks apply to the light reflected by Herapathite, according as the crystals are in air or in the mother-liquor. If a small portion of Quadratite (platinocyanide of magnesium) be dissolved on glass in a drop or two of water, and the fluid be allowed to evaporate, the tints reflected by the upper and under surfaces of the film of crystals are related to one another much in the same way as in the case of safflower-red. For a fine specimen of the salt last mentioned I am indebted to the kindness of M. Haidinger. I may mention in passing, that the platinocyanides as a class are of extreme optical interest. The crystals are generally at the same time doubly refracting, doubly absorbing, doubly metallic, and doubly fluorescent. By the last expression I mean that the fluorescence, which the crystals generally exhibit in an eminent degree, is related to directions fixed relatively to the crystal, and to the azimuths of the planes of polarization of the incident and emitted rays...

"I will here mention another instance of the connexion between metallic reflexion and intense absorption. I choose this instance because a different explanation from that which I am about to offer has been given of a certain phenomenon observed in the substance. The instance I allude to is specular iron. As it is already known that various metallic oxides and sulphurets possess the optical properties of metals, there is nothing new in bringing forward this particular mineral as a substance of that kind. It is to the chromatic variation of the metallicity that I wish to direct attention. If light polarized at an azimuth of about 45° be reflected from a scale of this substance at about the polarizing angle and the reflected light be viewed through a plate of calcareous spar and a Nicol prism, it will be found, by using different absorbing media in succession, that the change of phase, as indicated by the character of the rings, while it is very evident for red light, becomes much more considerable in the highly refrangible colors. Now specular iron is almost opaque for light of all colors, but as it gives a red streak it appears that the substance-color is red; and, in fact, it is known that very thin laminae are blood-red by transmitted light. Accordingly, the chromatic variation of the change of phase corresponds to that of the intense absorbing power.

"The light reflected by specular iron is not extinguished by analyzation, whatever be the angle of incidence; but at the angle of incidence which gives the nearest approach to complete polarization, a quantity of blue light is observed to remain. This has been explained by comparing specular iron to a substance of high dispersive power, so that the polarizing angle for red light is considerably less than for blue; and accordingly on increasing the angle of incidence, the light (which is here supposed to be analyzed so as to retain only the portion polarized perpendicularly to the plane of incidence), while it becomes much less copious near the polarizing angle, becomes at the same time of a decided blue color.[1] I believe, however, that the blue light is mainly due to the chromatic variation of the metallicity, the medium, considered optically, being much more metallic for blue light than for red, though it may in some measure be due to the cause previously assigned.

"Specular iron is a good example of a substance forming a connecting link between the true metals and substances like safflower-red. It resembles metals in the circumstances that the absorbing power, as inferred from the chromatic variation of the metallicity, and as indicated by the tint of the streak, is not subject to the same extensive chromatic variations as in the case of coloring matters like safflower-red. It resembles safflower-red in being sufficiently transparent with respect to a portion of the spectrum to allow the

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[1] See Dr. Lloyd's "Lecture on the Wave-Theory of Light," Part II, p. 18.

connexion between the metallicity and the substance-color to be observed; whereas the substance-color of metals is not known from direct observation, except, perhaps, in the case of gold, which in the state of gold-leaf lets through a greenish light."

"The instances in which substances appear colored by reflexion are comparatively rare. It is very common in chemical descriptions to read of a solution appearing of such a color by transmitted, and such a color by reflected light. In many cases, that is a positive mistake, and the color described as due to reflexion is really due to transmission. A chemist views a solution contained in a test-tube by transmission, and then by reflexion; and seeing, perhaps, some perfectly different color in the latter case, describes it as the color of the solution by reflexion, whereas it is merely the color by transmission due to a greater thickness, the light having been reflected at the back or bottom of the test-tube, and so having twice passed through the solution. In other cases the color described as due to reflexion really arises from fluorescence; and though the statement may be true in the sense intended, it seems objectionable to apply the term *reflexion* to a process so utterly different. It is only in the case of metals, such as gold and copper, and of certain other substances such as murexide, platinocyanide of magnesium, etc., that color is really seen as the result of reflexion....

"When this takes place in the case of non-metallic substances, they are found to be endowed, for the colors so reflected, with an intense opacity, comparable with that of metals; while for other parts of the spectrum they may be comparatively transparent, and these parts they reflect with an energy comparable to that of a vitreous substance only. The variations of absorbing power in passing from one part of the spectrum to another, and consequently the variations in reflecting energy, are frequently much more considerable, and accordingly the color by reflexion is much richer than in the case of metals.

"An excellent example of the intimate connexion between metallic reflexion and intense absorption is afforded by crystals of permanganate of potash. These crystals exhibit a green metallic reflexion, and when crushed yield a powder of an intense purple color by transmitted light. The color is too intense for spectral analysis but the solution has a similar color, merely less intense as corresponds with its smaller concentration, and the analysis of the light transmitted by the solution presents no difficulty. The green is quickly absorbed, but when the solution is sufficiently dilute, five eminently characteristic bands of absorption are seen in that part of the spectrum. A sixth band comes out with a greater thickness or else less strength of solution, but even the fifth is somewhat less strong than the others. When the light reflected from a crystal is analyzed, four bright bands are seen standing out on a generally luminous ground of inferior brightness. These bright bands correspond in position with the principal *dark* bands in the light transmitted by the solution, and therefore, it may be presumed, by the crystals themselves. When the angle of incidence has a suitable value, and the reflected light is analyzed by a Nicol's prism, with its principal plane in the plane of incidence, and then by a common prism, the spectrum is reduced to these four bright bands. A fifth bright band could perhaps be made out, in the case of a fine crystal with a fresh surface. Under the circumstances described, the Nicol's prism would extinguish the light reflected from a vitreous substance, and transmit much of that reflected from a metal. We see, therefore, that, as regards its relations to light, the crystallized body passes repeatedly from the condition of a vitreous to that of a metallic substance and back again, as the refrangibility of the rays, in relation to which it is considered, is continuously increased by a small amount.

"The same relation between intense absorption and metallic reflexion exists generally, though it cannot be always studied by means of a solution. The platinocyanides, for example, yield colorless solutions, so that the intense absorption which most of them exercise for certain parts of the spectrum must be attributed to the mode in which the molecules are built up in forming the crystals; but by attending to the color of the light transmitted by thin crystals, the law is found to be obeyed. Gold can only be obtained, in solution, as gold, by means of the opaque solvent mercury; but its color by transmission may be studied in gold leaf, or in a chemically deposited film, and is then found to be conformable to the law mentioned, the less refrangible colors, which are those which are the more copiously reflected, being also those which are the more intensely absorbed.

"When a body endowed with the property of colored reflexion, such as permanganate of potash, is dissolved, in consequence of the necessary dilution the opacity of the medium ceases to be, for any part of the spectrum, of that intense kind which is necessary for quasi-metallic reflexion; and accordingly the light reflected by the solution is colorless. Hence colored reflexion is not available for following a substance through mixtures containing it. The chemist ought, however, to be acquainted with its laws, in order to understand the changes of color which a substance possessing the property is capable of exhibiting in the solid condition, according to its state of aggregation.

"In order that the color due to reflexion should appear, it is necessary that the substance should have a certain amount of coherence. Thus indigo in the form of a fine loose powder is blue, even when viewed by reflexion. It would be erroneous, however, to describe the body as blue by reflexion, if we were speaking of the properties of the substance, and not the mere crude results of observation made under given circumstances. For though it is true that the light by which the blue color is seen has undergone reflexion (without which it would not have reached the eye) it is not *in reflexion* that the chromatic selection is made by virtue of which the powder appears blue, but *during transmission*. In fact it is only a small portion of the light that is reflected at the outer irregular surface of the mass; the greater part penetrates a little way, and is reflected at various depths, and in passing through the particles, in going and returning, suffers absorption on the part of the colored substance. Were the substance intensely opaque for *all* the colors of the spectrum, the powder would be not blue but black, as we see in the case of platinum-black. By burnishing, the powder is reduced to the state of a somewhat coherent mass, and it now begins to exhibit the copper color due to reflexion. The internal reflexions are at the same time greatly weakened, so that the part of the light which is reflected from beneath and undergoes absorption is much reduced. A pressed mass is not, however, an optically homogeneous medium, so that the color by reflexion obtained by burnishing cannot in general be quite pure. In the state of a fine crystalline powder, indigo exhibits a mixture of the copper color due to reflexion, and the blue color due to transmission, though observed in the light reflected from the mass as a whole; while if the substance could be obtained in large crystals, the color by reflection would be seen in perfection, and the color by transmission would disappear, the crystals being sensibly opaque."

Wood[1] says that substances which reflect selectively exhibit surface color. "The aniline dyes are excellent examples. A dye which in solution absorbs green light; appearing purple by transmitted light, in the solid state reflects green light selectively. Absorption, however, is not the only factor which determines this selective reflection, and we often find misleading statements in text-books on optics, it being frequently stated that the wave-lengths most copiously reflected are the ones most strongly absorbed. This is by no means the case. Cyanine, for example, has a strong absorption band in the yellow, while the color of the selectively reflected light is purple, not so very different in hue from that of the transmitted light. If we examine the spectrum of the reflected light, we find a very dark band in the green, the centre being not far from wave-length 0.0005. The distribution of intensity in the rest of the spectrum is not very different from what it would be in the case of reflection from

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[1] "Physical Optics," 440, 409, 417, 400 (1911).

glass, which shows that the peculiar color of the dye is not so much due to a very powerful reflection of certain waves as it is to its almost complete refusal to reflect a certain region of the spectrum."

"Not all absorption bands exhibit the phenomenon of quasi-metallic reflection, and it is of interest to inquire into the conditions governing its appearance. Absorption results from resonance vibration of the electrons, but in some cases they throw practically all of the energy back, and there is little or no true absorption. When we come to the consideration of metals, we shall see that there is a type of absorption resulting from the presence of free electrons which have no definite period of vibration. If these electrons are free to move without friction under the periodic forces of the light-waves, the electric intensity within the medium will be neutralized within the medium and we shall have complete reflection. This would be the case for a perfect conductor. If the electrons experience a resistance to their motion, the neutralization will not be complete and a portion of the energy will enter the medium and be absorbed or transformed into heat (ohmic heating). It is the surface layer only which contributes to the reflecting power; in other words, the resonators must be so densely packed that the wave is practically stopped within less than a wave-length of the surface. That this is so follows from the principle of interference. Suppose each layer of resonators to reflect a small percentage of the incident energy. The phases of the disturbances would not be in agreement; and they would destroy each other. Now we find that ultra-violet absorption bands, say those of glass or quartz, do not give rise to selective reflection. From this we should infer that the disturbance penetrates a short distance into the medium and is absorbed. Thin films of glass, only a few wave-lengths in thickness, are quite transparent, even to the extreme ultra-violet. They would, without doubt, be found to be absolutely opaque to the infra-red at 8.5 μ. It is possible to obtain scales of mica less than a wave-length thick, and it would be interesting to compare their transmission at 8.5 μ and in the remote ultra-violet, say at 0.2 μ. The absorption bands of many substances, both in the infra-red and visible region, are of the same nature as these ultra-violet bands, and cannot therefore be located by the method of residual rays. Selenite and alum belong to this class, as was found by Aschkinass. In some cases traces of selective reflection can be found by employing only a single surface. The residual rays are in this case much diluted with continuous spectrum, but they can be located if due precautions are taken. This method was adopted by Coblentz, who investigated the reflecting power of a large number of substances. Obviously in cases where the reflecting power is below 70 per cent, most of the energy would be lost after four or five reflections. For 50 per cent reflecting power, four surfaces would only give us $^1/_{16}$ of the total intensity of a band of residual rays....

"The selective reflection of powdered quartz in the infra-red has been investigated by A. Trowbridge. He found a *minimum* of reflecting power in a region of the spectrum corresponding to the absorption band at 2.95 μ, and a *maximum* at the absorption band at 8.5 μ. This is interesting, and shows us the difference in the behavior of the two types of absorption bands. The one at 2.95 μ is weak, and only manifests itself when a considerable thickness is traversed. The quartz therefore shows 'body color' by reflection, *i. e.*, a color resulting from absorption, the energy penetrating deeply into the powdered mass, and finally emerging as the result of repeated reflection and refractions among the particles, robbed of energy of wave-length 2.95 μ. The band at 8.5 μ is metallic in character, and the energy is selectively reflected from the upper surfaces of the particles. If the particles were very small and the surface flat, specular or regular reflection would appear. Trowbridge used a rather coarse powder, and studied the diffuse reflection. The distinction between the two types of bands must be taken into account in all investigations made with surfaces which permit of the formation of 'body color,' otherwise the results will appear to be very anomalous in character."

"Very little work has been done on selective reflection in the ultra-violet. In general the phenomenon of metallic reflection does not occur at the ultra-violet absorption bands. Some investigations, made by Martens, of the ultra-violet dispersion of certain organic compounds, indicate that traces of selective reflection exist in certain cases. Cassia oil, for example, which in the thinnest possible films, pressed between fluorite plates, is opaque to everything below wave-length 3360, exhibits the phenomenon. Light from the cadmium spark, reflected a number of times from its surface, is shown by the spectroscope to consist chiefly of the 2748 lines, no trace of the equally strong lines 2573 and 2321 appearing on the photograph. Fourfold reflection from a surface of monobromnaphthalene showed the lines 2321 and 2288 only. Bisulphide of carbon, investigated by Flatow, showed a reflection maximum at 2310. This is a subject which requires further investigation, and the work already done should be repeated. In working with ultra-violet rays, we are completely in the dark, and the high dispersion of all transparent substances in this region means wide angular separation of the rays at any refracting surfaces used. Great care must be taken to make sure that the rays of all wave-lengths have a chance to reach the spectroscope. Quantitative measurements of the reflecting power for different wave-lengths should be made at the same time and the transmission of the thinnest possible films examined. If the substance is in contact with glass, quartz, or some other transparent substance, we may have a selective reflection resulting from the difference between the values of the refractive index. This will modify the color of the reflected light in any case. In many cases the color of the light reflected is totally different from that most strongly absorbed. For example, the surface color of cyanine is purple, and the absorption band is in the yellow. Its purple color is due to its failure to reflect a region of the spectrum bordering the absorption band on the green side, resulting from the very low value of the refractive index. In contact with glass, viewed from the glass side, it reflects yellowish green light. Nitroso-dimethyl aniline, which has an absorption band in the violet, exhibits a brilliant blue reflection when in contact with glass (from the glass side), but practically no trace of color from the surface in contact with air. Selective reflection of this nature is chiefly the result of the high value of the refractive index, and cannot be used as a method of locating the position of the absorption band. Such experiments show us the care we should use in interpreting results found in the ultra-violet, where effects due to refractive index may be even greater."

"Stibnite, or natural sulphide of antimony, is a substance which exhibits very remarkable optical properties. It has a metallic lustre resembling that of freshly cut lead, and is opaque to visible light. Nevertheless, as Coblentz has shown, it is extremely transparent to the infra-red radiations, a slab 0.4 mm in thickness transmitting 46 per cent of the energy out to 12 μ while one 4.9 mm thick allowed 43 per cent to pass. This shows us that the absorption is very nearly nil, and that the rest of the energy is reflected at the surface. The reflecting power of the substance is about 37 per cent, and results from the very high value of the refractive index, which is 5.53 for blue light and 4.69 for red, according to the calculations of E. C. Müller, made from observations of the constants of elliptical polarization. Measurements made by the author with a Michelson interferometer, and by observing Newton's rings, with a film of stibnite obtained by cathode deposition, give the value 3 for yellow light, the lower value doubtless resulting from a lightly spongy condition of the deposit, which exhibited a lower reflecting power than the cleavage surfaces of the mineral."

Rayleigh[1] has discussed the particular question of reflection by metals. "The peculiarity in the behavior of metals towards light is supposed by Cauchy to lie in their opacity, which has the effect of stopping a train of waves before they can proceed for more than a few wave-lengths within the medium. There can be little doubt that in this

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[1] Phil. Mag., [4], 43, 321 (1872).

Cauchy was perfectly right; for it has been found that bodies which, like many of the dyes, exercise a very intense selective absorption on light, reflect from their surfaces in excessive proportion just those rays to which they are most opaque. Permanganate of potash is a beautiful example of this, given by Professor Stokes. He found that when the light reflected from a crystal at the polarizing angle is examined through a Nicol held so as to extinguish the rays polarized in the plane of incidence, the residual light is green, and that, when analyzed by the prism, it shows bright bands just where the absorption spectrum shows dark ones. This very instructive experiment can be repeated with ease by using sunlight, and instead of a crystal a piece of ground glass sprinkled with a little of the powdered salt, which is then well rubbed in and burnished with a glass stopper or otherwise. It can without difficulty be so arranged that the two spectra are seen from the same slit one over the other, and compared with accuracy....

"That a sufficient opacity is as competent as a high optical density to produce an abundant reflection is evident without any analysis. So long as the medium into which the light seeks to penetrate remains nearly at rest, the greater part of the motion must be thrown back without any regard to the *cause* of the approximate acquiescence. Whether the sluggishness be due to a great inertia or a correspondingly great friction is in this respect of no importance. In order, however, to account for the reflection from silver (90 or 95 per cent) without opacity, a very high optical density would be required, much higher than we have any reason to think at all likely. On the other hand, we know that the opacity of metals to light is very great.

"In this connection it is interesting to note that some, and probably many, non-metallic substances possess a quasi-metallic reflecting power for dark radiation. De la Provostaye and Desains long ago remarked on the large percentage of dark heat reflected from glass, which was much in excess of that calculated from Fresnel's formulas with the known refractive index. The observation seems to have remained uninterpreted; but we cannot well be wrong in attributing the extra reflection to an opacity to the rays of dark heat, which, always great, rises somewhere in the spectrum to such a magnitude as to damp the entering rays within a few wavelengths of the surface. Nothing but direct experiment can inform us what substances are sufficiently opaque to exercise an abnormal reflection; for the stoppage of radiant heat by a plate of ordinary thickness may well be complete to sense, and yet not sufficiently sudden to give any material assistance in reflection. I am glad therefore to be able to refer to the experiments of the late Professor Magnus, in which he investigates the proportion of heat reflected by plates of various substances, the incident radiation being derived from moderately heated plates of the same or of a different material.

"First let us see what fraction of the incident radiation (unpolarized) would be reflected from the surface of a substance having a refractive index of 1.5—about that of glass. If Q be the angle of incidence, and I the corresponding fraction, I find by calculating from Fresnel's formula the following:

Q = 0°	Q = 33°	Q = 45°	Q = 62°
I = 0.040	I = 0.042	I = 0.050	I = 0.100

This is for one surface. If the plate be quite transparent the reflection may be nearly the double of the above. Now for glass at an angle of 45°. Magnus found no smaller value of I than 0.084; and as this must be attributed almost, if not entirely, to the first surface, it is clear that something not taken account of in Fresnel's theory must have come into operation. But by far the most remarkable result was with fluor-spar for the reflecting, and rock-salt for the radiating plate. The reflection at 33° was no less than 0.23, at 45° it was 0.242 and at 62° it was 0.335; and to this the second surface cannot contribute sensibly. Unquestionably, therefore, the reflecting power of fluor-spar for a certain kind of dark radiation is greatly in excess of what can be accounted for without an extreme opacity, a result which is the more remarkable because for dark radiation in general fluor-spar is one of the most transparent things known. The reflection from a plate of rock-salt was found to be much the same as from glass; but here, I presume, we may consider both surfaces to be operative, in which case the result is normal.[1] It is curious that opacity first diminishes the reflection from a plate, and then, when extreme, increases it again and that without limit."

Wood[2] also discusses the question of metallic reflection. "While metals possess in general a high reflecting power, a considerable portion of the incident energy penetrates the surface and is absorbed. In the case of steel, for example, nearly one-half of the light is lost by absorption, while even silver absorbs 5 per cent. In the majority of cases the absorption is general, that is, it is not confined to a narrow range of wave-lengths, as is the case with the substances which we have examined thus far. It is to a certain extent selective, however, as is best illustrated by gold-leaf, which appears green by transmitted light, and thin films of chemically deposited silver, which appear blue. These silver films are fairly transparent to a limited range of ultra-violet radiations, which lie just beyond the limit of the visible spectrum. It is probable that the absorption of metals is due to the presence of two types of electrons—conducting ones which are free to move indefinitely under the influence of a steady electric force, and non-conducting ones which are similar to those which we have considered."

"The laws which govern the optical behavior of metals are very different from those which hold in the case of transparent substances and substances showing strong selective absorption. Metals exhibit in general a very high reflecting power, and in some cases, also a powerful absorbing action. We must distinguish carefully between absorption and reflection. If we examine a thin film of silver deposited on glass, we find that it transmits little or no light, and we might there-

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[1] According to the experiments of Masson and Jamin, the transmission of a perfectly transparent plate is always about 92 per cent, whether the material be glass, rock-salt, or alum. This is in agreement with the calculation in the text, as about 8 per cent would be reflected.

[2] "Physical Optics," 449, 456 (1911).

fore come to the conclusion that the metal absorbs strongly. A little further investigation will show, however, that over 90 per cent of the light has been reflected, the remaining 10 per cent having been absorbed. Platinum, however, has a much lower reflecting power, combined with equally great opacity; consequently we may regard platinum as possessing a stronger absorbing power than silver. Gold is, however, as compared to silver and platinum, extremely transparent, ordinary gold-leaf transmitting no inconsiderable amount of green light.

"While metallic absorption is not in general characterized by such marked selective action as is the case with the colored media which we have studied, the phenomenon of selective absorption is by no means absent, as the strong coloration of the light transmitted by gold-leaf proves: silver, too, while it appears to favor equally all wave-lengths in the visible spectrum, is fairly transparent to ultra-violet radiation comprised within the range 0.305–0.320: its reflecting power is correspondingly low for these same wave-lengths.

"The colors which metals exhibit are due to a selective reflecting power, which is especially marked in the case of gold and copper. If two gilded glass plates are mounted in parallel at a distance of a centimeter or so, with the reflecting surfaces opposed, and a beam of light caused to travel back and forth between them, suffering a number of reflections, the surface color is still more marked, the filament of an incandescent appearing as red as if seen through ruby glass. This method of bringing out the surface color is analogous to the method of Rubens and Nichols for isolating long heat waves by multiple reflections from surfaces of quartz and rock-salt. The same phenomenon can be seen in less marked degree by looking into the interior of a gilded goblet, the bottom of which appears of a fairly deep-red color. Glass plates can be easily gilded by exposing them to the discharge from a gold cathode in a vacuum tube; plates gilded by the application of gold-leaf, in the manner employed for lettering on windows, would doubtless answer as well, and can be readily obtained from a sign-painter.

"The phenomenon of elliptical polarization is exhibited in a high degree when light polarized in an azimuth of 45° is reflected obliquely from a metal surface. In the case of transparent substances, we have seen that this result can occur if the surface is contaminated with a film, but in the case of metallic reflection the presence of a surface film is not necessary."

The ratio of the intensity of the reflected light to that of the incident light at normal incidence is called the coefficient of reflection, R. For metals we have the equation

$$R = \frac{n^2(1 + k^2) + 1 - 2n}{n^2(1 + k^2) + 1 + 2n}$$

where k is the extinction coefficient.[1] In the case of metals $2n$ is small in comparison to $n^2(1 + k^2)$. If we neglect it, we get $R = 1$. In the case of silver 95 per cent of the incident light is reflected, *i. e.*, $R = 0.95$. The reflecting power will be greatest for the wave-lengths for which k has its greatest value; thus gold reflects red light much more powerfully than green. The best determinations of the reflecting power of different metals are those made by Rubens and Hagen.[2]

It is apparent from their results that the reflecting power of silver in contact with glass is somewhat less than that of silver in contact with air. The same is true for mercury.

"An easy way of exhibiting the loss of light by reflection from a metal is to half fill a test-tube with mercury and plunge it in a jar of clean water; the light reflected from the metal will appear quite dull in comparison with the light totally reflected at the glass-air surface.

"The values of R calculated from observations by katoptric methods (yellow light) were found in rough agreement with the values observed by Rubens. In the case of silver

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[1] Wood: "Physical Optics," 465, 440, 439 (1911).

[2] Drude's Ann., 1, 352 (1900); 8, 1 (1902).

the minimum at $\lambda = 316$ is very remarkable, the reflecting power of the metal for this wave-length being about that of glass for yellow light. The highest reflecting power appears to be possessed by metallic sodium, for which R = 99.7 according to Drude. This value was calculated, however.

"The most recent investigations of the reflecting and absorbing power of metals has been made by Hagen and Rubens. The films were deposited upon quartz plates, which permitted of investigations in the ultra-violet region, and their thickness determined by two different methods, weighing the film both before and after its conversion into the iodide and the interference method of Wernicke. They first investigated the dependence of reflecting power upon the thickness. From the data for gold we see that the reflecting power increases with the thickness, reaching its maximum value at about 80 $\mu\mu$ or 0.00008 mm, which is about one-eighth of the wave-length of red light, after which it remains constant. For red light this maximum value is 90 per cent; for green light it is less than 50 per cent. This explains the yellow color of gold and the green color of gold-leaf by transmitted light. In the ultra-violet it is necessary to use somewhat thicker films to get the full value of the reflecting power."

"In the case of absorbing media, the reflecting power depends both upon the refractive index and the coefficient of absorption. Now, absorbing media have a high refractive index on the red side of the absorption band and a low index on the blue side, consequently the spectrum of the reflected light will be brightest on the red side of the absorption band, since for these wave-lengths we have a large coefficient of absorption and a high refractive index. On the blue side, however, the low value of the index diminishes the reflecting power more than the augmentation due to the powerful absorption. The hue of the surface color thus depends on the refractive index of the medium in which the substance is immersed, for it is the relative and not the absolute refractive index in which we are concerned. Cyanine in contact with glass exhibits a yellowish green surface color, much more nearly resembling the hue of the absorbed light. If the dye could be brought in contact with a transparent substance having the same dispersion, the wave-lengths selectively reflected would be identical with those absorbed, since in this case the relative refractive index would be unity for all wave-lengths.

"An excellent way of showing the variable reflecting power of a film of cyanine is to compare it with glass in different parts of the spectrum. A little of the melted dye is pressed between two plates of hot glass, which are separated when cold. A spot is selected where the film has a good optical surface, and this spot is left on the glass, the rest being cleaned off. By holding the plate in the spectrum formed by a prism or grating, the reflecting power of the two surfaces can be studied. In some parts of the spectrum the cyanine reflects more strongly than glass; in other regions the reverse is true, while at wave-length 0.0005 the cyanine refused to reflect to such a degree that the film appears as a black spot on the blue field reflected by the glass.

"It is interesting to note the difference in the surface color of the dye when the reflection takes place at the surface in contact with the glass. A very convenient way of showing the yellowish green color in this case is to press out a film of the molten dye on one surface of a prism of 8 or 10 degrees angle.[1] In this way the light reflected from the dye can be obtained uncontaminated with the light reflected from the glass surface. The method is analogous to that employed by Lippmann in mounting his color photographs. The calculation of the curve of reflected intensities under these conditions makes a good exercise for the student."

"The colors of most natural objects result from absorption. The light penetrates their surfaces and then suffers internal

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[1] A suitable prism can be made in half an hour by grinding down a piece of thick plate window glass. A strip of thick glass cemented along one edge will be all that is necessary to make the glass take the required form. Grind on a piece of glass with a very coarse emery at first, then use finer grades, polishing with rouge at the end. Small scratches do no harm, and a high polish is not necessary.

reflections or refractions and emerges robbed of the rays which are most strongly absorbed. If this is to happen, it is clear that the substance must not be homogeneous, otherwise the reflections and refractions, which return the unabsorbed light, will not occur. It is thus incorrect to say that colored pigments reflect certain colors more strongly than others. If the pigment particles formed a continuous and homogeneous medium, no color whatever would appear in the reflected light, which would be white. If any color appeared, as it might if the pigments were a very powerful absorbent, it would be the tint complementary to the one exhibited by the powder.

"Since pigments produce color by absorption, it is at once apparent why a mixture of two pigments does not exhibit the color which we should obtain if we actually mixed the colored lights which they appear to reflect. The light reflected from the mixture is the residual color which remains after the dual absorption has taken place. For example, if we mix yellow light and blue light, we get white, while a mixture of a blue and yellow pigment appears green. The reason of this is, that the yellow pigment absorbs the blue and violet, the blue pigment the red and yellow, the mixture absorbing everything except the green."

Von Bezold[1] has called attention to the difference between colored substances which show selective absorption only and those which show selective reflection also. "Only in certain types of substances is the color due to absorption. There are other substances in which certain rays penetrate and certain others are reflected. Such substances have different colors in reflected and in transmitted light. The light which is reflected at the surface is colored and these substances are therefore said to have surface colors. The metals are typical of these substances. Very thin goldleaf is a beautiful blue-green by transmitted light, and very thin films of silver, such as one gets when making mirrors,

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[1] "Die Farbenlehre," 72 (1874).

are deep blue, while the mirror image of a white substance as seen on a golden surface is yellow, and orange-yellow after many reflections, while the image from a silver mirror is yellowish white. Many aniline colors show similar surface colors in the dry state. If one lets a small amount of a solution of one of these colors dry on a glass plate, the film appears completely metallic. For instance, magneta is a greenish gold color by reflected light and purple-red by transmitted light. Of the pigments used in painting very few show these colors and only to a slight extent. In a solid stick, indigo shows a slight trace of copper red and so does Prussian blue, though to a lesser extent."

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POTASSIUM AMMONOSODIATE, POTASSIUM AMMONOLITHIATE, RUBIDIUM AMMONOSODIATE AND RUBIDIUM AMMONOLITHIATE

BY EDWARD C. FRANKLIN

Introduction

It will be recalled that F. F. Fitzgerald was able to prepare an ammonozincate of potassium[1] by means of reactions taking place in liquid ammonia which are analogous to those which, in aqueous solution, result in the formation of aquozincate of potassium.[2] Fitzgerald found that just as an aqueous solution of potassium hydroxide dissolves zinc hydroxide or metallic zinc to form the aquozincate in accordance with the equations[3]

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O,$$
$$Zn + 2KOH = Zn(OK)_2 + H_2,$$

so potassium amide, the potash of the ammonia system, acts upon the amphoteric zinc amide and upon metallic zinc to form an ammonozincate of potassium as represented by the equations

$$Zn(NH_2)_2{}^4 + 2KNH_2 = Zn(NHK)_2 + 2NH_3,$$
$$Zn + 2KNH_2 = Zn(NHK)_2 + H_2.$$

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[1] Jour. Am. Chem. Soc., **29**, 56, 1274 (1907).

[2] Potassium zincate belongs to a water system of acids, bases and salts and is here referred to as the aquozincate in order to distinguish it from the ammonozincate, a similar salt of the ammonia system. For a detailed exposition of the ammonia system of acids, bases and salts, cf. Am. Chem. Jour., **47**, 285 (1912).

[3] Among the phenomena with which the student of chemistry early becomes familiar is the solubility of zinc hydroxide in solutions of potassium hydroxide and he soon learns to write confidently the first of the equations as representing the reaction which takes place, notwithstanding the fact that, apparently, a zincate of potassium has never been isolated. [Cf. Comey and Jackson: Am. Chem. Jour., **11**, 145 (1889); Förster and Günther: Zeit. Elektrochemie **6**, 301 (1900); Hantzsch: Zeit. anorg. Chem., **30**, 289 (1903); Wood: Jour. Chem. Soc., **97**, 878 (1910).]

[4] Zinc amide is to be looked upon as a tetrabasic acid which might be expected to react with potassium amide to form a mono-, di-, tri-, or tetra-potassium salt, though the likelihood that all the hydrogen in a weak polybasic acid,

The former reactions taking place in water solution and the latter in liquid ammonia are obviously strictly analogous. In the one case a weak aquo acid, zinc hydroxide, acts upon an aquo base to form an aquo salt; in the other, an ammono salt is formed by the action of an ammono acid on an ammono base.

The existence of an ammonia analog of aquozincate of potassium thus established it seemed almost a matter of course that an ammonoaluminate and an ammonoplumbite of potassium should be capable of existence, more especially in view of the fact that the precipitates formed by the action of potassium amide on liquid ammonia solutions of salts of aluminium and lead were found to be readily soluble on excess of the precipitant.

As was expected, the solution obtained by dissolving lead imide in a liquid ammonia solution of potassium amide was found to contain an ammonoplumbite of potassium. The compound,[1] formed in accordance with the equation

$$PbNH + KNH_2 = PbNK + NH_3,$$

separates from concentrated solution in the form of beautiful crystals of sharply definite composition, a behavior which is

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such as zinc amide must be assumed to be, could be replaced by potassium in the presence of ammonia is of course remote.

Fitzgerald obtained a beautifully crystallized dipotassium salt of the empirical composition $ZnN_4H_8K_2$, which may be formulated as an ammoniated dipotassium salt as represented by the formula $Zn(NHK)_2.2NH_3$, or it may be looked upon as a "molecular compound" of zinc amide and potassium amide and given the formula $Zn(NH_2).2KNH_2$. According to Werner (Neu. Anschau. Geb. anorg. Chem. 3te. Aufl., 123 (1913)) the formation of salts by the action of potassium hydroxide on the hydroxides of tin (stannic), lead zinc, aluminium, platinum, gold, etc., does not consist in the substitution of acid·hydrogen by the alkali metal but in the direct union (Anlagerung) of the basic hydroxide with the central atom of the heavy metal hydroxide as represented by the formula $[Zn(OH)_3]Na.2H_2O$ for the compound obtained by Comey and Jackson and by Förster and Günther from solutions of zinc hydroxide in aqueous sodium hydroxide. Such compounds Werner calls hydroxo salts. Analogously our potassium ammonozincate is an amido salt and, according to Werner, should be given the formula $[Zn(NH_2)_4]K_2$. Potassium ammonozincate loses ammonia on being heated but a well-defined deammonation product has not been obtained.

[1] Jour. Phys. Chem., 15, 509 (1911).

in marked contrast with water solutions of the aquo plumbite.[1]

The ammonia analog of aquoaluminate of potassium is undoubtedly formed when potassium amide is added in excess to a liquid ammonia solution of aluminium iodide but attempts to isolate the salt have been unsuccessful.[2]

Although strictly analogous compounds, the behavior of the aquozincate and aquo plumbite of potassium on the one hand, and the corresponding ammono salts on the other, towards the respective solvents, water and ammonia, is in striking contrast. The ammono salts are easily obtained pure in the form of beautiful crystals which show no apparent tendency to undergo ammonolysis in contact with liquid ammonia, whereas the aquo salts are highly hydrolyzed in aqueous solution even in the presence of a large excess of potassium hydroxide, and are isolable with difficulty or not at all.

In explanation of this striking difference in behavior it seems reasonable to assume that the ammonolyzing power of liquid ammonia is comparatively weak compared with the hydrolyzing power of water, an assumption which is supported by the fact that pure liquid ammonia is a very much poorer conductor of electricity[3] than is pure water. It follows, therefore, as a result of the very low concentration of amide ions in liquid ammonia as compared with the concentration of hydroxyl ions in water, that acids entirely too weak to form stable salts, even with strong bases, in water solution will, in liquid ammonia solution, form salts which undergo but slight ammonolysis.

Such considerations as these, together with the very satisfactory outcome of the work described above and with early observations showing that salts of a number of metals, such as silver, copper and thallium, in solution in liquid ammonia, when treated with potassium amide, give precipitates

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[1] Potassium plumbite is unknown except as it exists in the solution formed by dissolving lead hydroxide in potassium hydroxide.

[2] Jour. Am. Chem. Soc., 27, 849 (1905); 37, 847 (1915).

[3] Cf. Ibid., 27, 191 (1905).

which dissolve on adding the precipitant in excess led to a series of investigations planned to determine the extent to which the formation of salts by the action of potassium amide on the amides, imides and nitrides of other metals might be carried. The result of these investigations has been to show that a large number of metallic amides, including those of such strongly positive metals as magnesium, barium, strontium and calcium, react with potassium amide just as zinc amide does to form compounds which must be looked upon as salts in which these metals play the same part as zinc, lead and aluminium do in the compounds formed by the action of potassium hydroxide on the hydroxides of these metals.[1]

It will be shown below that the formation of this class of salts does not stop with the amides of the alkaline earth metals but extends even to the amides of sodium and lithium. These latter amides acting as ammono acids react with the strongly basic amides of potassium and rubidium to form salts which, it would seem, are properly designated by the names potassium ammonosodiate, potassium ammonolithiate, rubidium ammonosodiate and rubidium ammonolithiate.

A list of the compounds which have been prepared is given in the table which follows. Each compound is formulated first as an ammono salt of potassium containing "ammonia

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[1] It has probably frequently been assumed that the well-known solubility of many metallic oxides in fused potassium hydroxide is accompanied by salt formation. Certainly the existence of the list of ammono salts tabulated below lends considerable support to the view that in these fusions the aquo analogs of our ammono salts are present.

Some observations on the solubility of metallic oxides in fused potassium hydroxide gave the following results:

The oxides of barium, strontium, calcium, magnesium, zinc, cadmium, mercury, and silver dissolve to clear, colorless solutions. Metallic magnesium and calcium dissolve in fused potassium hydroxide with vigorous evolution of hydrogen. Cupric oxide gives a solution blue at lower temperatures and brown at higher. Nickel oxide gives a purple solution which changes to brown at high temperatures. Ferric oxide gives a purple solution when dilute, more concentrated solutions are very dark. Bismuth oxide dissolves abundantly to form a deep orange-colored solution. Metallic platinum gives a clear, yellow solution. Palladium dissolves from the palladium gold alloy known as "palau" to form a green solution, leaving the interior of the crucible yellow from exposed gold.

of crystallization." A second formulation is given the majority of them in accordance with which they are represented as "molecular compounds" of potassium amide with the acid or less basic amide. Finally, in so far as practicable, they are given formulas as amido salts, that is, as salts related to ammonia as Werner's hydroxo salts are related to water.

Potassium ammonostannate,[1]		
$Sn(NK)_2.4NH_3$	$Sn(NH)_2.2KNH_2$	$[Sn(NH_2)_6]K_2$
$Sn(NK)_2.NH_3$		
Potassium ammonozincate,[2]		
$Zn(NHK)_2.2NH_3$	$Zn(NH_2)_2.2KNH_2$	$[Zn(NH_2)_4]K_2$
Potassium ammonoplumbite,[3]		
$PbNK.2{}^1/_2NH_3$		
$PbNK.2NH_3$	$Pb(NH_2).KNH_2$	$[Pb(NH_2)_3]K$
$PbNK.NH_3$		
Potassium ammonothallite,[4]		
$TlNK_2.4NH_3$		
$TlNK_2.2NH_3$	$TlNH_2.2KNH_2$	$[Tl(NH_2)_3]K_2$
$TlNK_2.1{}^1/_3NH_3$	$Tl_3N.6KNH_2$	
Potassium ammonocuprite,[5]		
$CuNK_2.3NH_3$		
$CuNK_2.2NH_3$	$Cu(NH_2).2KNH_2$	$[Cu(NH_2)_3]K_2$
$CuNK_2.NH_3$		
Potassium ammonoargentate,[6]		
$AgNHK.NH_3$	$AgNH_2.KNH_2$	$[Ag(NH_2)_2]K$
Potassium ammononickelate,[7]		
$K_2N\text{-}Ni\text{-}NK\text{-}Ni\text{-}NK_2.\text{-}6NH_2$	$2Ni(NH_2)_2.5KNH_2$	
Potassium ammonocadmiate,[8]		
$Cd(NHK)_2.2NH_3$	$Cd(NH_2)_2.2KNH_2$	$[Cd(NH_2)_4]K_2$
Potassium ammonotitanate,[9]		
NTiNHK		

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[1] Jour. Am. Chem. Soc., 29, 1693 (1907).
[2] Ibid., 29, 660, 1274 (1907).
[3] Ibid., 27, 842 (1905); Jour. Phys. Chem., 15, 509 (1911).
[4] Jour. Phys. Chem., 16, 682 (1912).
[5] Jour. Am. Chem. Soc., 34, 1501 (1912).
[6] Ibid., 37, 852 (1915).
[7] Jour. Phys. Chem., 19, 559 (1915).
[8] Ibid., 19, 542 (1915).
[9] Jour. Am. Chem. Soc., 34, 1497 (1912).

Potassium ammonobariate,[1]		
$BaNK.2NH_3$	$Ba(NH_2)_2.KNH_2$	$[Ba(NH_2)_3]K$
Potassium ammonostrontiate,[1]		
$SrNK.2NH_3$	$Sr(NH_2)_2.KNH_2$	$[Sr(NH_2)_3]K$
Potassium ammonocalciate,[1]		
$CaNK.2NH_3$	$Ca(NH_2)_2.KNH_2$	$[Ca(NH_2)_3]K$
Potassium ammonosodiate,		
$NaNK_2.2NH_3$	$NaNH_2.2KNH_2$	$[Na(NH_2)_3]K_2$
Potassium ammonolithiate,		
$LiNK_2.2NH_3$	$LiNH_2.2KNH_2$	$[Li(NH_2)_3]K_2$
Rubidium ammonosodiate,		
$NaNHRb.NH_3$	$NaNH_2.RbNH_2$	$[Na(NH_2)_2]Rb$
$NaNRb_2.2NH_3$	$NaNH_2.2RbNH_2$	$[Na(NH_2)_3]Rb_2$
Rubidium ammonolithiate,		
$LiNHRb.NH_3$	$LiNH_2.RbNH_2$	$[Li(NH_2)_2]Rb$

Experimental

In the pages following is given a description of the manipulative details together with the analytical data which establish the existence of the four salts named in the title of this paper.

The reader is reminded that the reactions involved in the preparation of these salts are carried out in liquid ammonia solutions and entirely out of contact with air and water.

Di-Potassium Ammonosodiate, $NaNK_2.2NH_3$, *or* $NaNH_2.2KNH_2$ or $(Na(NH_2)_3)K_2$.—Experiments described in detail below show that this compound is formed by the action of potassium amide in solution in liquid ammonia on sodium amide;[2] by the addition of a soluble salt of sodium, such as sodium iodide, to an excess of potassium amide in solution in liquid ammonia; and by allowing a solution containing metallic sodium and potassium amide, the latter in large excess, to stand in contact with a small quantity of platinum black.

The reaction which takes place between potassium amide and sodium amide may be explained as resulting in the formation of a simple addition product in accordance with the equation

$$NaNH_2 + 2KNH_2 = NaNH_2.2KNH_2,$$

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[1] Jour. Am. Chem. Soc., 37, 2295 (1915).

[2] Sodium amide is very slightly soluble in liquid ammonia.

or it may be interpreted as the interaction of an acid and a base to form a salt as represented by the equation

$$2KNH_2 + NaNH_2 = NaNK_2 + 2NH_3.$$

The salt formed separates from solution with two molecules of ammonia of crystallization.

When solutions of potassium amide and sodium iodide are brought together in equivalent amounts, or when the latter is in excess, a crystalline precipitate of sodium amide is formed in accordance with the equation

$$NaI + KNH_2 = NaNH_2 + KI.$$

An equivalent of sodium iodide is mixed with an amount of potassium amide greater than one and less than three equivalents gives a precipitate which is a mixture of sodium amide and potassium ammonosodiate, while one equivalent of the salt added carefully to three or more equivalents of potassium amide results in the formation of pure potassium ammonosodiate. By the careful addition of sodium iodide to an excess of potassium amide the salt may be obtained in the form of beautifully developed crystals.

When a liquid ammonia solution containing metallic sodium and a large excess of potassium amide is allowed to stand in contact with a small quantity of platinum black the metallic sodium is rapidly converted into sodium amide which, instead of crystallizing out as such, reacts with the potassium amide to form the potassium salt of sodium amide.

The salt does not lose ammonia at 100° in vacuum. At higher temperatures it melts, loses ammonia and attacks the glass container, for which reason attempts have not been made to obtain definite deammonation products. The compound is decomposed by liquid ammonia solutions of acids with the formation of salts of sodium and potassium. For example, the action of ammonium nitrate[1] is represented by the equation

$$NaNK_2.2NH_3 + 3NH_4NO_3 = NaNO_3 + 2KNO_3 + 6NH_3.$$

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[1] Ammonium salts in liquid ammonia solution show the characteristic properties of acids.

It is vigorously attacked by water giving as hydrolytic products the hydroxides of sodium and potassium and ammonia.

Preparatory to analysis the compound is decomposed in vacuum by the action of water vapor, after which the hydrolytic products are dissolved in water and converted into chlorides by the addition of a slight excess of hydrochloric acid. The analytical procedure from this stage is the simple one of determining potassium, sodium, and ammonia in an aqueous solution containing potassium, sodium and ammonium chlorides. A description of this procedure is unnecessary.

Preparation I.—A liquid ammonia solution of potassium amide in large excess was poured from one leg of a reaction tube[1] upon pure sodium amide, prepared from about 150 milligrams of metallic sodium, in the other. Mere standing of the potassium amide solution in contact with the very slightly soluble sodium amide would undoubtedly, in the course of time, result in the complete conversion of the latter into potassium ammonosodiate. However, in the absence of any adequate evidence of complete reaction, it seemed advisable to recrystallize the product, a process which, because of the slight solubility of the salt, turned out to be a rather tedious task. Recrystallization was accomplished as follows: The solution containing the excess of potassium amide and saturated with the reaction product was poured into the second leg of the reaction tube and the tube was then so disposed, with the one leg immersed in tepid water and the other in an ice bath, that the ammonia from the solution was distilled back upon the reaction product. After boiling away the greater portion of the solvent a promising quantity of well-formed crystals had separated. The mother liquor was then poured over into the leg containing the distillate and the original reaction product. After saturating with the latter the solution was again transferred to the second leg of the reaction tube and again evaporated. A second portion of the pure compound was thus added to the first small crop of crystals. The operations thus described were repeated un-

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[1] These tubes have been described in earlier papers cited above.

til the whole of the reaction product was transferred to the second leg of the apparatus. The preparation, consisting of well-formed crystals, was washed several times with small quantities of solvent and dried in vacuum at 20° preparatory to analysis.

One-fourth of the specimen which weighed 0.9152 g gave 0.5595 g mixed KCl-$NaCl$-NH_4Cl, 0.3176 g mixed KCl-$NaCl$ and 0.7508 g K_2PtCl_6. Another fourth gave 0.0650 g N.

Preparation II.—This experiment was in all essential respects a repetition of the preceding. A crop of beautiful crystals was obtained. One-fourth of the specimen which weighed 0.5929 g gave 0.3661 g mixed KCl-$NaCl$-NH_4Cl, 0.2078 g mixed KCl-$NaCl$ and 0.4912 g K_2PtCl_6. Another fourth gave 0.0406 g N.

Preparation III.—A liquid ammonia solution of sodium iodide, contained in one leg of a reaction tube, was added very slowly to a solution of approximately four equivalents of potassium amide contained in the second leg. Early in this procedure crystals began to separate on the walls and bottom of the tube. With the exercise of care in mixing the solutions a crop of beautiful crystals was obtained which was washed several times with small quantities of liquid ammonia and dried in vacuum at 20° for analysis. The specimen weighed 0.1667 g. One-half gave 0.2052 g mixed KCl-$NaCl$-NH_4Cl and 0.1157 g mixed KCl-$NaCl$.[1] A test made of the other half of this preparation showed it to be free from iodine.

Preparation IV.—A second experiment conducted as above described gave an even more beautiful specimen of the salt which, dried in vacuum at 20°, weighed 0.2254 g. One-half gave 0.1560 g mixed KCl-$NaCl$,[1] the other half gave 0.0320 g N.

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[1] To establish the composition of the compound formed in this and the preceding experiment it was not deemed necessary to separate the potassium from the mixed chlorides as potassium chlorplatinate. Dependence was placed upon the determinations of the nitrogen content and the weight of the mixed potassium sodium chlorides.

In a further experiment a solution of potassium amide was run carefully into an excess of sodium iodide in solution in liquid ammonia in order to determine whether sodium amide is formed under these conditions. A crystalline precipitate was formed which analysis showed to consist of pure sodium amide. The analytical data are not given for the reason that sodium amide is a known compound.

The composition of potassium ammonosodiate calculated from the above given analytical data follows:

	Calculated for $NaNK_2.2NH_3$	Found			
		I	II	III	IV
K	52.3	52.7	53.2	....	....
Na	15.4	15.0	15.1	....	....
N	28.8	27.7–28.4	27.4–28.1	28.1	28.4
KCl-NaCl	139.1	138.8	140.0	138.8	138.8

Mono-Rubidium Ammonosodiate. $NaNHRb.NH_3$, $NaNH_2.RbNH_2$ *or* $[Na(NH_2)_2]Rb$.—With the existence of an ammonosodiate of potassium established one may assume almost as a matter of course, that a similar compound of rubidium would be formed by treating sodium amide with a liquid ammonia solution of rubidium amide. Experiments described below show that certainly one, and probably two, definite compounds may be so prepared. The compound whose existence has been definitely established differs from the potassium salt in that the latter contains two equivalents of potassium to each equivalent of sodium, whereas in the former the rubidium and sodium are present in equivalent quantities. The second compound whose existence is less certain corresponds in composition to that of potassium ammonosodiate. If it is legitimate to look upon the action between sodium amide and rubidium amide as that of an acid on a base, and it has been shown earlier in this paper that such a view is a reasonable one, then, since sodium amide or ammono sodic acid is a di-basic acid it should be capable of forming two salts by interaction with rubidium amide which is a monacid base. The one may be called acid or mono-rubidium ammonosodiate, the other normal or di-rubidium ammonosodiate. Both these salts are readily soluble in liquid ammonia. The di-rubidium salt is apparently incapable of existence in solution excepting in the presence of a large excess of rubidium amide. They are acted on violently by water giving as hydrolytic products rubidium and sodium hydroxides and ammonia and are decomposed by acids in ammonia solution just as is the corresponding potassium salt.

Preparation I.—Into the two legs of the familiar reaction tube were introduced, respectively, 93 milligrams of metallic sodium and 800 milligrams of metallic rubidium, each with a minute portion of platinum black which, it will be remembered, very greatly accelerates the conversion of the metals into the amides. When the solution of the readily soluble rubidium amide was poured into the leg containing the very slightly soluble amide of sodium the latter was found to dissolve much more readily than it does in a solution of potassium amide. By slowly evaporating the solvent from the concentrated solution a crop of beautiful crystals was obtained which was dissolved in fresh solvent and the solution thus obtained again evaporated to crystallization. The crop of crystals obtained was drained of mother liquor and washed several times with small quantities of solvent to insure its purity. The salt was dried in vacuum at 50°, hydrolyzed by exposure to water vapor and converted into a mixture of rubidium chloride, sodium chloride and ammonium chloride for analysis. The specimen weighed 0.1684 g. Two-fifths gave 0.0131 g N. Three-fifths gave 0.1289 g mixed RbCl-NaCl and 0.2059 g Rb_2PtCl_6.

Preparation II.—The mother liquor from the preceding experiment was transferred[1] to a new reaction tube in which it was evaporated to crystallization. The crop of crystals was washed three times with small portions of pure solvent

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[1] A description of the manner in which such transfers are made has been described in another place. Jour. Am. Chem. Soc., 36, 1460 (1915).

preparatory to analysis. Dried in vacuum at 20° the specimen weighed 0.1284 g. One-fifth gave 0.00508 g N. Four-fifths gave 0.2097 g mixed RbCl-NaCl-NH_4Cl, 0.1316 g mixed RbCl-NaCl and 0.2116 g Rb_2PtCl_6.

Preparation III.—A repetition of the procedure described above for making Preparation I, in which 40 milligrams of metallic sodium and 400 milligrams of metallic rubidium were used, gave a product which dried at 20° in vacuum weighed 0.1419 g. One-half gave 0.1446 g mixed RbCl-NaCl-NH_4Cl, 0.0907 g mixed RbCl-NaCl and 0.1457 g Rb_2PtCl_6 and 0.0353 g Na_2SO_4.

Preparation IV.—In the preceding experiments, excepting the first, the solutions worked with contained a large excess of rubidium amide. For certain reasons it seemed desirable to undertake the preparation of a specimen of the salt from a solution containing approximately equivalent quantities of the amides. Accordingly a solution of slightly more than one equivalent of rubidium amide was poured upon the sodium amide formed from 122 milligrams metallic sodium. The sodium amide dissolved readily and completely. On cooling the concentrated solution a good crop of crystals was obtained which, when washed and dried, that is, freed from solvent in vacuum at 20°, weighed 0.2409 g. Three-fifths gave 0.2930 g mixed RbCl-NaCl-NH_4Cl and 0.1845 g RbCl-NaCl.

Preparation V.—The mother liquor from the preceding preparation was concentrated and cooled to —33°. The crop of crystals formed was dissolved in pure solvent and the solution thus obtained evaporated to crystallization. The new crop was again dissolved and recrystallized and the final product thus obtained was washed with pure solvent and dried for analysis. The beautiful specimen weighed 0.2244 g. Two-fifths gave 0.01755 g N. Three-fifths gave 0.2718 g mixed RbCl-NaCl-NH_4Cl and 0.1716 g mixed RbCl-NaCl. In neither this nor the preceding experiment was it considered necessary to separate the sodium and rubidium in order to establish the composition of the compound.

The percentage composition of mono-rubidium ammonosodiate calculated from data given above follows:

	Calculated for $NaNHRb.NH_3$	Found				
		I	II	III	IV	V
Na	16.4	16.6	16.5	16.7–16.1	...	...
Rb	60.8	60.3	60.8	60.7	...	...
N	19.9	19.5	19.8–19.9	19.9	19.7	19.5–19.5
RbCl-NaCl	127.7	127.5	128.0	127.9	127.6	127.6

Di-Rubidium Ammonosodiate, $NaNRb_2.2NH_3$ or $NaNH_2.2RbNH_2$ or $[Na(NH_2)_3]Rb_2$

The mother liquors from preparations 2 and 3 which contained a very large excess of rubidium amide were transferred to a reaction tube and evaporated to crystallization at a low temperature with the object in view of determining whether under these conditions a di-rubidium salt might be formed. The crystals were distinctly different in appearance from those of the mono-rubidium salt and they seemed to be distinctly more soluble. The product was not recrystallized but was simply drained of the concentrated mother liquor and washed twice with small quantities of the pure solvent. The specimen dried in vacuum at 20° weighed 0.4716 g. One-fifth gave 0.01555 g N. Another fifth gave 0.01563 g N. Three-fifths gave 0.5270 g mixed $RbCl$-$NaCl$-NH_4Cl, 0.3474 g mixed $RbCl$-$NaCl$ and 0.6807 g Rb_2PtCl_6.

Calculated for	Na	Rb	N
$NaNRb_2.2NH_3$	9.5	70.7	17.3
Found	8.7	71.1	16.6–16.6

It should perhaps be said that the evidence for the existence of the di-rubidium salt is not entirely conclusive. The exhaustion of the supply of metallic rubidium prevented a repetition of this experiment.

Di-Potassium Ammonolithiate, $LiNK_2.2NH_3$, $LiNH_2 2.KNH_2$ or $[Li(NH_2)_3]K_2$

Because of the very slight solubility of potassium ammonolithiate several attempts to prepare the salt by the action of liquid ammonia solutions of potassium amide on lithium amide led to unsatisfactory results. The attempt was first made to obtain a specimen of the salt by transferring successive small portions to the second leg of the reaction tube in the manner described above for the first preparation of potassium ammonosodiate. The salt was found to be insufficiently soluble to make this procedure practicable. It was then decided to allow the solution of potassium amide to stand in contact with the practically insoluble lithium amide for several days, with occasional shaking, in the hope that thus the conversion of the latter into potassium ammonolithiate might be completed. The result, however, was unsatisfactory, for analyses of two specimens made in this manner showed them to be mixed with considerable amounts of lithium amide. Following these unsuccessful attempts to prepare specimens of potassium ammonolithiate the pure compound was obtained by the action of potassium amide on lithium iodide and also by allowing a mixed solution of the two metals in liquid ammonia to stand in the presence of platinum black.

The salt was obtained in the form of minute colorless crystals by the first method, slightly grayish by the second from the presence of platinum black. It is practically insoluble in liquid ammonia. Acids, that is, acid amides and ammonium salts of oxygen and halogen acids, decompose it with the formation of the corresponding salts of lithium, potassium and ammonium. It is energetically acted upon by water giving as hydrolytic products lithium and potassium hydroxides and ammonia. For the determination of the composition of the salt a weighed specimen was hydrolyzed in vacuum by water vapor. The potassium and lithium hydroxides and ammonia formed were dissolved in an excess of dilute hydrochloric and the aqueous solution of mixed chlorides analyzed by the well-known methods.

Preparation I.—A dilute solution of lithium iodide formed by the action of a liquid ammonia solution of ammonium iodide on metallic lithium was added in successive small portions to a large excess of potassium amide solution. After the addition of each portion of iodide it was thoroughly mixed with the concentrated solution of potassium amide before adding the next portion, thus avoiding the formation of lithium amide, which, once precipitated, is slowly converted into the double amide.

The crystalline precipitate obtained was washed well with pure solvent and dried in vacuum at 20°. The specimen weighed 0.2080 g. Three-tenths gave 0.0191 g N, one-half gave 0.1486 g mixed KCl-LiCl, 0.3721 g K_2PtCl_6 and 0.0451 g Li_2SO_4. Iodine was tested for and found to be absent.

Preparation II.—A third method for the preparation of potassium ammonolithiate was based on the hypothesis that the simultaneous conversion of metallic lithium and metallic potassium, the latter in large excess, in solution in liquid ammonia into their amides would result in the direct separation of the compound in view. Accordingly, the two metals, together with a minute portion of platinum black, were introduced into one leg of a reaction tube, ammonia was then distilled in upon the metals and the apparatus set aside until the reaction between the metals and the solvent was complete. A surprisingly small quantity of salt was found, a result due, as was realized later, to an error in using a much smaller quantity of lithium than had been intended. The crystalline product was grayish in color from the presence of platinum black. Well washed and dried in vacuum at 20° the specimen weighed 0.0479 g. The platinum black recovered weighed 0.0004 g. One-half gave 0.00758 g N. The other half gave 0.0341 g mixed KCl-LiCl.

Preparation III.—A repetition of the procedure described above, using 37 milligrams of lithium and 410 milligrams of potassium, gave a grayish but well-crystallized product which weighed 0.5323 g. From the specimen

0.0046 g Pt was recovered. One-fifth of the specimen gave 0.0332 g N. Another fifth gave 0.1517 g mixed KCl-LiCl and 0.3819 g K_2PtCl_6 and 0.0386 g LiCl. One-tenth gave 0.01668 g N, another tenth gave 0.0761 g KCl-LiCl and 0.1923 g K_2PtCl_6.

Preparation IV.—A fourth specimen of potassium ammonolithiate, made by the action of potassium amide on lithium iodide, gave on analysis the results found under IV below. The analytical data were not available when this paper was written.

	Calculated for $LiNK_2.2NH_3$	Found			
		I	II	III	IV
Li	5.3	5.5-5.5	....	5.5	5.3
K	58.7	57.6	....	58.3	58.6
N	31.5	30.6	31.9	31.5	31.6
LiCl-KCl	143.8	143.0	143.6	143.7	144.1

Mono-Rubidium Ammonolithiate, $LiNHRb.NH_3$ or $LiNH_2.RbNH_2$ or $[Li(NH_2)_2]Rb$

A pure specimen of this salt was prepared by the action of a solution of rubidium amide in excess on metallic lithium in the presence of platinum black in the following described manner:

Into the one leg of a reaction tube were introduced 500 mg of metallic rubidium together with a small quantity of platinum black, and into the other 20 mg of metallic lithium. Ammonia was then distilled into the apparatus to bring the metals into solution. After the lapse of a few minutes the rubidium was completely converted into the amide while the amount of lithium amide simultaneously formed in the absence of the accelerator was entirely negligible. As soon as the blue color of the rubidium solution had disappeared the solution of metallic lithium was poured into the leg containing the rubidium amide and platinum black. The metallic lithium was then generally converted into the amide in the presence of a large excess of rubidium amide, a condition which insured complete action between the two amides. The grayish[1] crystalline product was found to be so slightly soluble that no attempt was made to recrystallize it. It was simply washed several times with pure solvent to free it from mother liquor and dried in vacuum at 20° preparatory to analysis.

For analysis the compound was hydrolyzed by water vapor and then dissolved in dilute hydrochloric acid. In the aqueous solution of chlorides thus obtained the rubidium lithium and nitrogen were determined by the usual methods. The specimen weighed 0.3380 g. The platinum black filtered from the acidified aqueous solution of the mixed chlorides weighed 0.0026 g. One-fifth of the specimen gave 0.0148 g N. Three-tenths gave 0.0223 g N. One-half gave 0.2192 g mixed RbCl-LiCl, 0.3878 g Rb_2PtCl_6 and 0.0762 g Li_2SO_4.

Calculated for $LiNHK.NH_3$	Li 5.6	Rb 68.7	N 22.5
Found	5.6–5.8	68.4	22.1

It is interesting to note in passing that of the 20 mg of lithium used 19 mg were recovered in the preparation obtained while of the 500 mg of rubidium about 270 mg remained in the mother liquor as rubidium amide.

The existence of this compound was not confirmed by the preparation and analysis of a second specimen for the reason that our limited supply of metallic rubidium was exhausted.

Rubidium ammonolithiate has been obtained as a crystalline precipitate very slightly soluble in liquid ammonia. As do the other double amides described in this paper, it dissolves in liquid ammonia solution of acids and is vigorously attacked by water.

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[1] From intermixture of platinum black.

Isomorphous Mixtures of Rubidium Amide and Potassium Amide

Four unsuccessful attempts were made to separate a definite compound from solutions containing rubidium amide and potassium amide, both of which, it should be noted, are very soluble in liquid ammonia. From solutions of the mixed amides good crops of crystals were obtained on cooling the concentrated solutions nearly to the freezing point of ammonia, but in no case were rubidium and potassium present in these crystals in atomic ratios. Products containing the amides in ratios approximately represented by the formulas $KNH_2.3RbNH_2$, $KNH_2.2.5RbNH_2$, $KNH_2.1.5RbNH_2$, and $KNH_2.RbNH_2$ were obtained. It must therefore be concluded that these two amides form isomorphous mixtures. It is interesting to note that the crystals are obtained relatively richer in rubidium than the solutions from which they are deposited. In one experiment recrystallization repeated three times gave a preparation which was nearly pure rubidium amide from a solution containing relatively a large quantity of potassium amide.

Summary

In the introductory part of this paper attention is called to the existence of a considerable number of potassium salts of metallic amides which are related to ammonia as the alkali zincates, plumbites and aluminates are related to water. A list of the compounds which have been prepared is given.

In the experimental part is given a description of the manipulative details together with the analytical data which establish the existence of the four salts named in the title of this paper.

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NEW BOOKS

Forced Movements, Tropisms, and Animal Conduct. *By Jacques Loeb. 21 × 15 cm; pp. 209. Philadelphia: J. B. Lippincott Company, 1918. Price: $2.50.*—The titles of the chapters are: introduction; the symmetry relations of the animal body as the starting-point for the theory of animal conduct; forced movements; galvanotropism; heliotropism; an artificial heliotropic machine; asymmetrical animals; two sources of light of different intensity; the validity of the Bunsen-Roscoe law for the heliotropic reactions of animals and plants; the effect of rapid changes in intensity of light; the relative heliotropic efficiency of light of different wave-lengths; change in the sense of heliotropism; geotropism; forced movements caused by moving retina images; stereotropism; chemotropism; thermotropism; instincts; memory image and tropisms.

The following selections, pp. 7, 21, 31, 45, 66, 72, 82, 126, 131, 163, 171, give a fair idea of the book. Animal conduct is known to many through the romantic tales of popularizers, through the descriptive work of biological observers, or through the attempts of vitalists to show the inadequacy of physical laws for the explanation of life. Since none of these contributions are based upon quantitative experiments, they have led only to speculations, which are generally of an anthropomorphic or of a purely verbalistic character. It is the aim of this monograph to show that the subject of animal conduct can be treated by the quantitative methods of the physicist, and that these methods lead to the forced movement or tropism theory of animal conduct, which was proposed by the writer thirty years ago, but which has only recently been carried to some degree of completion.

"Physiologists have long been in the habit of studying not the reactions of the whole organisms but the reactions of isolated segments (the so-called reflexes). While it may be justifiable to construct the reactions of the organism as a whole from the individual reflexes, such an attempt is in reality doomed to failure, since reactions produced in an isolated element cannot be counted upon to occur when the same element is part of the whole, on account of the mutual inhibitions which the different parts of the organism produce upon each other when in organic connection; and it is, therefore, impossible to express the conduct of a whole animal as the algebraic sum of the reflexes of its isolated segments."

"E. P. Lyon has shown that if the tail in a normal shark be bent to one side (without changing the position of the head) the eyes of the animal move as promptly as compass needles in association with the bent tail around the same axis in which the bending occurs, but in an opposite sense. On the convex side of the animal, the white of the eye is more visible in front, on the concave side it is more visible behind; hence the former has moved backward, the latter forward. This was observed not only in the normal fish but also when the optic and auditory nerves were cut. The central nervous system acts as one unit. R. Magnus and his fellow-workers have shown that an alteration in the position of the head of a dog inevitably alters the tone of the muscles of the legs. These and other associations and mutual inhibitions make possible that simplification which allows us to treat the organism as a whole as a mere symmetry machine, a simplification which forms the foundation of the tropism theory of animal conduct. It would, therefore, be a misconception to speak of tropisms as of reflexes, since tropisms are reactions of the organisms as a whole, while reflexes are reactions of isolated segments. Reflexes and tropisms agree, however, in one respect, inasmuch as both are obviously of a purely physico-chemical character."

"The importance of these forced movements caused by lesion of the brain for the explanation of the conduct of normal animals lies in the fact that the latter is essentially a series of forced movements. The main differences between the forced movements after brain lesion and the conduct of the normal animal lies in the fact that the former are more or less permanent; while in the normal animal conduct the changes in the relative tone of symmetrical muscles leading to a temporary forced movement are caused by a difference in the velocity of chemical reactions in symmetrical sense organs or other elements of the surface."

"All the phenomena of galvanotropism are, therefore, reduced to changes in the tension of associated muscles or contractile elements, as a consequence of which the motion of the organisms toward one pole is facilitated, while the motion toward the opposite pole is rendered difficult. Galvanotropism is, therefore, a form of forced motions produced by the galvanic current instead of by injury to the brain.

. "Heliotropic curvature of sessile animals can be shown equally well in a hydroid, *Eudendrium*. It is necessary to cut off the old polyps at once when the animal is brought into the laboratory and to put the stem into fresh, clear sea water. In a day or two new polyps are formed by regeneration and these polyps will bend toward the light until their axis of symmetry is in the direction of the rays of light. The region at the base of the polyps is contractile and when light strikes the polyps from one side only, the stem on the side of the light contracts more than on the other side, and this results in a bending of the stem, whereby the polyp is put into the direction of the rays of light. As soon as the axis of the polyp is in the direction of the rays of light (provided there is only one source of light), the tension of the contractile elements is the same all around, and there is no more reason for the organism to change its orientation. It, therefore, remains in this orientation to the light.

"The muscle tension theory of animal heliotropism is, therefore, proved for all classes of the animal kingdom, infusorians, hydroids, annelids, crustaceans, etc. It would be wrong to state that the theory holds only for insects."

"Garry has shown that when a fly with one eye blackened is put on a vertical stick, it still walks upward, but in spirals around the stick, instead of in a straight line. The asymmetry of locomotion changes only the geometrical nature of the path in which the animal moves, from a straight line to a spiral, but does not alter the forced movement character of the reaction. Bancroft has pointed out that when in a positively heliotropic amphipod one eye is blackened and the legs of the same side are cut off, the animal's path would be a combination of a circus motion induced by the blackening of the eye and of a rolling motion around its longitudinal axis. Both effects combined would result in the animal swimming in a spiral path, and if the animal is positively heliotropic it would swim in such a path toward the light. This is the path which aquatic, asymmetrical positively heliotropic organisms, such as the flagellate *Euglena*, describe in their motions to the light."

"It has been suggested by the anthropomorphic interpreters of animal conduct that the motion of an animal to a source of light is the same phenomenon as when a human being who has lost his way in the dark is attracted by an illuminated human habitation. As Bohn pointed out, the definite path in which a positively heliotropic animal moves when under the influence of two lights, shows that the anthropomorphic interpretation is as erroneous in this as in any other case. A human being would go to one of two illuminated houses and not toward a point between them, determined by the relative intensity of the two lights."

"When an animal, *e. g.*, a shark or a pigeon is rotated on a turntable, *during* rotations a nystagmus is observed in the motions of the eyes and sometimes also of the head. If the rotation is not too rapid the eyes move slowly in the same plane but in the opposite direction from the rotation of the turntable, until they form a maximum angle with their normal position in the head; then they rapidly swing back and the whole phenomenon is repeated. This phenomenon is called nystagmus. It depends upon the nerve endings in the semicircular canals, but is not dependent upon the motion or pressure of the lymph in the canals, since the cutting out of the canals in the shark or the plugging up of the canals in the pigeon leaves the phenomenon unaltered. When after some rotation the motion of the turntable suddenly stops, a nystagmus of the eyes or head in the same plane but in the opposite direction as during the rotation is observed.

"Maxwell has shown that if *Phrynosoma* is rotated on a horizontal plane with constant velocity and the eyes of the animal are closed, compensatory motions of the head are produced as soon as the angular velocity exceeds a certain value which was 8 seconds for a rotation through an angle of 45°."

"When a human being has been rotated passively to the right for some time, at the interruption of the passive motion the eyes move slowly to the right and return rapidly to the left. Only the slow motions give rise to the sensation of an apparent motion of the objects and hence after the sudden stopping of a passive rotation to the right the objects seem to such a person to move to the left. The geotropic after-effect, after passive rotation to the right, consists in inducing passive compensatory motions to the right, *i. e.*, in the opposite sense of the orientation caused by the apparent motion of the visual objects. Hence in the after-effect the orientation effect of the retina image and the centrifugal effect weaken each other.

"Lyon has shown that the phenomena which were formerly described as rheotropism in fish are due to the orientating effect of moving retina images. The reader is familiar with the fact that many fish when in a lively current have a tendency to swim against the current. This phenomenon was believed to be due to the friction of the water. Lyon showed that fish orient themselves just as well when they are put into a closed glass bottle, which is dragged through the water, although in this case they are not under the influence of any friction from the current. When the bottle is not moved the fish swim in any direction inside the bottle. It is obviously the motion of the retina images of the objects on the bank of the brook which causes the "rheotropic" orientation of fish.

When driven backward by the current or when dragged backward in a bottle through the water, the objects on the bank of the river seem to move in the opposite direction. The animal being compelled to keep the same object fixed, an apparent forward motion of the fixed object changes the muscles of the fins in such a sense as to cause the animal to follow the fixed object automatically. When such rheotropic fish were kept in an aquarium and a white sheet of paper with black stripes was moved constantly in front of the aquarium the fish oriented themselves against the direction in which the paper and its stripes moved. The phenomenon was more marked in young than in older specimens. All the phenomena of rheotropism ceased in the dark or when the fish were blind."

"These few examples may suffice to show that the theory of tropisms is at the same time the theory of instincts if due consideration is given to the rôle of hormones in producing certain tropisms and suppressing others. A systematic analysis of instinctive reactions from the viewpoint of the theory of tropisms and hormones will probably yield rich returns. As an example we may quote the fact that diurnal depth migrations of aquatic animals, consisting in an upward motion during the night and a downward motion during the day are in all probability determined by a periodic change in the sense of heliotropism."

"This tentative extension of the forced movement or tropism theory of animal conduct may explain why higher animals and human beings seem to possess freedom of will, although all movements are of the nature of forced movements. The tropistic effects of memory images and the modification and inhibition of tropisms by memory images make the number of reactions so great that prediction becomes almost impossible and it is this impossibility chiefly which gives rise to the doctrine of free will. The theory of free will originated and is held not among physicists but among verbalists. We have shown that an organism goes where its legs carry it and that the direction of the motion is forced upon the organism. When the orientating force is obvious to us, the motion appears as being willed or instinctive; the latter generally when all individuals act alike, machine fashion, the former when different individuals act differently. When a swarm of *Daphnia* is sensitized with CO_2 they all rush to the source of light. This is a machine-like action, and many will be willing to admit that it is a forced movement or an instinctive reaction. After the CO_2 has evaporated the animals become indifferent to light, and while formerly they had only one degree of freedom of motion they now can move in any direction. In this case the motions appear to be spontaneous or free, since we are not in a position to state why *Daphnia a* moves to the right and *Daphnia b* moves to the left, etc. As a matter of fact, the motion of each individual is again determined by something but we do not know what it is. The persistent courtship of a human male for a definite individual female may appear as an example of persistent will, yet it is complicated tropism in which sex hormones and definite memory images are the determining factors. Removal of the sex glands abolishes the courtship and replacing the sex glands of an individual by those of the opposite sex may lead to a complete reversal of the sex instincts. What appears as persistent will action is, therefore, essentially a tropistic reaction. The production of heliotropism by CO_2 in *Daphnia* and the production of the definite courtship of the male A for the female B are similar phenomena differing only by the nature of the hormones and the additional tropistic effects of certain memory images in the case of courtship. Our conception of the existence of 'free will' in human beings rests on the fact that our knowledge is often not sufficiently complete to account for the orienting forces, especially when we carry out a 'premeditated' act, or when we carry out an act which gives us pain or may lead to our destruction, and our incomplete knowledge is due to the sheer endless number of possible combinations and mutual inhibitions of the orienting effect of individual memory images." *Wilder D. Bancroft*

Coal and Its Scientific Uses. *By William A. Bone. 22 × 15 cm; pp. xv + 491. New York: Longmans, Green and Co., 1918. Price: $7.00.*—In 1865 Jevons said that "Coal in truth stands not beside, but entirely above, all other commodities. It is the material source of energy of the country, the universal aid—the factor in every thing we do. With coal almost any feat is possible or easy; without it we are thrown back into the laborious poverty of early times. . . The progress of science, and the improvement in the arts will tend to increase the supremacy of steam and coal." The author has treated the subject under the following headings: introductory; the origin and formation of coal; the chemical composition of coal; the combustion of coal; the principles governing combustion and heat transmission in boilers; domestic heating; the smoke nuisance and its abatement; general considerations relating to the use of gaseous fuels derived from coal; the carbonization industries; the complete gasification of coal; water gas and its applications; fuel economy in the manufacture of iron and steel; economy of fuel attainable in the blast furnace by the use of dry blast; power production from coal; surface combustion.

The following extracts, pp. 23, 68, 164, 178, 221, 224, 438 give some idea of the book.

"Although many classes and varieties of coal occur in Nature, all of them represent some stage or product of the primary decomposition and subsequent transformations, under the combined influence of slowly increasing pressure, and possibly also of temperature, of the vegetable debris of primaeval forests and swamps. This process has gone on in several of the great geological periods, and, so far as its early stages are concerned, is being repeated to-day under somewhat different conditions in our modern peat bogs and deltas, where enormous masses of water-logged vegetable debris are decomposing under bacterial influence.

"A consideration of the geographical distribution of the world's principal coalfields shows that all the important fields adjacent to the North Atlantic and Arctic areas (which include nearly all the fields of the North-West Europe and in the eastern part of North America) originated in what geologists call the Carboniferous Period of the Primary Era; while what may be termed the 'Indian Ocean' group of coalfields (which include those of China, India, Australia, and South Africa) originated in the somewhat later Permo-Carboniferous Period. Mesozoic coals are found in the interiors of North America and Asia (intracontinental group); while Tertiary coals are chiefly found in what may be termed the Pacific borderland (west of North America, Japan, and New Zealand), as well as in regions bordering on the Gulf of Mexico and the Mediterranean.

"The great coalfields of the Carboniferous System originated in a new monster vegetation flourishing in a rich virgin soil, with an equable if not subtropical climate, and large areas of shallow sea, to which great quantities of sediment were borne from rivers. Vegetable tissue has in all ages, then as now, been built up by the action of chlorophyll under the influence of sunlight, stimulated by minute quantities of mineral salts drawn in by the roots, upon atmospheric carbon dioxide and moisture, which action sets up a complex series of chemical changes, with the intermediate formation of sugars and starches, ultimately resulting in the production of celluloses and ligno-celluloses, as the basis of all woody tissue."

"In selecting coal for any particular purpose, the following points may usefully be borne in mind:

"1. The best gas-coals are those in which the O:H ratio is approximately 2.0. They usually yield 32 to 38 percent of volatiles at 900° (reckoned on the dry ashless coal), and a fairly porous coke.

"2. The best coking coals usually yield between 20 and 30 percent of volatiles at 900° C. They are strongly caking, and have a ferruginous ash.

"3. The best steam-coals are found among those which yield between 10 and 20 percent of volatiles at 900° C; they are non-caking, or only feebly so and they should have a non-ferruginous ash.

"4. For gas generation, where the whole of the coal is to be gasified in a 'producer' under the influence of a mixed steam-air blast for the making of 'Producer Gas,' it is best to select, whenever available, either a non-caking or feebly caking coal with, if possible, an infusible non-ferruginous ash. Strongly caking coals are to be avoided.

"5. The coals freest from sulphur, arsenic, and with the *purest and lowest ash contents* are the anthracites."

"When a fresh charge of raw coal is introduced into the furnace of, say, a boiler, it first of all undergoes a destructive distillation, whereby a number of combustible gases, tarry vapors and steam are expelled. The gaseous products consist chiefly of hydrocarbons (methane with smaller proportions of ethylene, benzene, and probably also ethane), hydrogen, and carbon monoxide, whilst the tarry vapours are mingled with a certain proportion of finely divided carbon (soot). The 'volatile' combustion constituents thus evolved from the upper portion of the fuel bed will amount in all to between 15 and 25 percent of the weight of the ash-free coal charged, and the oxygen needed for this combustion must be furnished by what is sometimes termed a 'secondary' air supply which is usually introduced through adjustable openings in the doors of the furnace, or (may be) also at the fire-bridge, in such a manner that it mixes with the combustible gases and vapours at or near the top of the fuel bed. The ensuing combustion causes the well-known development of smoky flames in the furnace after each addition of fuel.

"The combination of the residual coke (carbon) takes place in the lower layers of the fire by means of the 'primary' air supply drawn in through the fire-bars, the evidence of which may be seen by looking at the incandescent mass of fuel in the furnace towards the end of the interval between two successive chargings of the coal.

"Accepting this as an approximately true view of the outward and visible sequence of events in the furnace, it is at once evident that we have to deal with at least two distinct cases of combustion, namely (1) that of solid carbon in the lower layers of the fire, and (2) that of the combustible 'volatiles' (gases and vapours) in or above the upper layers."

"The combustion of the heavier hydrocarbons which constitute the tarry vapours produced by the distillation of the coal is a much more difficult matter, inasmuch as their complex more molecular constitution renders them not only more resistant to oxygen attack, but also prone, under the roasting influence of heat, to form still denser molecular aggregates by a series of internal condensations. Without doubt the production of the mixture of soot and dense hydrocarbons which constitute black smoke is largely due to this circumstance. The best way of counteracting it is to ensure a uniform supply and distribution of 'preheated' air, so as to keep the interacting gaseous medium well above the ignition point of the tarry vapours it contains, and to ensure that all parts of it are sufficiently, though not excessively, supplied with the necessary oxygen for the maintenance of vigorous combustion. Also, devices which will cause the burning mixture to impinge on incandescent fire-brick surfaces in the furnace, thereby accelerating combustion, will undoubtedly minimize, even if they do not altogether prevent, smoke production.

"It is obvious that, so long as a coal is 'free-burning,' the smaller the amount of volatile matter it contains the less will be its liability to cause smoke, and, inasmuch as smoke production is always a sign of incomplete combustion, the more efficiently can it be burnt. Hence arises the good reputation of the celebrated semi-bituminous Welsh 'steam-coals,' containing from 10 to 15 percent of volatile matter, which burn almost smokelessly. As, however, such smokeless coals are only available in certain favoured localities, it has been frequently suggested that, as a good means of preventing smoke, suitable bituminous coals might be submitted to a preliminary process of expelling or decomposing their smoke-producing constituents by low temperature distillation in a separate apparatus before being burnt in boiler furnaces and the like. If such a process could be carried out economically so as to yield 'semi-coke' of sufficient strength, the problem of boiler firing with solid fuel would be much simplified. Even then, however, the achievement of really efficient combustion would still depend upon the proper regulation and distribution of both primary and secondary air supplies, and the maintenance of uniform conditions in the furnace. And for this purpose, both a good draught and effective means of regulating it, are absolutely essential as a prime condition of success."

"Some idea of the wastefulness of our British open fireplaces and kitchen ranges may be gained from the fact that, whereas with a population of 46 millions we annually consume in our houses about 36 million tons of coal, in Germany, with its population of 67 millions and its severer winter climate, where closed stoves and ranges are universally employed, only 17 million tons are so burned. In other words, each inhabitant of the United Kingdom requires a domestic consumption of 15 cwts. of coal per annum, as against only 5 cwts. in Germany."

Many reforms in the construction of house firegrates are due to the pioneering work of Mr. Teale. In a pamphlet published in 1883, he tells us that "his ideas embody a combination of two conditions, namely, one, that no current of air should pass through the grate at the bottom of the fire; the other, that the space or chamber under fire should be kept hot. He laid down seven rules to be observed in the construction of fireplaces, which in substance are as follows:

"1. As much firebrick and as little iron as possible to be used.

"2. The back and sides of the fireplaces should be constructed of firebrick.

"3. The back of the fireplace should lean or arch over the fire so as to become heated by the rising flame, whereby smoke is consumed, and much more heat is radiated into the room.

"4. The bottom of the fire or grating should be deep (9 to 12 in.) from before backwards, in order that the fire may be made horizontal and slow-burning instead of vertical and quick-burning.

"5. The slits in the grating should be narrow ($^1/_4$ to $^3/_8$ in. in width).

"6. The bars (if any) in front should be narrow (less than $^1/_2$ in. thick) and not more than four in number for an ordinary fire.

"7. The chamber beneath the fire should be closed in front by a shield or 'economizer,' so as to stop all currents of air that would pass *under* the grate and *through* the fire."

"On the assumption that power may be most efficiently applied to industry by the medium of electricity, the Committee [on Coal Conservation] are of the opinion that the present system of electrical power distribution throughout the country, which is undertaken by over 600 authorities in as many separate districts, is both technically wrong and commercially uneconomical. The present average size of generating stations is stated to be only 5000 H. P., or about one-fourth of what should now be the smallest generating machine in a power station. The Committee accordingly made a number of recommendations for the supervision of the present system by a comprehensive scheme for Great Britain, of which the first six may here be quoted:—

"1. It is essential that the present inefficient system of over 600 districts should be superseded by a comprehensive system in which Great Britain is divided into some sixteen districts, in each of which there should be one authority dealing with all the generation and *main* distribution.

"2. Centres, or sites, suitable for electric generating purposes should at once be chosen on important waterways as the future main centres of supply for each of the districts into which the country is to be divided.

"3. The sites so chosen should be as large as possible, having in view the land available in suitable localities, and should have ample water and transport facilities. Land is required, not only for the power stations themselves—which for the sake of security and safety would have to be suitably subdivided, that is they would not be contained all in one building—but for the processes involved in the extraction of by-products from the coal before it is used for the production of power, where such extraction is found to be justified. It is also required for the development of electro-chemical processes, which may be most conveniently carried on in close proximity to the power plant. This condition entails the sites being chosen outside, not inside, towns. The health of the great industrial centres and the congestion of the railway lines in their neighborhood would be radically improved by arranging that the conversion of coal into motive power was carried out away from the densely populated centres.

"4. Plans should be prepared for the construction immediately after the war on these sites of the first instalment of large super-power plants capable, first, of supplying through a comprehensive electric power distribution system which must also be arranged for, the existing demands of the community; and, secondly, of supplying electrical energy at the lowest possible price for new processes and manufactures.

"5. Such plants would be designed so that, as methods are perfected for extracting by-products from the fuel, before using it for the purpose of the production of electric power, the by-product plant can be combined with the power plant. Each site should be laid out with this in view, and with a view to the unrestricted extensions of the plant as required.

"6. Power available from surplus gas or waste heat should be turned into electrical energy on the spot in local plants which would feed into the main distribution system. As regards waste coal, *i. e.*, coal which it does not at present pay to bring to the surface—this could, where transport was the ruling consideration, also be used on the spot."

Wilder D. Bancroft

Practical Physiological Chemistry. *By Philip B. Hawk. Sixth edition, revised and enlarged. 24 × 17 cm; pp. xiv + 661. Philadelphia: P. Blakiston's Son and Co., 1918. Price: $3.50.*—"The book has been thoroughly revised in an attempt to bring it strictly up to date. In view of the great clinical importance of the chemical phases of the phenomena of acidoses a new chapter on acidosis has been introduced. The chapters on metabolism, blood analysis, gastric digestion, and quantitative analysis of urine have been expanded considerably, and the question of growth has been treated experimentally. Two radical changes in the quantitative section are the substitution of Van Slyke's procedure for all former methods for the determination of acetone bodies in urine and the elimination of all methods for the determination of urea, except those based upon the use of urease."

The titles of the chapters are: enzymes and their action; carbohydrates; salivary digestion; proteins (2); nucleic acids and nucleoproteins; gastric digestion; gastric analysis; fats; pancreatic digestion; intestinal digestion; bile; putrefaction products; feces; blood and lymph; blood analysis; acidosis; milk; epithelial and connective tissues; muscular tissue; nervous tissue; urine (5); metabolism.

"Of all the various elements of the protein molecule, nitrogen is by far the most important. The human body needs nitrogen for the continuation of life; but it cannot use the nitrogen of the air or that in various other combinations as we find it in nitrates, nitrites, etc. The nitrogen in the protein molecule occurs in at least four different forms, as monamino acid nitrogen, as diamino acid nitrogen or basic nitrogen, as amide nitrogen, and as guanidine residue (p. 64)."

From reliable experiments made upon lower animals and man it is evident that the gastric juice is secreted as the result of stimuli of two forms, psychical stimuli and chemical stimuli. The psychical form of stimuli may be produced by the sight, thought, or taste of food; and the chemical stimuli may be produced by certain substances, such as water, milk, the excretives of meat, etc., when coming in contact with the stomach mucosa. The stimulatory power of water has been demonstrated very strikingly. The claim that the drinking of water with meals is harmful, because such a procedure causes a dilution of the gastric juice, has no basis in fact. The drinking of water with meals by normal individuals has been found to be accompanied by a more economical utilization of the ingested proteins, fats and carbohydrates. Various other desirable, and no undesirable, features have been demonstrated as accompanying or following such dietary procedure. No experimental evidence has been submitted which can justly be interpreted as showing any harmful influence to accompany or follow the drinking by normal persons of all large quantities of water at meal time (p. 138)."

"The processes involved in the coagulation of the blood are not fully understood. Several theories have been advanced and each has its adherents. The theory which appears to be fully as firmly founded on experimental evidence as any is the following. Blood contains a zymogen called prothrombin which combines with the calcium salts present to form an enzyme known as thrombin or fibrin-ferment. When the blood is drawn from a vessel the fibrin-ferment at once acts upon the fibrinogen present and gives rise to the formation of fibrin. This fibrin forms in shreds throughout the blood mass and holding the form elements of the blood clot. The fibrin shreds contract gradually, the clot assumes a jelly-like appearance, and the yellowish serum exudes. If, immediately upon the withdrawal of blood from the body, the fluid be stirred rapidly or whipped thoroughly with a bundle of coarse strings, twigs, or a specially constructed beater, the fibrin shreds will not form a network throughout the blood mass; but instead will cling to the device used in beating. In this way the fibrin may be removed and the remaining fluid is termed defibrinated blood (p. 260)."

"The difference between the freezing-point of normal urine and that of pure water varies ordinarily between —1.3° and —2.3°. It is subject to very wide fluctuations when conditions are unusual. For instance, following copious water or beer drinking, the difference may be only —0.2° whereas it may be —3° or more on a diet containing much salt and deficient in fluids. The freezing-point of normal blood is generally about —0.56° and is not subject to the wide variations noted in the urine, because of the tendency of the organism to maintain the normal osmotic pressure of the blood under all conditions. Variations between —0.51° and —0.62° may be due entirely to dietary conditions; but any marked variation can, in most cases, be traced to a disordered kidney function (p. 393)."

"As a result of the work of different experimenters, certain accessory food substances, 'growth-promoting substances,' or vitamines, as they are variously termed, have been shown to be of great importance in nutrition. The exact character of these substances has not been established. There are two distinct accessory food substances, one soluble in fats and called 'Fat-Soluble A,' the other soluble in water and called 'Water-Soluble B.' The substances have a rather wide distribution. The fat-soluble vitamine is present in milk fat, egg yolk fat, beef fat, cod liver oil, 'oleo oil,' margarins, cabbage and alfalfa leaves, rye, and the seeds of flax, hemp, millet, and sunflower. The water-soluble vitamine occurs in milk, rice (unpolished), yeast, peanuts, pancreas, and kidney bean. Certain animal and vegetable products contain both the vitamines. Among these are whole milk, cotton seed, soy bean, the kernel of maize and oat, and the kernel and embryo of wheat. In order that a diet may be adequate for growth, it must contain a satisfactory quota of these accessory food substances in addition to protein, proper in kind and amount, suitable inorganic matter, and enough fat and carbohydrate to yield the required energy (p. 385)."

The reviewer would have welcomed a discussion of the possible reasons why a fat man utilizes his food quite differently from a thin man. This is the most important problem in metabolism and we know practically nothing about it, which makes it the more necessary that the problem should be formulated and brought to the front as often as possible. *Wilder D. Bancroft*

Electro-Analysis. *By Edgar F. Smith. Sixth edition. 20 × 14 cm; pp. 13 + 344. P. Blakiston's Son and Co., 1918 Price: $2.50.*—In the preface to this edition the author says: "The methods of electro-analysis are finding their way into all laboratories; indeed in many works every provision has been made to apply them. Since the appearance of the last edition of this book, comparatively few new fields or new and important advances have been made, so that in the present revision, while making place for references to all contribution which have been published, there are comparatively few additions to the main text. Attention is directed particularly to the improved double cup, p. 316, in which hundreds of halides have been analyzed successfully. The new device ensures complete success and removes every doubt which may have arisen in regard to the efficacy of the apparatus first suggested in the determination of anions and cations. Other additions to the text will be noticed at once, so that in its present form there is presented the most recent and complete picture of the subject to which the book is devoted; not that electro-analysis has attained perfection, for this would be, in no sense, true as so much remains for study; but the book brings together all that has been found reliable, by the test of experience, and offers simultaneously the latest results gathered in recent years from widely removed centers." *Wilder D. Bancroft*

Introduction to Organic Chemistry. *By J. T. Stoddard. Second edition. 18 × 13 cm; pp. x + 423. Philadelphia: P. Blakiston's Son and Co., 1918. Price: $1.50.*—"The book is considerably smaller than many of the text-books on the subject; but it is believed that it is none the less complete in all the essential matter which is properly presented in a first course. The larger text-book is apt to bewilder the student by brief descriptions of too many compounds of minor importance, or to fill too many pages with discussions which can be conducted to better advantage by the lecturer." The sections which have been rewritten in the second edition are those on the natural oils and fats, on uric acid and the purine bases, and on the proteins.

There are a few points which the reviewer at least would like to see amplified. Why do ethyl and methyl chlorides, p. 32, burn with a green-edged flame? The alumina method of making ethylene is better than the phosphoric acid one, p. 46. Why does fusel oil, p. 67, distill with alcohol though having a much higher boiling-point? Since the vapor of acetic acid is hardly decomposed when led through a red-hot tube, p. 97, why is it so difficult to oxidize acetaldehyde to acetic acid above 100°? Reference might well have been made to the difference between calcium and sodium hydroxides in causing the hydrolysis of fats. *Wilder D. Bancroft*

ETHYLENE

BY WILLIAM MALISOFF AND GUSTAV EGLOFF

Introductory

Of the vast family of hydrocarbons the unsaturated members have had a stronger affinity for the chemical imagination than any others, and of these most and longest of all the relatively simplest one, ethylene. The solution of the problem of its unsaturation from a thoroughly modern physico-chemical point of view will dissolve a host of complacent, though convenient, conceptions, as chains, cycles, bonds, strains, etc., which are, so to speak, *statically untrue*, and hence almost of the nature of prejudice. The proper understanding of the synthesis, decomposition and the reactions of ethylene contains in its essence the answer to the general questions which are the sole "natural right" of the scientist.

The aim of the present communication is to collect the data on ethylene on a logically convenient basis, and to point out the numerous practical and theoretical considerations which will constitute the problems for a series of papers on researches of the authors.

A. Physical Characteristics of Ethylene.
  1. Physical Constants.
  2. Specific Properties.
  3. Gas Properties.
  4. Application of Physical Characteristics Industrially.

B. Chemical Characteristics of Ethylene.
  1. Solubility of Ethylene in Various Solvents.
  2. Solubility in Ethylene.
  3. Combustion and Explosion of Ethylene.
  4. Reactions Proper.
    a. Simple addition reactions.
    b. Oxidations.
    c. Formation of other compounds.
    d. Halogenation.

C. The Formation of Ethylene in Chemical Reactions by Decomposition.
  1. Formation by Electrolysis.
  2. Formation by Simple Decomposition of Compounds other than Alcohol.
  3. Formation by Double Decomposition.

D. The Decomposition of Ethylene.
  1. Heat Decomposition.
  2. Electro Decomposition.

E. Catalysis.
  1. Catalytic Decomposition.
  2. Catalytic Formation.
  3. Catalysis of Alcohol.
  4. Electrosynthesis.
  5. Catalytic Oxidation.
  6. Hydrogenation.
    a. Direct.
    b. Catalytic.

F. Miscellaneous on Ethylene.
  1. Analytical.
  2. Biological Data.
  3. Miscellaneous.

G. Research Possibilities on Ethylene—Summary.

A. PHYSICAL CHARACTERISTICS OF ETHYLENE

1. Physical Constants

The specific gravity of ethylene (referred to air as 1) is 0.9784 as reported by Carius.[1] On the other hand, Saussure[2] states the theoretical density to be 0.9683 and reports an observation of 0.9852. He gives the weight of 1 liter of the gas at 0°, 760 mm, sea-level, 45° latitude as 1.2519 grams. This conflict in data is evidently a very unsatisfactory one and it is difficult to weight the figures. The value, of course, is one needed for all sorts of calculations.

Cailletet[3] gives the boiling point at —105° C, but is contradicted by Wroblewsky and Olszewsky,[4] who place it between —102° and —103°. The latter used a hydrogen thermometer, whereas the former used a carbon disulphide one. This probably accounts for the discrepancy, for Ladenburg and Krügel,[5] at a later date, report a boiling point of —105.4° at 760 mm. For another pressure they get at 756.9 mm —102.65°. The boiling point has also been given by Travers[6] as 102.6° and by Wroblewsky and Witkowsky[7] as —103.6°.

Maass and McIntosh[8] (1914) report the boiling point as —102.5° and the density at this boiling point as 0.5650, but the specific gravity of the liquid at the boiling point —102.7°, according to Ladenburg and Krügel,[9] is 0.6095; at —169° it is 0.6585 and at —105.4° it was found to be 0.5710. The liquefaction of ethylene as determined by Carius under different temperatures was as follows:

Temperature	Atmospheres
1°	45
4°	50
8°	56
10°	60

The melting point is given by Ladenburg and Krügel[10] as —169°.

Olszewsky's[11] value for the melting point of ethylene checks that of Ladenburg and Krügel.[12] He obtained solid ethylene (m. p. —169°), a white, crystalline, somewhat transparent mass, by allowing the liquid to boil under a pressure of 1 mm at the boiling point of oxygen (—181.4°).

Burrell and Robertson[13] describe in detail an apparatus for determining the saturated vapor pressure of gases. The values for the vapor pressure and boiling points of ethylene under various pressures as determined by them were as follows:

Avg. temp. Deg. C	Observed pressure Mm	Calculated pressure Mm
—103.9	760	760
—104.8	730	726
—105.4	700	701
—106.8	650	643
—108.0	600	595
—111.0	500	512
—114.1	400	400
—118.2	300	300
—123.6	200	200
—132.2	100	98
—135.3	75	74
—139.6	50	49
—144.3	31	30
—149.4	17	17
—154.8	9	9
—159.9	4	4

The equation of the curve they obtained is:

$$\log P = -762.52/T + 1.75 \log T - 0.00532\ T + 4.3910$$

The authors place the b. p. of ethylene at —103.9° (or 169.2° absolute). The saturation pressures of ethylene with corresponding boiling points as given by Villard[14] follow:

Temp. Deg. C.	Atmosphere pressure
—104.0	1.00
— 85.0	2.85
— 80.0	3.55
— 60.0	7.50
— 40.0	14.30
— 30.0	18.70
0.0	40.20
6.0	46.10
9.5	49.50
9.9	50.10

The following table is given by Olszewsky[15] for the boiling points of ethylene under different low pressures:

Pressure Mm	B. p.
750	—103.0
546	—105.0
441	—108.0
346	—111.0
246	—115.5
146	—122.0
107	—126.0
72	—129.7
56	—132.0
31.0	—139.0
12.0	—148.0
9.8	—150.4

The melting point and boiling point of ethylene, if checked, may be safely used as standards, for they are said to be particularly constant and reliable, due to the high degree of purity of the gas. Furthermore, these facts serve as indication that the latent heats of fusion and of evaporation for ethylene are larger than for liquids used in low temperature work.

In their work on liquefied gases and their saturated vapors, Cailletet and Mathias[16] give the following density values for ethylene:

Temp. Deg. C	Density of saturated vapor
—28.0	0.0378
— 7.5	0.0660
— 1.5	0.0785
11.8	0.1140
6.1	0.1230
8.9	0.1500

Temp. Deg. C	Density of liquid
—21.0	0.414
— 7.3	0.342
— 3.7	0.353
4.3	0.332
6.2	0.306

According to Beilstein[17] the density of liquid ethylene is

0.386 at 3°
0.361 at 6°
0.335 at 8°

Maass and McIntosh[18] find a straight line relation between the density and temperature of ethylene. Their figures are:

Temp. Deg. C	Density
—114.2	0.5752
—107.7	0.5696
—105.9	0.5674
—105.0	0.5669
—103.3	0.5657
— 99.4	0.5631

By comparing the figures for ethane, ethylene and acetylene, the authors found that, considering the atomic volume of hydrogen as 5.5, the atomic volumes of carbon for different linkages are:

Single	10.9
Double	13.8
Triple	15.5

The molecular volume of ethylene at its boiling point is, according to their figures, 49.6.

2. Specific Properties

Carius[19] gives the critical temperature as 13°. Values given by others vary from 8.8° to 13.0°.

t_k	p_k	v_k	d_k	$a \times 10^5$	$b \times 10^6$	Authority
9.2	58.0			777	2228	Van der Waals[20]
13.0						Cailletet[21]
10.1	51.0					Dewar[22]
		0.21	0.00569			Cailletet and Mathias[23]
10.0	51.7					Olszewsky[24]
9.5	50.7					Cardoso[25]
8.8	48.5	0.212				Amagat[26]

Cardoso and Arni,[27] working with ethylene, prepared from sulphuric acid and ethyl alcohol and purified by washing and fractional distillation, found the following constants which are probably the most reliable: m. p. —169°, b. p. —104.3°, t_c 9.50° ± 0.1°, p_c = 50.65 ± 0.1 atm. The critical opalescence extended from 9.05° to 9.50°.

Berthelot[28] reports the heat of formation from amorphous carbon to be —9,400 cals. The negative heat of formation is very much like that of acetylene. Favre and Silberman[29] report —8,000 cals.; Thomsen[30] again reports H. F.$_p$ as —2,710 cals. He reports the H. F.$_v$ —3,290 cals. Such large differences can hardly be accidental. The heat of combustion is given by Thomsen[31] at 333,350 cal. at 18°, Berthelot's[32] value being 341,400 cals.

W. G. Mixter[33] determined the heat of dissociation of ethylene by exploding a mixture of acetylene and ethylene and correcting for the thermal effect of the acetylene. The heat of combustion is 345,800 cal., under constant pressure, and 344,600 cal. under constant volume. The heat of dissociation of ethylene, by exploding with molecular equivalent of acetylene, was 17,000.

Of interest may be the general value given by P. Lemoult.[34] He states that the molecular heat of combustion for hydrocarbons of the olefin series is (157n + 28) Cal., which checks quite closely, giving 342,000 calories for ethylene.

8. Gas Properties

The dielectric constant of ethylene at 0° and 1 atmosphere is given by Klemencic[35] as 1.001456 and by Boltzmann[36] as 1.0001312. Dielectric conditions are then about the same as for air provided no decomposition of ethylene occurs.

The compressibility coefficients $\left(\frac{p_0v_0}{pv}\right)$ are given for a series of conditions by Winckelmann,[37] of which some are indicated as follows:

At 0° C mm Hg	Coefficient	At 100° C mm Hg	Coefficient
731.9 to 1407.0	1.00545	746.7 to 1451.3	1.00265
714.3 to 2067.8	1.01390	746.7 to 2083.7	1.00381

Amagat[38] gives a number of values of *pv*; the value for 0° and 1 atmosphere being 1; at 50 atm. and 0° determined as 0.176; and under 1000 atmospheres and 0° the value of 2.289 was found.

The speed and dimensions of the gas molecule are given by Breitenbach[39] at 0°:

t	Ω	Lt × 10^8	Qt	Qt (corr.)	6 × 10^9	t_B
0	45,420	546	42,400	23,200	33	0

The viscosity is variously reported by Obermayer,[40] Graham,[41] and Breitenbach.[42]

Temperature	$\eta t \times 10^7$
21.5	851
0.0	966
20.0	1090
302.6	1826

For mixtures of ethylene and air, Breitenbach[43] reports:

Percent ethylene	(15° C) $\eta \times 10$
90.31	1078
54.00	1345
13.65	1695

Zimmer[11] measured the viscosity coefficient of ethylene between 13.8° and —75.7° by the transpiration method. The values of η observed agree with those calculated by Sutherland's formula. It is

$$\frac{\eta_2}{\eta_1} = \frac{(T_2)^{3/2}}{(T_1)} \cdot \frac{T_1 + C}{T_2 + C}.$$

The value of the constant C with data on the change of viscosity of the gas with temperature (Landolt, p. 101) are as follows:

$\eta_0 \cdot 10^7$	α	$\beta \cdot 10^5$	η	C (Sutherland) formula	Range	Observer
922.2	0.003665	350	0.958		—21.5 to 53.5	Obermayer[46]
				272.0		Sutherland[46]
961.3				225.9		Breitenbach[47]

As to the relation between the viscosity coefficient of a gas and the temperature, they agree only down to —20°, below which temperature the observed values are much larger than computed. Density measurements show that ethylene begins to deviate from the Boyle-Gay-Lussac law at the same temperature. This seems to indicate a *polymerization of the gas.*

For a general discussion of the relation of viscosity to physical properties in the case of double bonds and triple bonds, see Hilditch and Dunstan.[48]

S. Loria[49] determined the refractive indices by an interferometer method through the range of wave-lengths from 5230 to 6677. The value for ethylene being 1.0006571 for the D_1 line at 0° and 760 mm. The results are thought *not* to support the theory of dispersion electrons and valency electrons. The values in the equation

$$\eta - 1 = a\,(1 + b/\lambda^2)$$

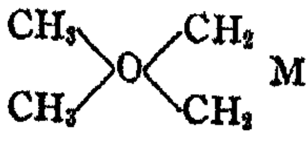
are given by him as $a = 0.0006303$ and $b = 1.477 \times 10^{-10}$. Values possibly a little better than Loria's are given by L. Stuckert.[50]

Lieveing and Dewar[61] give the refractive indices for liquid ethylene. At —100°,

$$\frac{\mu_D - 1}{d} = 0.627 \text{ and } \frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.384.$$

The corresponding numbers for gaseous ethylene are given as 0.578 and 0.385.

In a series of researches on the fusibility curves of gaseous mixtures Baume and German[52,53] found that the oxonium compound



$Me_2O.C_2H_4$

is formed at —163.2°—which is not stable in contact with the solution and melts with decomposition.

The spectrum of ethylene is given by Wesendonck.[54]

M. Moulin[55] has used ethylene along with other gases to study ionization by α-rays.

4. Applications of Physical Characteristics Industrially

It is a noteworthy fact that Wroblewsky and Olszewsky froze alcohol and liquefied oxygen by allowing ethylene to boil in a vacuum. The temperature attained by them was —136° C. No doubt, as the field of low temperature work increases, ethylene will have to be considered more and more.

The melting and boiling points are *very constant* and therefore should be introduced by all means for the calibration of thermometers. Pure ethylene is, moreover, not very difficult to prepare.

Compressed ethylene (pure) can be put on the market without any great difficulty. The demand is certain to be large in view of the important developments the chemistry of ethylene has undergone and is bound to undergo. With an explosibility which under practical conditions is nil and with a ready compressibility (see figures above), the operations bound up with its liquefaction and storing under pressure are not likely to be expensive or difficult.

Even the luminosity of ethylene may be utilized in this connection, since it may be added to natural gas poor in luminants without any great trouble or cost. However, the strong conservation movement throughout the United States at the present time, to convert the gas standards of cities from an illuminating to a heat standard is well under way, so that the addition of ethylene to *add* illuminating value to a natural gas may not be commercial.

B. CHEMICAL CHARACTERISTICS OF ETHYLENE

1. Solubility of Ethylene in Various Solvents

Carius[56] gives the solubility in water at 0° as 0.25 and the solubility in alcohol at 0° as 3.6 percent, also working out the formula in alcohol (sp. gr. = 0.792 at 20°) as $C = 3.59498 - 0.057716t + 0.0006812t^2$. Winckler, Landolt and Börnstein Tabellen[57] give the following data on the solubility of ethylene in alcohol:

Solubility in Alcohol

$t°$	Vols. C_2H_4 per 100 vols. alcohol
0	359.5
4	337.5
10	308.6
15	288.2
20	271.3

Levi[58] determines the solubility of ethylene in methyl alcohol and in acetone with the following results in terms of the Ostwald solubility expt.

$$l\,f = \frac{\text{Vol. of gas absorbed}}{\text{Vol of absorbing liquid}}'$$

$t°$	Methyl alcohol	Acetone
0	3.3924	4.0652
10	2.8831	3.3580
20	2.3718	2.6278
25	2.1154	2.2500
30	1.8585	1.8680
40	1.3432	1.0852
50	0.8259	0.2772
60	0.3506	....

The formulas from which the above figures were calculated are:

In methyl alcohol $f = 3.3924 - 0.05083t - 0.00001t^2$
In acetone $f = 4.0652 - 0.06946t - 0.0000126t^2$

F. Heinrich[59] has recalculated the temp. equations for the absorption coefficients of gases by means of the method of least squares from Bunsen's experiments. His results are as follows: ethylene in water $C = 0.25487 - 0.0088312t + 0.000174l7t^2$. Ethylene in alcohol gave $C = 3.5846 - 0.56153t + 0.00062369t^2$. The probable errors of these equations are much less than those of the equation given by Bunsen. Bunsen[60] gives $C = 0.25629 - 0.0091363t + 0.000188108t^2$.

Bohr[61] states that the relation between the absorption coefficient and temperature is given by the equation

$$a(T - n) = k$$

where a is the absorption coefficient, T the absolute temperature, and n and k constants for each gas (the expression given may be simplified to $at - a_0/(1 - kt)$, and this form of expression is found to give good agreement with the observed values in the cases of hydrogen, oxygen, nitrogen, carbonic oxide, carbonic anhydride, nitric oxide and ethylene in water; and of carbonic oxide, carbonic anhydride, nitric oxide, methane, nitrous oxide and ethylene in alcohol.

Tucker and Moody,[62] in their search for an analytical separation of C_2H_2 and C_2H_4, found that ammoniacal cuprous chloride dissolves ethylene quite readily. The gas is but slightly soluble in a solution of ammonia, and is fairly soluble in alcohol, but not in ammoniacal chloride of silver.

Lean and Bone[63] observed that alkaline pyrogallol and strong potash do not absorb ethylene at all, even on prolonged standing.

McDaniell[64] found the solubility of ethylene to be in:

	A_{25}
Benzene	2.9281
Hexane	2.9896
Heptane	3.4061
Acetone	2.4834

2. Solubility in Ethylene

Interesting is the fact that solids and liquids will dissolve in ethylene (as well as other gases) under pressure. P. Villard[65] reports a series of experiments, finding that ethylene, under 300 atmospheres pressure, takes up sufficient iodine to color it a very deep violet to a thickness of 2 mm. But in time the color disappears as combination ensues. Compressed ethylene also dissolves paraffin (abundantly above 150 atmospheres), stearic acid and camphor; the latter volatilizes readily under small pressure; and when the pressure is increased to 150 atmospheres, the unvolatilized camphor becomes liquid, but continues volatilizing as the pressure is further increased. On releasing the pressure, the same phenomena ensue, but in the reverse order.

It is suggested that these observations may find application for the distillation of substances which are decomposed by heat, when taken up under pressure in a suitable gaseous medium and redistilling by relieving the pressure might, in some cases, prove more advantageous than distilling in a vacuum.

3. Oxidation, Combustion and Explosion of Ethylene

Schutzenberger[66] noted that ethylene, heated to 400° with an insufficient quantity of oxygen for complete combustion, yielded formaldehyde. The exclusive production of formaldehyde, under the above conditions, is explained by Nef[67] on the assumption that the hydrocarbon is dissociated into methylene.

Bone and Andrew[68] investigated the effect of moisture on the interaction of hydrocarbons and oxygen. Two similar tubes containing, respectively, thoroughly dried and undried, equimolecular mixtures of a hydrocarbon (acetylene, ethylene, ethane) and oxygen, were heated under similar conditions for the same length of time, comparative experiments being also made with electrolytic gas dried and undried, in order to insure that the degree of dryness attained was such as would practically inhibit the combustion of hydrogen. It was found that the exclusion of moisture had little, if any, influence on the rate of oxidation of the hydrocarbons.

Bone and Drugman[69] found that when a paraffin undergoes combustion there is a considerable separation of carbon and a large formation of steam; the gaseous products contain, besides carbon dioxide and hydrogen, between 8–10 percent of methane and fair proportions of acetylene and ethylene. Evidently, the theory of preferential combustion of carbon does not hold in case of a saturated hydrocarbon.

Experiment with ethane, ethylene and acetylene shows that when ethylene or acetylene was exploded with oxygen, there was a sharp explosion, with no separation of carbon or condensation of moisture when product was cooled.

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

In case of ethane, a lurid flame filled the explosion bulb, accompanied by a dense cloud of carbon particles and formation of steam. The ratio P_2/P_1 of a nitrogen-free mixture at first to final was 1.5 instead of 2.5, as demonstrated by the relation

$$C_2H_6 + O_2 = 2CO + 3H_2.$$

The rinsings gave a formaldehyde reaction. The gaseous product contains acetylene, ethylene and about 10 percent of methane. The total heat evolved by the ethane was greater than that evolved by the ethylene.

When ethylene is exploded with less than its own volume of oxygen, it burns with a lurid flame, carbon separates and water condenses when products are cooled. The rinsings give a strong aldehydic reaction, and the gas contains both methane and unsaturated hydrocarbon. Even when large amounts of hydrogen were introduced according to $C_2H_4 + 4H_2 + O_2$, under various initial pressures, there is no separation of carbon, and only a slight condensation. A hydrocarbon does not appear to be decomposed to any great extent in the flame, much less resolved into its elements except in a limited amount of oxygen.

Lesher[70] found that a mixture as rich in hydrogen as

$C_2H_4 + O_2 + 8H_2$ could be exploded without the decomposition into carbon and without a trace of acetylene.

Bone, Drugman[71] and Andrew[72] ignited ethylene and oxygen in vessels having different surface areas per unit volume, with the view of discriminating between the various combustion products, it being argued that the greater the cooling effect of the walls of the containing vessel the larger will be the proportion of primary products of combustion. The results obtained were entirely in accord with the view previously put forward that combustion, both above and below the ignition point, involves the initial formation of hydroxylated molecules.

Lean and Bone[73] note the historical development of the study of explosive combustion.

Dalton,[74] on exploding equal volumes of ethylene and oxygen, noted an increase in volume from 200 to 300, carbonic oxide and hydrogen being formed.

In 1861, Kersten[75] obtained similar results on exploding ethylene with (1) electrolytic gas (2) deficiency of air. He found that carbonic oxide was formed before the hydrogen burnt.

Teclu[76] and Smithells and Ingle[77] (1892) observed in the ethylene-air flame interconal gases that there was some acetylene.

Similarly, V. B. Lewes[78] observed that in the inner zone of coal-gas flame, hydrocarbons are heated up by the combination of hydrocarbons and methane, and are resolved to acetylene which, at higher temperatures, break up into carbon and hydrogen.

W. G. Mixter,[79] investigating the combustion phenomena by means of a weak electric spark discharge, has proven that ethylene with oxygen can yield acetic acid besides other products as carbon dioxide, and that the pressure factor is highly important during the reaction.

Lean and Bone[80] describe a series of experiments, giving the results of explosive combustion under varying conditions. Mixtures of ethylene, with its own or a less volume of oxygen, were fired in a coil. Their results are in agreement with those of Dalton, Kersten and Mayer, and show that when fired with about its own volume of oxygen, ethylene yields mainly carbonic oxide and hydrogen as the final result; but they have also observed that methane, acetylene and carbon are produced.

The following are the tabulated results of the analyses:

	Starting mixture				
	C	D	E	F	G
Ethylene	56.03	54.18	49.77	48.64	49.41
Oxygen	39.46	41.52	45.81	45.84	47.69
Nitrogen	4.51	4.30	4.42	4.52	2.90

	Percent of reaction products				
	C	D	E	F	G
Unsaturated hydrocarbons	5.53	3.77	2.78	2.14	—
Methane	5.96	3.77	2.52	2.55	1.01
Carbon dioxide	1.63	2.80	1.24	0.94	0.33
Carbon monoxide	38.85	44.84	47.79	46.53	49.11
Hydrogen	43.30	41.72	43.32	45.35	48.78
Nitrogen	5.16	3.10	2.35	2.49	1.01

Lean and Bone's conclusions were:

(1) When ethylene is fired with its own volume of oxygen, carbon monoxide and hydrogen are eventually obtained,

$$C_2H_4 + O_2 = 2CO + 2H_2. \qquad (1)$$

(2) When ethylene is fired with less than its own volume of oxygen, methane is formed. The quantity formed increases as the oxygen decreases.

$$C_2H_4 = CH_4 + C \qquad (2)$$

or

$$2C_2H_4 + O_2 = 2CH_4 + 2CO.$$

(3) Carbon is liberated.

(4) Unsaturated hydrocarbons are formed, especially acetylene; from (1) and (2).

$$2C + 2H = C_2H_2.$$

Along these lines E. von Meyer[81] reports that acrolein, $CH_2 : CH.CHO$, is formed when ethylene is exploded with insufficient oxygen in a eudiometer. The odor is very distinct. 100 volumes of ethylene and 60 volumes of oxygen (one-fifth of that necessary for burning) were sparked. There was a separation of carbon and an increase of volume. The combustion could be seen with the eye, the speed being 300–350 or 400–450 mm per second, depending on the width of the apparatus used. The oxygen reacted with the carbon to form carbon monoxide. The equation is then

$$C_2H_4 + CO = C_3H_4O.$$

On the other hand, he was unable to get any acrolein by sparking C_2H_4 and CO. He was, however, of the opinion that the silent electric discharge would give acrolein according to the surmised equation.

Ozone reacts very vigorously with ethylene. Studies have been consequently made at low temperatures, notably by J. Drugman.[82] The mode of action of ozone on a saturated and an unsaturated hydrocarbon is very different. Ozone acts, at the ordinary temperature, very slowly on saturated hydrocarbons such as methane and ethane. The process is one of gradual hydroxylation. In the case of ethane, ethyl alcohol is the first product formed. The reaction in the case of an unsaturated hydrocarbon, such as ethylene, is instantaneous, even at temperatures far below 0° C. A very explosive addition compound is first formed, which decomposes extremely readily, giving oxidation products containing only one carbon atom. The carbon chain is broken at the double bond. Comparison with the results of Harries'[83] work on ozonides makes it appear probable that the addition product is an ozonide, but the decomposition of this is more complex than that usually obtained with a liquid or solid ozonide. The following equations probably represent the process:

$$(1)\ C_2H_4 + O_3 = C_2H_4O_3 = \begin{cases} (a)\ CH_2O + HCO_2H \\ (b)\ CH_2O + CO + H_2O \end{cases}$$

$$(2)\ C_2H_4O_3 + H_2O = 2CH_2O + H_2O_2$$

HCOOH, CH_2O, CO, H_2O_2 were all obtained.

Hauzeau and Renard[84] exploded ethylene in the cold with weakly ozonized oxygen, and found formic acid and carbon dioxide.

According to Otto,[85] ethylene, treated with ozonized oxygen containing less than 50 mg of ozone per liter, yielded acetaldehyde and acetic acid; neither ethyl alcohol nor glycol could be detected among the products of oxidation.

Berthelot and Gaudechon[86] have tried the ultraviolet rays on ethylene and oxygen. A 100-volt lamp at a distance of 4 cm produced, in four hours, the following compounds: carbon dioxide, carbon monoxide, acetylene and formic acid.

4. REACTIONS PROPER

(a) Simple Addition Reactions

The simple addition reactions are of more than ordinary interest because of the complexities that are made possible. It is certain that as soon as the commercial needs become evident, many processes will be built up which will find their points of originality in the simple reactions of ethylene.

A good instance of what is likely to happen is with the compounds of various inorganic acids with ethylene.

Berthelot[87] started a series of such researches and found that ethylene combines at 100° with strong hydrogen iodide and hydrogen bromide, but not with hydrogen chloride. The reactions were carried out in rather awkward apparatus and heating carried on for periods of 50–100 hours. Hydrogen bromide gave ethyl bromide much less readily than ethyl iodide, from hydrogen iodide and ethylene. The first reaction required 100 hours' heating at 100°, whereas the latter needed 50 hours at the same temperature. From 20 cc of saturated hydrogen iodide and 1 liter of gas he obtained 4 grams of ethyl iodide.

Such reactions are rather unsatisfactory, but results begin to look brighter when catalysts are used. For example, Landolph[88] reports the ready formation of ethyl bromide at 0° from ethylene and hydrogen bromide in the presence of aluminum bromide. The possibilities which become evident have not as yet been made real. Similarly with the addition of hypochlorous acid, Carius[89] obtained a small yield of addition product. Butleroff,[90] after some trouble, increased the yield, but only slightly. Carius used hypochlorous acid 2–3 percent concentration in cold water, working in the dark, and reported what he called "good yields." Butleroff, at best, obtained only one-third of the theoretical yield, the reactions running on for 70–80 hours at 12° C, obtaining 1 gram of glycol-chlorhydrin per liter of ethylene.

Subsequent to this, Umnova[91] has published some work on the action of higher ethylene hydrocarbons, which may be applied to the case of ethylene. The developments are still but fragmentary.

N. J. Demjanow[92] has a series of observations on the reactions of ethylene. With the oxides of nitrogen as N_2O_4 he obtained ethylene nitrosite, $C_2H_4.N_2O_3$, which, on reduction with tin and hydrochloric acid, gives ethylene diamine. With nitrogen pentoxide he obtained ethylene nitrate (or, as he calls it, ethylene-glycol-nitric acid-ester), $C_2H_4N_2O_6$, which interesting substance gives, on reduction, acetaldehyde, ethylene diamine and $CH_2OH.CH_2.NH_2$. He suggests the following structure for the compound, $O_2NO.H_2CCH_2.ONO_2$.

The formation of ethyl-sulphuric acid from ethylene and sulphuric acid is the only reaction that has been made good use of. Discovered by Faraday,[93] Hennel,[94] and developed in the hands of Berthelot,[95] it received great importance in recent times on a commercial scale.

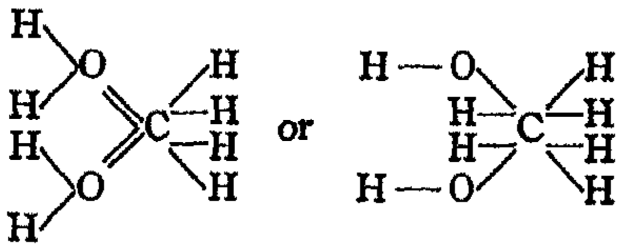
No record has been found as to the nature of the addition compound with phosphoric acid and other acids. Along these lines, deservedly or undeservedly, much more attention has been directed to the less important (it would seem) members of the ethylene family.

The reactions of ethylene with sulphuric acid and phosphoric acid lead to the subsequent formation by hydrolysis of alcohol or ether. (The commercial side of the question is too extensive to be treated here.)

According to Villard,[96] ethylene, like methane and acetylene, forms a hydrate with water. The pressures of the hydrate are 7 atm. at 0° and 58 atm. at +17°. The formula, apparently, has not been determined. If one were free to venture a guess, it might well be surmised to be $C_2H_4.4H_2O$. This would give a gradation:

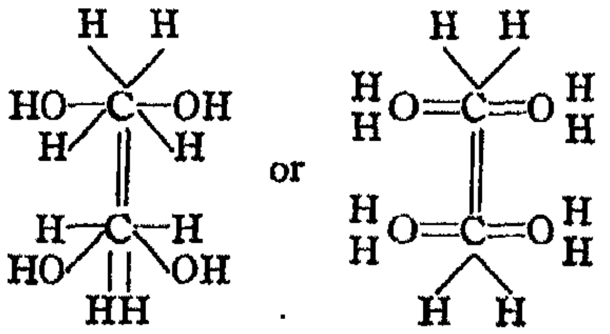
Methane	CH_4, $2H_2O$
Ethylene	C_2H_4, $4H_2O$
Acetylene	C_2H_2, $6H_2O$

The valency of carbon may be considered as 8, thus



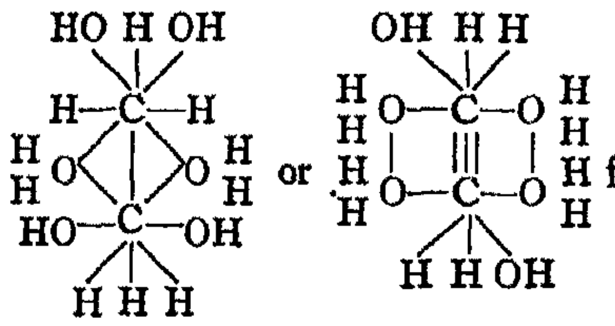
(Oxonium structure)

for the methane hydrate



(Oxonium structure)

for the ethylene hydrate



for the acetylene hydrate.

De Forcrand and Thomas[97] also report a mixed hydrate of ethylene, and carbon tetrachloride. In general, the mixed hydrates of acetylene, carbon dioxide and sulphur dioxide, with carbon tetrachloride, are more stable than the simple hydrates. Other halogen derivatives in place of carbon tetrachloride may be used.

Metallic salts also form quite a variegated number of compounds with ethylene. M. G. Kutscheroff[98] reports that a substance having the composition $2C_2H_4.HgCl_2.HgO$ is precipitated when ethylene acts on an aqueous solution of mercuric chloride. It is slightly soluble in water and in alcohol, easily soluble in alkalis, and regenerates ethylene when treated with acids.

Later, Hoffmann and Sand[99] made a rather comprehensive study of the behavior of mercuric salts toward olefins. Their conclusions were that by the action of ethylene on solutions of mercuric salts, compounds of the following kinds are obtained:

1. Ethenemercury salts $CH_2 : CH.HgX$
2. Ethanolmercury salts $OH.CH_2.CH_2.HgX$
3. Ethyl ether mercury $(C_2H_3HgX)n$

The formation of all compounds is explained on the supposition that the mercury salt HgX_2 splits up into the ions X and HgX, which then combine with the ethylene, converting it into the saturated compound $XHg.CH_2.CH_2X$. If this then loses the elements of hydrogen haloid, ethenemercury salts are obtained, while, if it undergoes hydrolysis, ethanolmercury salts result; and if this hydrolysis is only partial, condensation of the product of hydrolysis and the original compound, with loss of hydrogen haloid, gives rise to compounds of Type 3. Strong acids, especially hydrochloric, readily decompose all these compounds into ethylene and mercury salts. The addition of potassium iodide to the solution of ethylene in gradually neutralized mercuric nitrate gives rise, not to an ethenol derivative, but to ethenemercury iodide, $CH_2 : CH.HgI$, which separates from ethyl alcohol in beautiful, silver plates melting at 147°; it being readily soluble in hot alcohol, and suffers decomposition by the action of hydrochloric acid or potassium cyanide.

Buckton[100] found the following reaction taking place for mercury salts with ethylene, which are examples of the above type:

$$C_2H_4 + HgCl_2 \rightleftarrows Cl.Hg.C_2H_4.Cl$$
$$Cl.Hg.C_3H_4.Cl + H_2O \rightleftarrows Cl.Hg.C_2H_4.OH + HCl$$
$$C_2H_4 + Hg.(NO_3)_2 \rightleftarrows O_3N.Hg.C_2H_4.NO_3$$
$$O_3N.Hg.C_2H_4.NO_3 \rightleftarrows O_3N.Hg.C_2H_3 + HNO_3.$$

Schoeller, Schrauth and Essers,[101] working with mercuric acetate and alcohols as solvents, noticed that a suspension of 20 g $Hg(OAc)_2$ in 100 cc of methyl alcohol absorbs 1 mol. ethylene after 1 hour's shaking at 22° under 760 mm, the mercuric acetate dissolving completely, giving 14 g of acetatemercuriethyl methyl ether, $AcOHgCH_2CH_2OMe$, m. p. 42°, easily soluble in water and organic solvents, producing blisters on the skin; gives with diluted hydrochloric acid the chloride which decomposes in excess of hydrochloric acid, especially on gentle warming with evolution of ethylene. Towards acid, the ether is more stable, sodium hydroxide has no perceptible effect on it; ammonium sulphide gives a white amorphous sulphide which decomposes on standing, more quickly on warming, with formation of mercuric sulphide; $SnCl_2$ in alkali at once ppts. mercury; aqueous permanganate and iodine in ether are decolorized; potassium bromide in aqueous alcohol yields the bromide $BrHgCH_2CH_2OMe$ as needles, m. p. 58°. The iodide forms leaves which are quite unstable.

Further work may be found along similar lines by Sand[102] on the constitution of the compounds of ethylene and allyl alcohol with mercuric salts; also by Hofmann and Sand.[103] A general discussion of the chemical statics and kinetics of mercuric ethylene compounds is given by Sand and Breest.[104] An isolated study by Manchot and Brandt[105] on copper compounds states that ethylene forms a compound with cuprous chloride. The true structural formula has not been determined, as copper is not separated easily from carbon, nor does the chlorine break off from the carbon readily, hence $CuCH_2 — CH_2Cl$ is probably not the correct formula. In absence of water, cuprous chloride does not react with ethylene nor does combination occur in the presence of absolute ethyl alcohol.

According to Birnbaum,[106] a solution of platinum chloride in concentrated hydrochloric acid solution forms $C_2H_4PtCl_2$. The same compound is formed by boiling platinic chloride with alcohol, Zeise.[107] It is a yellow mass, slightly soluble in water and decomposed by light. In aqueous solution it is unstable unless hydrochloric acid is present. Potassium hydroxide precipitates on warming, an explosive powder. It formed the following combinations:

($NH_3C_2H_4PtCl_2$: Yellow precipitate) -- ($NH_4ClC_2H_4PtCl_2$ aq. : lemon-yellow prisms) - ($KClC_2H_4PtCl_2$ aq.-$KBrC_2H_4PtBr_2$ aq.: pale-yellow needles (Chojnacki[108]). - $C_2H_4Pt_2Cl_4(Et_3PO_3)_2$ (Schützenberger[109]).

The corresponding $NH_4ClC_2H_4IrCl_2$ and $(KClC_2H_4)_2IrCl_2$ may also be prepared (Sadler[110]).

When ethylene is passed into concentrated aqueous ferrous bromide in sunlight, there are formed greenish deliquescent crystals of $C_2H_4FeBr_2$ 2 aq. (Chojnacki[111]). The corresponding $C_2H_4FeCl_2$ 2 aq. is obtained by heating ether (50 g) with Fe_2Cl_6 (5 g), P (0.2 g) and CS_2 (0.4 g) at 100° (Kachler[112]).

According to Landolph,[113] ethylene and BFl_3 in the sunlight at 25°-30° gives $C_2H_3BFl_2$, b. p. 124-125°, sp. gr. 1.0478 at 23°. It is decomposed by water to boric acid and possibly ethylfluoride.

The effect of aluminum halides has been studied to some extent. Henderson and Gangloff[114] state that when aluminum chloride in alcohol is saturated with dry ethylene and allowed to stand in a closed vessel, crystals appear in five days; they are hygroscopic, soluble in most solvents, and decompose very easily, evolving ethylene. With acids, ethylene and hydrogen chloride are evolved on standing. Analysis indicates the composition $AlCl_3.3C_2H_4H_2O$. In a later study[115] they obtained the following ethylene compounds: $AlCl_3.C_2H_4.2C_2H_5OH$ and $AlCl_3.C_2H_4.CH_3OH.H_2O$.

G. Gustavson[116] obtained addition products with aluminum halides, and using also hydrogen halides. He states that when dry ethylene and hydrogen bromide are passed over aluminum bromide, a liquid product is obtained, together with a gas consisting of paraffins. A current of dry carbonic anhydride is passed through the liquid to remove free hydrogen bromide, ethylene and ethyl bromide. The compound, on analysis, was found to have the formula $AlBr_3.C_4H_8$. It is an orange-colored liquid, insoluble in light petroleum and carbon bisulphide and miscible with methyl bromide. Water decomposes it with formation of liquid unsaturated hydrocarbons, boiling between 150°–300°. An analogous compound, $AlCl_3.C_4H_8$, was obtained from aluminum chloride in a similar manner. The compound $AlBr_3.C_4H_8$ is also obtained by heating aluminum bromide (1 mol.) and ethyl bromide (4 mols.) at 60–70°. When treated with ethylene and hydrogen bromide at 0°, a gas is obtained, consisting of hydrocarbons, C_nH_{2n+2} with some unchanged ethylene. Beilstein[117] reports the formation of $C_4H_8AlBr_3$ at this temp. from C_2H_4, $AlBr_3$ and HBr. The utility of such researches is obvious in that, first, a convenient method for the absorption of ethylene may be developed. The decomposition of the compounds may give different and necessary compounds.

Various compounds and elementary gases form addition compounds with ethylene.

E. Lippmann[118] reports that phosgene will give chlorpropionylchloride ($C_3H_4OCl_2$), which compound, when hydrolyzed with water, gives hydrogen chloride and monochlorpropionic acid. The formation of this compound, like that of phosgene, occurs in the sunlight.

Chloride of sulphur, according to Guthrie[119] and Spring and Lecrenier,[120] forms $S_2(CH_2.CH_2Cl)_2$, also $C_2H_4.SCl_2$.

Chlorine monoxide forms chiefly chlor-ethyl-chloroacetate, $CH_2Cl.CO.O.CH_2CH_2Cl$, along with ethylene chloride, as stated by Mulder and Bremer.[121]

According to Beilstein,[122] chlorine dioxide gives chloroacetic acid, and hypochlorous anhydride gives $C_2H_2ClO_2$, C_2H_4Cl.

In the dark according to Fürst,[122a] a mixture of chlorine dioxide and ethylene remains unaltered, but in diffused daylight quickly becomes colorless, forming oil drops which solidify over sulphuric acid. By carefully neutralizing with calcium carbonate, yields of crystals of calcium glycollate are formed. This is formed by the decomposition of monochloracetic acid, which, in its turn, is derived from monochloracetyl chloride, the primary product of the reaction of the gases

$$2ClO_2 + C_2H_4 \longrightarrow C_2H_4ClOCl + H_2O + O_2.$$

Combinations with Other Hydrocarbons

Ethylene may be made to combine with other hydrocarbons. Berthelot[123] reports that ethylene, when heated in a glass tube to dull redness with an equal volume of acetylene, appears to form butylene. He also stated that the hydrocarbons thus obtained are identical with erythrene or pyrrolylene (divinyl : 1 : 3-Butadiene; $CH_2 : CH.CH : CH_2$). In one-half hour, 66 cc of each of the gases, acetylene and ethylene, combined.

The reactions with cyclic hydrocarbons are, in general, similar; a splitting off of hydrogen, however, occurring at the time of combination.

Barbier[124] obtained thus, by a heat reaction, anthracene from ethylene and diphenyl. He also reports the formation of phenanthrene from benzene and ethylene. He writes the diphenyl reaction

$$C_2H_4 + C_{12}H_{10} = C_{12}H_8,C_2H_2 + 2H_2.$$

Ferko[125] obtained styrene from toluene vapor and ethylene.

Berthelot obtained styrene, using benzene instead of toluene. He also recovered anthracene and naphthalene. Styrolene, naphthalene and anthracene are obtained at a red heat. A typical equation is

$$C_6H_6 + C_2H_4 = C_8H_8 + H_2.$$

For the formation of naphthalene, the equation would be

$$C_6H_6 + 2C_2H_4 = C_{10}H_8 + 3H_2.$$

For anthracene

$$2C_6H_6 + C_2H_4 = C_{14}H_{10} + 3H_2.$$

Berthelot[128] also mentions a hydrocarbon, boiling at 260°, formed probably from three molecules of ethylene and one of benzene. Ferko, who did not use temperatures as high as Berthelot, recovered no naphthalene in the benzene experiment. Some of his results on benzene, toluene, and naphthalene reactions with ethylene follow:

1.5 : 1 Benzene and Ethylene

Unchanged	80 g
Styrol	17 g
Diphenyl	300 g
Phenanthrene	10 g
Anthracene	15 g

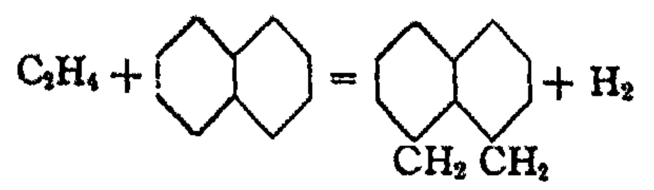
Toluene $1^1/_4$: 1 Ethylene

Benzene	200 g
Toluene	160 g
Styrol	10 g
Naphthalene	35 g
Oil (b. p. 270°–280°)	13 g
Anthracene	20 g

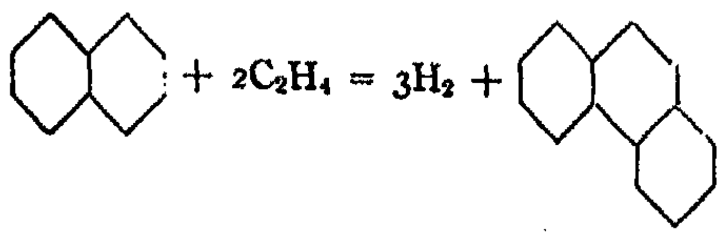
Naphthalene and Ethylene from "Good Naphthalene"

Unchanged	400 g
Acenaphthene	0.5 g
Phenanthrene	1 g
Dinaphthylene	125 g

The formation of acenaphthene is explained as follows:



For the formation of phenanthrene from naphthalene:



b. OXIDATIONS

Reactions with Oxidizing Acids

Watts[127] mentions the fact that fuming nitric acid absorbs ethylene, forming oxalic acid. The action of dilute acid apparently has not been studied.

Baumstark,[128] working with chlorosulphuric acid ($ClSO_3H$), states that it absorbs dry ethylene with rise of temperature; at 90° isethionic anhydride, $C_2H_4SO_3$, is formed, but if the sulphuric chlorhydrin be kept cool and the product poured into water, an oil, $C_2H_5SO_3Cl$ (154° b. p.), smelling like mustard oil, is obtained; this oil is converted by water at 100° into isethionic acid, and by dry ammonia into deliquescent tables of $C_2H_7NSO_3$.

Ludwig[129] has stated that chromic acid solution oxidizes ethylene to carbon dioxide, whereas Othmar and Zeidler[130] report the formation chiefly of oxalic and acetic acids. Chapman and Thorpe[131] reported the complete oxidation to water and carbon dioxide in a sealed tube, formic and acetic acids, too, being formed at ordinary temperatures. The action is weak for dilute solutions, more formic acid relatively being formed than for strong solutions. Berthelot[132] further reports the formation of some acetaldehyde. Working with a concentrated solution of chromic acid he obtained at 100° for many hours no effect; even carbon dioxide was not given off. At 120°, however, he recovered aldehyde, but did not state the yield obtained.

Truchot[133] and Berthelot[134] report that a potassium permanganate solution containing sulphuric acid is decolorized by ethylene and carbon dioxide, formic and acetic acids being formed. Neutral and alkaline potassium permanganate form chiefly oxalic acid and carbon dioxide, together with a little formic acid.

Wagner[135] states that neutral potassium permanganate acting on ethylene also gives glycol. He also reports formic acid but not a trace of acetic acid. This contradicts Zeidler's work. Since in neutral solutions glycols do not turn to aldehydes or ketones, it is possible that Zeidler obtained acetic acid because he distilled with sulphuric acid.

Zeidler and Othmar reported:

Chromic acid at 100° gave carbon dioxide, acetylene and perhaps some aldehyde and a little of formic and acetic acids.

Chromic acid with sulphuric acid gave carbon dioxide, formic and acetic acids, possibly aldehyde and oxalic acid.

From $2^1/_2$ liters of ethylene they obtained, using neutral potassium permanganate, 1.6 g calcium oxalate and some formic acid.

$KMnO_4$ and H_2SO_4 gave traces of oxalic acid, carbon dioxide, formic and acetic acids.

$KMnO_4$ and NaOH gave oxalic acid, carbon dioxide, formic acid and acetaldehyde.

Berthelot[136], using very concentrated (fuming?) nitric acid, forms $C_2H_4N_2O_5$ with ethylene.

According to Butlerow,[137] with sulphuric anhydride ethylene forms carbyl sulphate, $C_2H_4(SO_3)_2$. The formation of ethyl sulphuric acid by heating concentrated sulphuric acid at 160°–170°, or fuming sulphuric acid in the cold with ethylene, was noted by Butlerow[138] although the first observations were made by Faraday[139] and Hennel.[140]

C. OTHER COMPOUNDS

Reactions with Carbon Dioxide

An observation, which has not been sufficiently exploited, was made by Schützenberger[141] that ethylene and carbon dioxide react at 400° to give acetaldehyde.

Reaction with Nitrogen

Reactions of ethylene with nitrogen in itself has not been particularly studied. Berthelot[142] reports the formation of hydrocyanic acid. This indicates that of the numerous patents for the manufacture of synthetic cyanides from hydrocarbons, ethylene may well be used.

Schützenberger[143] also reports the formation of hydrocyanic acid.

d. HALOGENATION OF ETHYLENE

Ethylene burns in chlorine with a smoky flame, $C_2H_4 + 2Cl_2 = 2C + 4CHl$. In the dark and in the cold, however, it forms $C_2H_4Cl_2$, sometimes called "Dutch liquid." It was discovered by four Dutch chemists, van Deimann, Paets van, Troostwyk, Bondt and Lauwerburg,[144] who also discovered ethylene.

Other ways of producing it are described by Liebig,[145] Dumas,[146] Wöhler,[147] Laurent,[148] Regnault,[149] Limpricht,[150] Malaguti,[151] and Pierre.[152] By admitting ordinary ethylene and moist chlorine simultaneously into a large globe, ethylene dichloride is produced. It may be prepared by passing ethylene through a slightly heated mixture of manganese dioxide, sodium chloride and sulphuric acid, which is generating chlorine. It is also formed by passing ethylene into antimony pentachloride. Smythe[153a] combines ethylene and chlorine in the presence of calcium chloride, which he believes is analogous to chlorination by means of sunlight.

Balard,[153] Löwig,[154] Serullas,[155] D'Arcet,[156] Regnault,[157] and Hofmann,[158] Read and Williams,[159] describe the action of bromine on ethylene, Erlenmeyer and Bunte[160] give a convenient laboratory procedure, E. B. R. Prideaux[161] has devised an apparatus using the principle of counter currents for large-scale laboratory production. The ethylene is prepared by passing ethyl alcohol vapor through phosphoric acid in three flasks connected in parallel. It meets the bromine in a nearly horizontal condenser. The apparatus has the advantages of continuous operation, complete conversion and yielding the product free from bromine.

Faraday[162] describes the direct combination of iodine and ethylene in sunshine. Regnault[163] produced the same result by heating to 60°. An interesting mode of preparation is given by Semenoff,[164] who saturated a pasty mixture of iodine and absolute alcohol with ethylene, agitating and adding fresh quantities of iodine from time to time. Other halogen derivatives (chlorine) of ethylene, which, however, are not made from ethylene, have had commercial applications as solvents and as substitutes for benzene, and as analytical reagents.

Clarke, Meyers and Acree,[165] in a study of the ethylene electrode, gave preliminary experiments to determine whether ethylene combines with bromine, chlorine, hydrogen, etc., through electronic transfer which could be used to develop an e. m. f. A cell was set up as follows:

$$C_2H_4 - Pt - 0.1\ N\ HCl \text{ ——— } 0.1\ N\ HCl - Pt - Cl_2$$

The reaction could be represented by

$$CH_2 : CH_2 + Cl_2 \longrightarrow CH_2^+ CH_2^+ + 2Cl^- \longrightarrow CH_2.Cl.CH_2.Cl.$$

The properties of halogen derivatives of ethylene are given by Staedel[166] and Denzel.[167]

The chlorine derivatives may be made in many ways other than the direct combination of ethylene with chlorine which cannot be considered here.

Boron fluoride, it was claimed by Landolph,[168] at 30° in sunlight forms $C_2H_3BF_2$, an ethereal liquid (125°), d. (23°) 1.0478, V. D. 2.55, and which fumes in the air. It is decomposed by water into ethylene, boric acid and hydrogen fluoride. This "fluoboroethylene" reacts with camphor at 200° to form a hydrocarbon of empirical formula $C_{12}H_{18}$.

In 1894, however, Gasselin[169] repeated some of the work of Landolph without checking him at all points. Genther and Thorpe[170] showed that ethylene and dry iodonechlorine form ethylene dichloride and iodine.

Ross and Race[171] reported that ethylene practically does not react with n/100 iodine solution; however, with strong iodine in potassium iodide it is gradually absorbed, forming $C_2H_4I_2$ but complete absorption takes weeks.

B. T. Brooks and D. F. Smith.[172] In the thermal decomposition of gas oil, the oil gas formed is subjected to liquefication and then distilled to recover ethylene and propylene free of hydrogen and methane. The ethylene and propylene with chlorine are passed through solvents as $CHCl_3$, CCl_4, CS_2, $C_2H_2Cl_4$, in which ethylene dichloride and propylene dichloride are formed.

C. THE FORMATION OF ETHYLENE IN CHEMICAL REACTIONS BY DECOMPOSITION

1. Formation by Electrolysis

Acetates, succinates, malonates, and propionates have given among their decomposition products on electrolysis, ethylene and other hydrocarbons. Apparently no other organic acids or their salts have been investigated.

In 1868 Bourgoin,[173] on electrolyzing an alkaline solution of potassium acetate, obtained the formate and proved the presence of ethane and ethylene. He thereby demonstrated the mode of occurrence of characteristic oxidations, indicated by Löb[174] as follows:

$$\begin{array}{ll} CH_3 + CO & \\ & O - O = 2CO_2 + C_2H_6 \\ CH_3 + CO & \end{array}$$

Shortly after, Kolbe and Kämpf[175] checked the results, and reported besides, ethylene, ethane, and carbon dioxide, also acetic methyl ester and formic methyl ester at the anode.

Hopfgartner,[176] upon electrolyzing sodium acetate, recovered methyl acetate, 49.28 percent carbon dioxide; 1.17 percent ethylene; 21.06 percent ethane; 0.16 percent oxygen and 27.85 percent hydrogen. Potassium acetate gave similar values.

From propionates the yield of gases was 45.74 percent carbon dioxide; 8.01 percent ethylene; 0.16 percent oxygen; 15.24 percent butane; and 31.07 percent hydrogen.

As the temperature conditions were increased the ethylene yield decreased, whereas with increase of current density greater yields of ethylene were obtained.

In general, for the electrolysis of acetic acid, Petersen[177] writes five equations:

I. $2CH_3COOH = 2CH_3COO + H_2$
II. $2CH_3COO + H_2O = 2CH_3COOH + O$
III. $2CH_3COO = C_2H_6 + 2CO_2$
IV. $2CH_3COO = CH_3COOCH_3 + CO_2$
V. $2CH_3COO + O = C_2H_4 + H_2O + 2CO_2$

Equations I and III predominate, but V is always traceable. Concentration, current density and temperature have an important bearing on the reactions. In any case the yield of ethylene is small. For example, after 331 hours of electrolysis the author obtained only 3 cc of ethylene bromide.

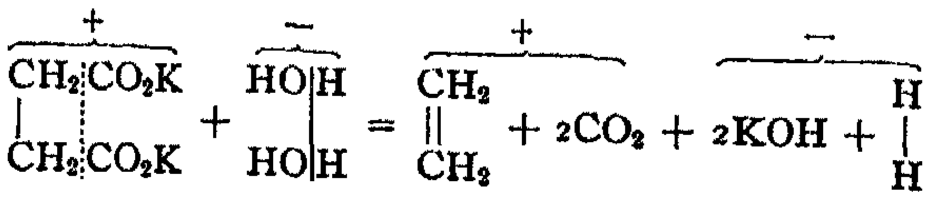
Similarly, for the electrolysis of a slightly acid solution of potassium succinate, Petersen's[178] formulation is:.

I. $C_2H_4(COOH)_2 = C_2H_4(COO)_2 + H_2$
II. $C_2H_4(COO)_2 + H_2O = C_2H_4(COOH)_2 + O$
III. $C_2H_4(COO)_2 = C_2H_4 + 2CO_2$

In this case particularly, small variations in the conditions of the experiment, as well as in the degree of acidity, the temperature, and the kind and size of electrodes exert a great influence on the course of the electrolysis. For example, an increase of concentration of the salt from 5 percent to 40 percent causes the ethylene yield to jump from 0.25 percent to 23.70 percent at 0° C. An increase of current from 5 amperes to 6.3 amperes causes the ethylene yield to change from 2.9 percent to 11.03 percent for a 20 percent solution at 0° C.

A similar electrolysis of a succinate in alkaline solution is reported by Clarke and Smith,[179] to have given not only oxygen, carbon monoxide, carbon dioxide, ethylene and methane, but also tartaric and oxalic acids.

Richter[180] writes for the electrolysis of concentrated potassium succinate:



$$\overbrace{\begin{array}{l}CH_2\vdots CO_2K\\ |\quad\ \vdots\\ CH_2\vdots CO_2K\end{array}}^{+} + \overbrace{\begin{array}{l|l}HO&H\\ &\\ HO&H\end{array}}^{-} = \overbrace{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + 2CO_2}^{+} + \overbrace{2KOH + \begin{array}{c}H\\ |\\ H\end{array}}^{-}$$

Kekule[181] also electrolyzed a concentrated solution of sodium succinate. Miller,[182] in electrolyzing malonates, was able to detect some ethylene. Petersen's[183] equation therefore is

$$2CH_2(COO)_2 = C_2H_4 + 4CO_2.$$

Bunge[184] observed a similar formation in electrolyzing a neutral solution of potassium propionate. Jahn,[185] working with concentrated solutions of sodium propionate, obtained, when the density of the current was not too great, hydrogen, ethylene, carbon dioxide, and a little butane. His results were again confirmed by Petersen,[186] who noted further that the amount of ethylene formed increased with increased dilution to a maximum which is reached at a concentration of the electrolyte corresponding to about 14 percent of sodium propionate.

The following equations indicate what goes on:

I. $2C_2H_5COOH = 2C_2H_5COO + H_2$
II. $2C_2H_5COO + H_2O = C_2H_5COOH + O$
III. $2C_2H_5COO = C_4H_{10} + 2CO_2$
IV. $2C_2H_5COO = C_2H_5COOC_2H_5 + CO_2$
V. $2C_2H_5COO + O = 2C_2H_4 + H_2O + CO_2$

Apparently all of the electrolyses are of similar type.

In all cases the acid radical decomposes into a saturated hydrocarbon and into carbon dioxide, or by oxidation to water, an unsaturated hydrocarbon (olefin) and carbon dioxide. We have here, then, a general method for the formation of hydrocarbons of two series. Here is an opportunity of working up the methods by a proper study of all the conditions, and to throw some added light on the subject of the electrolysis of organic acids.

The chances for commercial application, however, are, as a rule, small, because electrolysis of such solutions is not very economical. Not only the value of the product sought would have to be quite high, but also the difficulties of making it by other methods insurmountable, for electrolysis to claim its own at present.

2. Formation by Simple Decomposition of Compounds other than Alcohol

Reiset and Millon[187] state that by the thermal decomposition of ether passed through glowing tubes, they obtained ethylene, acetaldehyde, hydrogen and water. At 300°–350° no decomposition of ether vapors occurred. Wilde[188] found that ethyl ether under reduced pressure gave ethylene, carbon, and other gases.

Liebig[189] observed also the formation of methane under the above conditions; and Jahn[190] was able to break up ether at 300°–350° by using zinc dust as a catalyst. He obtained ethylene, hydrogen and a little methane and carbon monoxide. Various other organic compounds yield ethylene. Worstall and Burwell[191] report ethylene among the products obtained on heating the vapor of heptane to 900°.

Ipatieff and Dowgelewitch[192] found ethylene as a product from the thermal decomposition of hexane.

Noyes[193] passed isobutylene through a tube heated to a dark red and recovered methane, ethylene, propylene, C_4H_6, benzene, toluene and naphthalene.

Berthelot[194] thermally decomposed pure ethane and at the beginning of the experiment giving small yields of acetylene and ethylene, which at the end of the experiment gave polymerization hydrocarbon products, as $C_{10}H_{18}$. Stepski[195] formed it by passing *n*-hexane or isobutyl alcohol mixed with air over heated platinum. Ipatieff[196] reported that ethane and ethylene are among the products of heat decomposition of isopropyl and isoamyl alcohols. He found that isoamyl alcohol, in the presence of zinc dust and pumice or pieces of "so-called" graphite crucible, at a temperature between 380°–420°, decomposes almost completely to ethylene.

The "graphite" catalyst consists of clay, graphite and a small amount of iron and other impurities. *Pure graphite* free of iron possessed no catalytic action.

Wurtz[197] obtained both ethylene and acetylene from the decomposition of the vapor of amyl alcohol.

Haber[198] gives the following figures for the decomposition of trimethylethylene at 930°–940°:

	Percent
CH_4	27.72
C_2H_4	8.10
H_2	1.76
Gaseous by prod.	4.96
C_2H_2	0.30
C	5.09
C_6H_6	8.00–13.41
Tar	33.71–39.12

Olefines were obtained by cracking quite a number of paraffins.

Müller[199] obtained ethylene by decomposition of *phenol* and *cresol*. He explains the formation of oil gas by reactions of the following type:

$$\left.\begin{array}{l}C_6H_5CH_3\\ \\C_6H_5CH_3\end{array}\right| = \left|\begin{array}{l}C_6H_6\\ \\C_6H_6\end{array}\right. + C_2H_4$$

One of his decomposition examples is:

Gas from Creosote Oil

	Percent
CO_2	0.2
C_nH_{2n}	2.0
CO	36.5
H_2	26.3
CH_4, etc.	21.7
Air	13.3

Watts[200] states that upon the dry distillation of barium formate, ethylene, together with methane and butylene, was found.

An important decomposition product of acetone was discovered by Schmidlin and Bergman,[201] which showed a 10–14 percent yield of ketenes at 500° to 600°, but at a higher temperature a secondary reaction takes place as follows:

1. 500°–600°:

$$2CH_3.CO.CH_3 \longrightarrow 2CH_2 : CO + 2CH_4$$

2. At higher temp.:

$$2CH_2 = CO \longrightarrow 2CO + C_2H_4$$

Sabatier and Mailhe[202] worked out a metallic oxide decomposition of organic esters forming ethylene as one of the products.

$$C_6H_5COOC_2H_5 + (ThO_2)\ 400° \longrightarrow C_6H_5COOH + C_2H.$$

Ebelmen[203] heats (1 pt.) alcohol with fused (4 pt.) B_2O_3, forming ethylene.

Dilthey[204] gets both ethylene and ethane among the products of the dry distillation of the calcium salt of isovaleric acid. From 100 g of the material he obtained about 5 liters of gas, which analyzed:

	Percent
CO	23.00
H_2	23.40
CH_4	20.97
C_2H_6	20.61

and 5.5 g of olefin bromides, principally of propylene and a little of ethylene.

Gossin[205] reports ethylene among products of distillation of calcium lactate.

A. Perrot[206] noted that ethylene is among the products formed by passing methyl chloride through a hot tube (porcelain). He obtained it along with naphthalene, methane, carbon monoxide, etc.

Joist[207] also observed that acetyl chloride breaks up on heating.

$$2CH_3COCl = 2HCl + 2CO + C_2H_4.$$

The decomposition of ether and of the alcohols, both aliphatic and cyclic, is clearly in essence similar to that of ethyl alcohol itself, plus an added reaction. The production of ethylene from the salts of fatty acids, and from methyl chlorides, seems to depend simply on the possible ways in which those compounds can split up and not necessarily on the fact that they may be derivatives of ethylene. Reversing the reaction would be a difficult matter. The decomposition of acetyl chloride, however, does show chances of reversibility, and acetyl chloride is in a sense a double addition product of ethylene, and hence the reaction is of the type of the splitting up of alcohol.

8. Formation by Double Decomposition

Ethylene from inorganic sources has been of considerable interest, in that the aim was to produce alcohol. Now it is more important that acetic acid be produced. A short review on the production of ethylene via acetylene from carbides is given by Tucker and Moody.[208]

Mixtures of aluminum carbide and calcium carbide were used with water for the formation of ethylene, but only methane and acetylene were obtained. Trials were made with a charge of 100 g of witherite, 60 g silica and 43 g of coke. This was mixed with a carbide charge of 150 g of witherite and 25 g of coke, both mixtures being incorporated and subjected to heat at 150 amp. and 60 volts for seven minutes. The product was blackish, gave off gas slowly in cold water, but vigorously in warm water. Fifty cc of this gas was found to contain 15 percent ethylene (average 8–15 percent). An increase of the carbide content diminished the quantity of ethylene to 2 percent, and a decrease of the carbide content to a fraction of 1 percent. Substitution of strontianite for witherite, with increase of heating and the presence of an oxidizing agent such as chromic acid, had no effect. The use of calcium instead of barium brought the yield down to 2 percent of ethylene. In the reaction the use of dilute acids is undesirable.

According to Berthelot,[209] cerium, lanthanum, yttrium and uranium carbides give ethylene along with other gases by interaction with water. Moissan[210] obtained similar results, especially uranium carbide giving good yields. This probably is of little significance from a commercial point of view, but may throw considerable light on the development of a catalyzer in reactions of a different type leading to the synthesis of ethylene.

To Lefebvre[211] we owe an interesting observation as to the effect of passing methyl alcohol, ethyl alcohol, isobutyl alcohol, or amyl alcohol instead of water over calcium carbide heated to 500° C. In such cases there is a formation of ethylene and acetylene, due no doubt to the dehydration of the alcohols, their heat decomposition, and the reaction of the carbide with water.

The formation of ethylene from the halogen derivatives of ethane is of interest simply in the preparation of the pure gas for laboratory purposes. The conditions of ethylene formation have been worked out by Sabaneyeff[212] for very pure gas by the action of zinc on ethylene dibromide.

Gladstone[213] uses the same method, but has copper present in the dilute alcoholic solution of ethylene bromide and regulates by cooling.

Nef[214] obtained ethylene from carbon tetrabromide, by acting on it with excess of alcoholic potash. This was mixed with carbon monoxide, the total yield of gas being 175 cc from 5 g of tetrabromide.

Very early work done by Hermann[215] on bromoform showed that with alcoholic potash ethylene was formed. The reaction is very violent when the concentration is large. Long's[216] experiments established the fact that the proportion of carbon monoxide and ethylene is about 3 : 1 for any concentration of reagents used. This indicates the proportion in which the three components react. The ethylene no doubt comes here as well as in Nef's reaction from the alcohol, which is easily dehydrated under these circumstances.

P. Schorigin[217] found that sodium alkyls and ethers formed ethylene as one of the products according to the following reaction:

$$Hg(C_2H_5)_2 + 2Na + 2(C_2H_5)O \longrightarrow$$

$$Hg + 2C_2H_5OH + 2C_2H_4 + 2C_2H_6$$

$$2Hg + 2C_2H_5Na \longrightarrow 2NaHg + C_2H_4 + C_2H_6$$

$$2C_2H_5Na + (C_2H_5)_2O \longrightarrow C_2H_5ONa + C_2H_6 + C_2H_4$$

Berthelot[218] notes that ethylene is among the products formed by passing a mixture of carbon disulphide with hydrogen sulphide and phosphine over heated copper. Besides he[219] observed methane and hydrogen in the proportion of 1 : 5 to 1 : 3 and naphthalene, etc. Similarly passing the above mixture over iron at a dark red heat he obtained the same products. However, more ethylene was formed when carbon monoxide was added instead of phosphine. It seems that no clear explanation of this has been suggested. Possibly the temperature of reaction is just right for the formation of ethylene.

Le Bel and Greene[220] carried out a series of experiments with zinc chloride. When alcohol is dropped on heated zinc chloride, hydrogen, a trace of ethane, mostly ethylene, considerable aldehyde, traces of ether, and a small quantity of liquid hydrocarbons are formed. Reduction, dehydration, and condensation go on at the same time. Experiment showed that the amount of aldehyde corresponded closely to the ethylene disengaged:

$$2C_2H_6O = C_2H_4O + C_2H_4 + H_2O + H_2$$

Similarly, methyl alcohol also gave a little ethylene. Acetone produced some. Acetic acid produced considerable ethylene, and aldehyde passed in a thin stream gave similar results.

Miller and Tschitschkin[221] showed that other organic acids may give ethylene, for example, azelaic acid on distillation with soda lime.

The general classical procedure in which two or more substances are made to interact in order to produce two or more other substances of which one is wanted, is then applicable by the above methods, to ethylene.

According to Tollens[222] ethylene is made from ethylene chloride $CH_3.CHCl_2$ and sodium. This method, even for laboratory purposes, is not as feasible as Sabaneyeff's. Frankland and Dobbie[223] record the following reaction:

$$2C_2H_5I + Zn = 2C_2H_4 + ZnI_2$$

H. Denham,[224] in synthesizing cupric iodide from cupric oxide and methyl iodide or ethyl iodide, obtained, besides ether, a mixture of gases containing oxygen, carbon monoxide, ethylene, methane and homologues. When ethyl iodide was used 50 percent ethylene was formed.

Formation from Acetylene Chemically

Ethylene has been made variously from acetylene. Moissan[225] reports a reduction by means of sodammonium.

In an interesting article on the production of ethylene from inorganic sources, Tucker and Moody[226] succeeded in obtaining ethylene by a reduction of acetylene as it is formed *in situ*. Barium silicide reacts with water and if this be intimately mixed with barium carbide, hydrogen so formed acts on the acetylene, and ethylene is produced. The mixture is obtained by heating in an electric furnace witherite, silica, and coke, and the gas produced by the action of water contains up to 15 percent of ethylene. On replacing the barium by a corresponding strontium or calcium mixture, the proportion of ethylene formed sinks to 5 percent in the former case and 2 percent in the latter.

Ethylene, according to a patented process by Atterbury,[227] is formed by the reduction of copper acetylide with zinc. Acetylene, produced from carbide or otherwise, is passed into a vessel containing finely divided copper or a copper compound or other suitable metal or metallic compound in suspension in water—or carbide is added to the water containing the copper; and acetylene generated *in situ*. Copper acetylide is thus formed, and for the production of ethylene this compound may be transferred to another vessel containing water, where it is mixed with zinc, in order to decompose it by means of nascent hydrogen. For this purpose the copper acetylide is mixed with the decomposing chemical, either alone or together with oxide, hydrate, or carbonate of one of the metals, alkali or alkaline earths.

The use of chromous salts is patented by Coudert[228] for the manufacture of alcohol, via ethylene. Acetylene obtained from calcium carbide is brought into contact with a solution of reducing salt, such as the double ammonium chromous sulphate, ethylene being produced which is absorbed by sulphuric acid.

After the addition of water to the solution of ethylsulphuric acid, alcohol is obtained by distillation. The reducing agent is regenerated by the action of nascent hydrogen electrolytically produced. A suitable apparatus is also described.

An application of the above is found in the Villon[229] process for the manufacture of alcohol. The raw materials are limestone and coke, which are ground together and heated in an electric furnace. The calcium carbide obtained is decomposed with water in the usual manner, and the acetylene converted into ethylene by allowing it to pass through a solution of chromium and ammonium sulphates, maintained at a temperature of 40° C. The ethylene is absorbed in sulphuric acid and the hydrogen ethylsulphate produced is distilled upon the addition of water. The ethyl alcohol obtained in the distillate is stated to be of a very pure character.

Along similar lines there are several patents by Traube:[230,231,232]

(1) In the manufacture of ethylene from acetylene, with the aid of chromite in acid medium, the chromite being added in theoretically insufficient amount, the chromium compound is regenerated by a suitable reducing process.

(2) Acetylene is reduced with chromous chloride and the like in acid medium.

(3) Acetylene is reduced to ethylene under pressure with hydrogen chloride, chromous chloride and zinc.

D. THE DECOMPOSITION OF ETHYLENE

1. Heat Decomposition

Dalton[233] was the first to notice formation of carbon and hydrogen from ethylene. March and Magnus[234] had noticed that ethylene decomposed on heating to carbon, hydrogen and methane. Berthelot[235] noticed also ethane and acetylene. Magnus obtained about 90 percent methane at red heat and almost pure hydrogen at white heat. Berthelot[236,7,8,9,40] mentioned similar results in several communications, and found that 100 C_2H_4 gave 25.15 H_2; 4.35 C_2H_4; $(C_8H_{14})_n$ and formerly obtained a fluid $C_{20}H_{16}$.

Before the work of Day,[241] investigators satisfied themselves almost entirely with very approximate estimates of the temperatures of decomposition of hydrocarbons. By regulating the supply of gas to a furnace and by means of the mercury in the pressure gauge of an air thermometer, which at the same time registered the temperature, Day[212] found that ethylene may be heated at 344° for several hours continuously without change of volume or of odor. At 350°-355° the gas slowly suffers contraction, amounting to about 1/20, and acquires an odor of impure kerosene; it is free, however, from marsh-gas or hydrogen, and the new product is, therefore, a simple condensation product. Heated at 400°-408° for 171 hours, the contraction amounted to a little more than one-half, and a few drops of liquid were formed. This combined readily with bromine, and no benzene was present. The residual gas was free of hydrogen, and contained in 62.7 volumes: ethylene hydrocarbons, 15.6; ethane, 24.8; and methane, 23.3. At 450° ethylene is more rapidly acted upon, the action ceasing after 72 hours; a very slight amount of carbon being deposited. The residual gas of 55.67 volumes contained ethylene hydrocarbons, 15.37; ethane, 35.6; and methane, 4.7. He thus observed the formation, under 500°, of unsaturated condensation products, liquid and gaseous, a series of saturated hydrocarbons, and a small liberation of carbon, but no hydrogen.

That it is possible to obtain aromatic hydrocarbons from ethylene, but only after prolonged action, was demonstrated by Norton and Noyes.[213]

Ethylene was slowly passed through a hard glass tube heated to dull redness, the escaping gases passing through condensing tubes, ammoniacal cuprous chloride and bromine samples of the gases being ultimately collected. After a month, 15 cc of liquid had been condensed, and was found to contain benzene, naphthalene and anthracene; only a very slight precipitate was formed in the cuprous solution. There were about 300 g of bromides of unsaturated hydrocarbons, consisting largely of ethylene bromide, but methylene, propylene and butylene bromides were also present, as well as a solid bromide.

The solid bromide is identical in composition and properties with the crotonylene tetrabromide obtained from coal-gas and from oil-gas. The escaping gases consisted of methane and ethane. The authors believe that the aromatic hydrocarbons are formed directly from the ethylene without the intermediate formation of acetylene.

Present-day work on the catalytic condensation of ethylene seems to confirm this opinion, though more than one reaction may take place.

V. B. Lewes[311] performed an extensive series of experiments on ethylene. In these he passed ethylene, both alone and with hydrogen, and at various rates, through 140 mm of platinum tube 2 mm in diameter, heated to various temperatures, the temperatures being determined by a Le Chatelier platinum-rhodium pyrometer inserted in the tube. Experiments were also made to test the point which showed that platinum had no special action on the hot gases and could therefore be safely used. Experiments were also made on the effect of similar heating, upon methane, ethane and benzene and probable products of the reactions. Below 800° C practically no action takes place and at this temperature traces of acetylene were formed. Between 800°–900° C the ethylene decreases in quantity, and large quantities of methane are generated, accompanied by liquid products. This action increases until just below 1,200° C, when hydrogen begins to appear among the products of decomposition, while at the same moment deposition of carbon commences and the formation of oil begins to decrease, until at 1,500° the decomposition of ethylene is practically complete and the products are mainly hydrogen and carbon, with a little undecomposed methane. The quantity of acetylene polymerizing so readily between 900° and 1,300° C, produces the oils found. Methane was found to be very stable at 1,000° C, slowly decomposed between that and 1,300° C, and rapidly at 1,500°. Benzene began to decompose rapidly above 1,000°. Ethane decomposes even below 900° C with liberation of hydrogen and formation of ethylene and acetylene. This latter fact shows that ethane cannot be a primary decomposition product of ethylene, or hydrogen would have been formed below 1,200° C when that gas was heated. As the result of his experiments the author concludes that the primary action of heat on ethylene is expressed by the equation

$$3C_2H_4 = 2C_2H_2 + 2CH_4$$

while the final decomposition is

$$C_2H_4 = 2C + 2H_2,$$

and that between these two extremes there occur a large number of reactions due to the polymerization of the acetylene formed from the ethylene, and also at higher temperatures, from the methane, according to the equation

$$2CH_4 = C_2H_2 + 3H_2.$$

Thus the author showed that ethylene, when subjected to heat, was converted into acetylene and methane according to

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

the acetylene resulting therefrom either at once polymerizing into secondary products or decomposing, to carbon and hydrogen, according to the temperature at which the reaction is being conducted.

In many case of destructive distillation ethylene is one of the principal products; it is therefore of great importance to ascertain the precise causes of its formation. Another series of experiments[245] were instituted to ascertain the effect of:

1. Rate of flow.
2. Area of heated surface.
3. Dilution.

The apparatus and analytical methods were the same as those previously employed, except that the platinum tube was 736 mm long, with a diameter of 14 mm. Temperatures were, as before, measured by the Le Chatelier thermocouple.

The results of the numerous experiments may be summarized as follows: The initial decomposition of ethylene, by heat, is very rapid, and requires but a short flow through a heated zone; such primary decomposition, however, being but slowly completed, owing to secondary reactions, which tend to re-form ethylene, the decomposition, which nearly all occurred in the first inch tube, was as under different heated lengths and rates of flow in the following table:

PERCENTAGE OF ETHYLENE DECOMPOSITION

Length of tube heated	1 inch	6 inches	18 inches
Rate of flow 5 cc per min.	80.10%	85.48%	93.76%
Rate of flow 15 cc	70.83	79.42	90.31
Rate of flow 40 cc	50.58	63.17	87.15

Dilution has but little effect in retarding the amount of decomposition of ethylene, unless it be very large (over 75 percent). Increase in rate of flow diminishes the amount of decomposition, when the heated area is small, but rapidly diminished in effect as the rate of flow through a heated area increases. Radiant heat and not contact with heated surfaces, is the chief cause of the decomposition of ethylene.

That this is so is proved especially by the experiments, in which diluted ethylene is passed through the heated tube; for, if contact had been the active factor, dilution, by reducing the number of impacts of hydrocarbon molecules with the heated surface, would have led to a considerable decrease in the decomposition effects.

Bone and Coward[246] state that the ultimate resolution of a hydrocarbon into its elements at high temperature cannot be regarded in general as the immediate result of a chemical change was proved by Marchand.[247] Lewes concluded that ethylene was primarily resolved into equal volumes of acetylene and methane,

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that acetylene subsequently polymerizes or is resolved into its elements, according to the temperature used. Acetylene is the chief product of decomposition of ethylene but not of either methane or ethane. At comparatively low temperature acetylene exhibits a strong tendency to polymerize, forming benzene, etc. Tendency to polymerize reaches a maximum at 600°–700°, but there is little evidence of polymerization at 1,000°.

Acetylene exhibits a tendency to combine with hydrogen at low temperature, forming ethylene and ethane, but the importance of this factor, which is not very great, diminishes above 1,000°.

In cases of ethane and ethylene, the primary effect of high temperature is to cause an elimination of the bond between the carbon atoms giving rise to residues such as $:CH_2$ and $:CH$. These residues may subsequently form $H_2C:CH_2$ and $HC:CH$ or break down into carbon and hydrogen or be hydrogenized to methane.

Bone and Coward found, in an experiment of heating ethylene at 570°-580°, acetylene, methane, ethane, hydrogen and aromatic hydrocarbons formed, but at 900°, as shown in the following table, the time factor profoundly modifies the percentage of reaction product and indicates the course of the thermal decomposition of ethylene.

Time in minutes	1	5	15	60
Percent hydrogen	25.90	7.30	1.35	0.00
Percent acetylene	4.20	2.70	0.00	0.00
Percent ethylene	2.65	0.70	0.00	0.00
Percent ethane	15.00	35.30	37.65	43.00
Percent methane	52.25	54.00	61.00	57.00

2. Electro Decomposition of Ethylene

a. Spark Discharge.—Buff and Hofmann[248] were among the earliest experimenters on the effect of the spark discharge on ethylene. They used an inductive machine with platinum terminals and obtained the elements carbon and hydrogen. They did not find methane, quite evidently because the temperature was too high. They apparently noted the effect of pressure on the reaction without showing, however, that they were aware of the simple explanation. They remarked that "the reaction slows down as the rate of increase of the hydrogen formed."

Quet[249] reported similar results with a Ruhmkorff coil. Wilde,[250] in his experiments, thought that acetylene is first formed and then decomposed into its elements. At a somewhat later date, Dalton,[251] Hofmann and Buff[252] reiterated the observation that decomposition occurs into the elements. These effects, it may be observed, are *purely thermal.* The work of Thenard and Berthelot[253] with the spark discharge indicates an advance. They report besides the elements also a fluid and a solid product, without, however, identifying them. Thenard[254] found the solid product to be insoluble in all solvents.

b. Silent Electric Discharge.—Work of prime interest was initiated by S. Losanitsch and Milorad Z. Jovitschitsch,[255] who observed that unsaturated hydrocarbons are converted into polymeric substances. Thus ethylene yields a thick, yellow liquid $(C_2H_4)_n$, which boils above 200°. They used a current strength of 3·5 amperes with 70 volts(?). Considerably later we find Jovitschitsch[256] trying desperately to account for a mysterious deficiency of carbon in the condensation products of ethylene. That something remarkable occurs the following experiments attest: Pure dry ethylene and acetylene were in turn brought under the influence of the silent electric discharge, and the condensation product in each case analyzed.

The product obtained from ethylene was shown to have probably the formula $C_{30}H_{54}$ and to be a cyclic condensation product. It is oxidized by bromine in ethereal solution forming a brown, sticky product, which when heated with silver nitrate and nitric acid at 100° yields the silver salt of a nitro derivative.

When treated with nitric acid at 50°–60° the condensation product yields two nitro derivatives; one of $C_7H_{11}NO_2$ is soluble while the other, $C_6H_9NO_2$, is insoluble in hot alcohol.

The condensation product from acetylene is probably $C_{30}H_{26}$ and forms a dibromide, $C_{30}H_{26}Br_2$, with bromine at ordinary temperature, and it also reacts with fuming nitric acid, forming a product, $C_{30}H_{25}N_3O_{30}$.

Both products ($C_{30}H_{54}$ and $C_{30}H_{26}$) are strongly radioactive, which is ascribed to *a third element formed under the influence of the silent discharge upon ethylene and acetylene.*

The purest chemical reagents were employed in the combustions. From several determinations the percentage of carbon and hydrogen taken together fell below the theoretical 10 percent; in the case of the ethylene product a 7 percent and in that of the acetylene product a 22 percent deficiency was noted. This loss in the amount of hydrogen and carbon required by the formulas of hydrocarbons has been accounted for by Berthelot in the possibility of oxygen absorption from the atmosphere. However, the author has excluded this possibility by working with dry gases and preserving the products in hermetically sealed tubes immediately upon their formation. It is stated also that condensed ethylene loses no carbon on exposure to the air and that condensed acetylene is hardly affected by many weeks' standing. The analysis of the products from sealed tubes and those exposed for some time to the air were in agreement with each other. The possible intake of oxygen during the removal from the tubes is practically nil, owing to the rather insoluble nature of the compounds and the absence of any change in their appearance. These facts present us with a scientific riddle, a chemical anomaly, which, the author believes, can be explained only through experimental errors or through the *transformation of elements*. As great care and precision were taken in all of the determinations, the author is more convinced of the latter possibility, especially since these condensation products, notably that of acetylene, possess strong radioactive properties. These products, therefore, may be considered, not as simple hydrocarbons, but as compounds of these with known and unknown elements here brought into existence through the action of the silent electric discharge upon gaseous ethylene or acetylene.

Berthelot[257] has shown that a silent electric discharge acting upon saturated or unsaturated hydrocarbons will split off hydrogen in varying quantities from the molecules and instead of polymerization products, condensation products will result, and (confirmed by Losanitsch[258]) Jovitschitsch reports the work upon ethylene and acetylene under these conditions. The pure, dry gases were introduced into a synthetizer, an ozonizer with manometer attachment. In the case of ethylene the condensation product is soluble in ethyl alcohol, and ether gives a high mol. wt. of 420. This corresponds to a formula approaching $C_{30}H_{54}$. The action of bromine and nitric acid upon this product leads to its classification with cyclic compounds. The acetylene condensation product is extremely insoluble hence no mol. wt. determination could be directly obtained. The compound is similar in chemical properties to the preceding one, and is undoubtedly of ring structure. The deficiency in percentage of carbon in these compounds is worthy of note. An explanation for the same was given in the preceding paragraph.

Subsequent work, more successful at least as far as definiteness goes, has been done by means of catalyzers. The synthetic possibilities, arising from condensation reactions so favored by the silent discharge, merit much greater attention than has been paid to them heretofore.

E. 1. Catalytic Decomposition of Ethylene

Sabatier and Senderens[259] have practically monopolized the work on the catalytic decomposition of ethylene. In a long series of articles they investigated quite a series of products and conditions.

A layer of nickel reduced by hydrogen, if heated to 300° and upwards, completely decomposes pure, dry ethylene passed over it. The products are only carbon, hydrogen, and methane, in varying proportions, the hydrogen yield increasing with the temperature. Freshly reduced iron, copper, cobalt, and spongy platinum and palladium were inactive, and nickel filings less active than the reduced metal. The nickel and ethylene appear to form an unstable compound which decomposes into carbon, methane, and nickel; hydrogen being formed by a secondary reaction. The explanation offered by Moissan and Mauren of the decomposition of acetylene by reduced metals in the cold., *viz.*, that it was due to the heat of absorption of the gas, by the porous metal provoking decomposition of the endothermic gas, cannot apply in the present case.

When a slow current of pure ethylene is passed over the surface of nickel reduced by hydrogen, and heated to above 320° C, the gases obtained after removing traces of undecomposed ethylene by means of bromine are found to consist of a mixture of ethane, methane, and hydrogen, with possibly an infinitesimal trace of higher hydrocarbons.

When ethylene is passed with moderate rapidity over nickel previously reduced in hydrogen, and heated to a temperature not exceeding 325°, the issuing gas is a mixture of about 10 volumes of hydrogen with about 60 volumes of ethane and 30 volumes of methane. At higher temperatures the proportion of ethane diminished, and only traces remained when the temperature approached a dull red heat. It would seem that the first change in the decomposition of ethylene is into carbon and ethane, the latter, at higher temperature, being converted into carbon and methane, the methane ultimately splitting up into carbon and hydrogen. Direct experiments show that ethane is partially decomposed by nickel at 325°, and that pure methane is also decomposed, especially above 390°. A long column of nickel has practically the same effect on ethane as an increase of temperature, and even at 325° ethylene can be converted almost completely into methane, mixed with a small quantity of hydrogen. In order to prepare ethane, a mixture of hydrogen with an excess of ethylene is passed over reduced nickel, heated at a temperature not exceeding 150°, and the process may go on for several hours with a comparatively small quantity of nickel. The process has, therefore, the advantage over Wilde's[260] method, in which platinum is used but has to be continually renewed. Reduced cobalt, iron or copper cannot be substituted for the nickel. Under similar conditions, ethylene shows no tendency to combine with either water or ammonia.

Finely divided platinum and copper have no action on ethylene below 400°, but cobalt above 300° partially decomposes it into ethane, methane, and hydrogen, together with carbon, but without any acetylene. Iron above 350° has less action but decomposes a small part of the gas into ethane, hydrogen and carbon.

While nickel at 300° C acts readily on ethylene, depositing carbon, and giving a gaseous mixture of methane, ethane, and hydrogen, platinum black and copper have no action on it. Cobalt and iron, however, behave like nickel, only much more slowly; both metals need to be heated to about 400° C and even then action is slow, especially in the case of iron.

Analyses of gases using cobalt and iron:

	With cobalt	With iron
Ethylene	67.4	58.8
Ethane	13.4	4.8
Methane	4.4	
Hydrogen	14.8	9.4

A rather different type of catalysis of ethylene is described by Ipatieff and Rutala,[261]— a catalysis by zinc chloride leading to a very interesting polymerization, which no doubt throws some light on the polymerization in the silent electric discharge. Ethylene (40 liters) under 70 atm. in the presence of 5-6 g zinc chloride, begins to polymerize at 275°, the pressure decreasing for 50-60 hours, when it falls to 30-35 atm. at room temperature. The residual gas consists of 3.0 percent hydrogen, 36 percent of C_nH_{2n} and 61 percent of C_nH_{2n+2} hydrocarbons. The liquid reaction product (320 g) is like naphtha, of a brownish color, $d_{15°}$ 0.7512; 61 percent of it having boiling points 20°-300°. It consists of the same mixture of hydrocarbons as was formerly obtained without a catalyzer. With commercial aluminum chloride as catalyzer, polymerization takes place at 240° with formation of only small amounts of liquid products; at 280°, only a carbonaceous residue is obtained and the gas has the composition: C_nH_{2n}, 4.0 percent; hydrogen, 10.0 percent; C_nH_{2n+2}, 86 percent. With freshly prepared aluminum chloride, the polymerization takes place at room temperature with formation of a greenish red, fluorescent liquid, $d_{15°}$ 0.7842, which contains considerably less naphthenes than the product obtained with zinc chloride.

2. Catalytic Formation of Ethylene

Mostly, ethylene is formed by catalytically reducing acetylene. This, however, will be treated under acetylene. As representative may be mentioned a patent of Karo.[262] He specifies: The manufacture of ethylene from acetylene and hydrogen in the presence of a catalyzer, employing as catalyzer the mixture of at least one metal of the platinum or palladium group with at least one metal of the series iron, nickel, cobalt, copper, silver, magnesium, zinc, cadmium and aluminum.

Reference may be made to the important work of Sabatier and Senderens[263] (to appear in an article on "Acetylene") and the earlier work of Wilde[264] and the later work of Pool[265] and his co-workers.

G. Orlof[266] reports on one of the specialties of the Russians, on the catalytic synthesis of ethylene from carbon monoxide and hydrogen; and also with carbon dioxide. Coke, pieces in size of hazel nuts, was soaked in nickel nitrate, dried and ignited. It was then treated in the same manner with palladium chloride and finally reduced in a copper tube, by means of methyl alcohol. When a mixture of hydrogen and carbon monoxide is passed over the prepared coke at 95°-100°, the issuing gas consists of carbon monoxide, hydrogen, air, ethylene and methane. At higher temperatures, or in contact with reduced nickel alone, both ethylene and methane are produced.

3. Catalytic Decomposition of Alcohol to Form Ethylene

Jahn and Ipatieff,[267] in a series of communications, obtained both ethylene and methane by passing ethyl alcohol through hot tubes of glass, platinum, iron, zinc, brass, oxides of zinc, tin, etc., and even plumbago crucible pieces.

Jahn,[268] by passing the vapors of alcohol through a heated hard glass tube at 700°, found scarcely any change, finding only a trace of aldehyde; at 800° gases form with acetaldehyde; at 800°-820° of 140 g alcohol, 50 g were decomposed mainly into aldehyde and hydrogen with a little ethylene, the analysis of the gas being:

Gas	Percent
Ethylene	5.0
Carbon monoxide	18.9
Methane	26.2
Hydrogen	41.3

At 820°-830°, 140 g alcohol gave 45 g ethylene bromide which boiled at 130°-132°. The higher the temperature, the greater the yield of aldehyde, but also the greater the decomposing tendency.

In the presence of platinum 100 g alcohol had decomposed 70 g at 780° in an iron pipe, 10 g into ethylene and water, and the balance into aldehyde and hydrogen. The gas analysis gave 10.8 percent ethylene, about 14 percent of the alcohol decomposed into ethylene and water, and about 86 percent into aldehyde and hydrogen.

$$C_2H_5OH = C_2H_4 + H_2O$$
$$C_2H_5OH = CH_3CHO + H_2.$$

Using pure zinc as catalyst, 54 g of 144 g alcohol heated at 660° gave 32 g of acetaldehyde and less than a gram of ethylene.

Zinc dust heated with 134 g alcohol at 550° gave 76 g ethylene bromide, which is one-half of the alcohol decomposed into ethylene and water; the other half giving aldehyde and hydrogen. At 300° ethylene predominates in presence of zinc dust.

At red heat the products formed are mainly hydrogen, carbon monoxide and methane.

In the presence of brass (33 percent zinc and 67 percent copper) of 144 g alcohol decomposed at 650°, 49 g decomposed, giving 5 g of ethylene and water, the balance analyzed aldehyde, carbon monoxide and methane.

Ipatieff[269] reports good yields by the catalytic action of heated alumina or fire clay on alcohol vapor.

In this connection the researches on the decomposition of ethyl alcohol in a porcelain pipe at 750°–780° of 141 g of alcohol gave 7 g of aldehyde and 12 g of ethylene bromide. In a copper pipe of 140 g of alcohol at 780°–800° gave 12 g of aldelene and 10 g of ethylene bromide.

An aluminum pipe heated to 700° melted the pipe, but no decomposition of alcohol occurred. At 700° in an iron pipe there was energetic decomposition with a separation of carbon but no ethylene was obtained.

In the presence of metal oxide, the oxide is reduced and formed into a fine state, making it more contact active. At 630° of 148 g of alcohol 15 g of ethylene bromide and 18 g of aldehyde were obtained with tin oxide. At 650°, with 146 g of alcohol, 22 g of acetaldehyde and 12 g of ethylene bromide were obtained. In the presence of brass, at 660°–680° in a glass pipe 146 g of isobutyl alcohol gave 67 g of aldehyde and 25 g of a mixture of ethylene and propylene bromides. In the presence of brass isopropyl alcohol at 840°–850° in a glass pipe gave 45 g bromide, mostly propylene bromide, with some ethylene present.

Bouveault[270] has used pumice stone, impregnated with copper, reduced from its nitrate, and bullets made of clay and copper oxide. *Complete* decomposition of alcohol occurs under these circumstances at 300° C.

C. Sprent[271] indicates the best condition for aluminum oxide catalyst as at 360°. A higher temperature causes the decomposition of the ethylene and ruins the catalyst while a lower temperature causes the formation of ether, which is an intermediate product, to pass on with the ethylene.

Engelder,[272] in a study of contact catalysis, found experimental verification of Bancroft's[273] theory that "if a substance may react in two ways, that reaction will predominate for which the reaction products are most strongly adsorbed by the catalytic agent."

This is illustrated by the dehydration and dehydrogenation of alcohol:

Reaction 1: $CH_3CH_2OH \longrightarrow H_2O + CH_2 : CH_2$
Reaction 2: $CH_3CH_2OH \longrightarrow H_2 + CH_3CHO$

According to Grigorieff,[274] Sabatier and Maihle,[275] reaction 1 is almost exclusive with thoria at 340°–350°, and alumina at the same temperature gave a dehydrating effect practically as reaction 1, with a slight tendency toward reaction 2, showing 1.5 percent hydrogen.

Engelder[276] has tabulated the results of Sabatier and his co-workers on the dehydrating effect of oxide of various metals below 350° upon alcohol. Thoria (ThO_2) gave practically 100 percent ethylene; alumina and tungstic oxide each gave 98.5 percent, and Cr_2O_3, SiO_2, TiO_2, BeO, ZrO_2, UO_2, M_2O_5 (blue), Fe_2O_3, V_2O_3 and ZnO gave percentage yields from 5 to 91 of ethylene. They state that silica prepared from SiF_4 and quartz gave no catalytic action, but from Na_2SiO_3 and HCl at 380° a yield of 84 percent ethylene and 16 percent hydrogen was obtained.

Engelder passed 25 percent, 50 percent and absolute alcohol at temperatures 380°, 420° and 490° over catalyst of Al_2O_3, SiO_2, ZrO_2, TiO_2 and Ni and Al_2O_3; and also passed aldehyde; hydrogen and aldehyde; ethylene and hydrogen; and ethylene over TiO_2, and ether over TiO_2 and Al_2O_3 to determine the displacement equilibrium of these reactions. This work is of highly theoretic and industrial importance in catalytic reactions for the production of ethylene, acetaldehyde, acetic acid and hydrogen. Some of his conclusions are as follows:

1. It has been shown that in the catalytic decomposition of alcohol the water-ethylene equilibrium can be displaced with Al_2O_3, SiO_2, ZrO_2 and TiO_2 as catalysts by adding water vapor to the system.

2. Silica is a poor catalyst for the decomposition of alcohol, but alumina prepared from $Al(NO_3)_3$ retains its activity indefinitely.

3. It was found possible to reduce the ethylene content from 84.2 percent to 68.6 percent by adding water to the alcohol over SiO_2.

4. Zirconia, obtained by calcining the nitrate, is an active catalyst. With absolute alcohol it yields a gas containing 63.6 per cent C_2H_4 and 3.5 percent H_2. With aqueous alcohol mixtures the composition changes to 42.5 percent C_2H_4 and 49 percent H_2.

5. When hydrogen is mixed with alcohol vapors and passed over TiO_2, the amount of hydrogen formed decreases from 53.9 percent to 47.0 percent.

6. Ethane forms from ethylene and hydrogen when alcohol is decomposed over TiO_2.

7. Ethyl ether results from the dehydration of ethyl alcohol with Al_2O_3 at 210° and Engelder believes that ether is an intermediate product in the decomposition of alcohol.

Bancroft's [277] conclusions on catalysts apply very pointedly to the type of catalysis here discussed.

1. Only those substances which are adsorbed by a solid are catalyzed by it.

2. While catalytic action of solids may be solely the result of the increased surface concentration in some cases, this is not always the only factor.

3. A solid catalytic agent may be considered as equivalent to a solvent and may therefore displace the equilibrium.

4. As a result of selective adsorption we may get different reaction products with different catalytic agents.

5. A catalytic agent tends to produce the system which it adsorbs the most strongly.

4. Electrosynthesis

(a). The Spark Discharge

Though ethylene is decomposed by the spark discharge into its elements, it may under proper conditions be formed to some extent from its elements, and also by the decomposition of various compounds.

Melly and Lowemel[278] report the formation of both acetylene and ethylene by the decomposition of ethyl alcohol by the spark.

Truchot,[279] working on the Perkin synthesis of hydrogen cyanide by the action of the induction spark on ether and ammonia, noted that ethyl ether liquid is decomposed by the spark to methane, hydrogen, acetylene and ethylene. Klobukow[280] performed his experiments with ether vapor heated to 250°-300°. In the induction spark it gave carbon monoxide hydrogen, methane, ethylene, acetylene and their homologs. At ordinary temperatures there was no trace of hydrocarbon decomposition. Wilde's[281] experiments were conducted under reduced pressure. He also obtained ethylene along with other gases and carbon.

The induction spark with its brilliant scenic and chemical effect has been studied but little. The reactions carried on under its influence are the results of thermal and electrical energy liberations. The above experiments carried upon ether alone indicate that a host of possibilities have unfortunately been slurred.

b. The Silent Electric Discharge

Maquenne,[282] in his studies on the effect of the silent electric discharge on various substances, obtained ethylene from ethyl alcohol, methyl alcohol, acetic acid and formic methyl ester.

ETHYL ALCOHOL

Pressure	2 mm	110 mm
CO_2	2.2	0.0
CO	11.0	0.0
C_2H_2-C_2H_4	14.0	14.8
C_3H_6	30.1	10.3
H_2	42.6	0.4

METHYL ALCOHOL

Pressure	3 mm	100 mm
CO	24.3	19.6
CO_2	0.0	0.0
C_2H_2-C_2H_4	4.3	0.9
CH_4	51.0	36.7
H_2	20.4	42.8

FORMIC METHYL ESTER

Pressure	100 mm Percent
CO_2	8.1
CO	46.8
C_2H_4	0.5
CH_4	20.6
H_2	24.0

The same products were obtained from acetic acid. With increased pressure there was noted an increase in hydrogen and carbon monoxide and a decrease in carbon yields.

Berthelot,[283] working with other compounds, also obtained ethylene. It was formed from pure ethane at the start of the experiment and as the experiment goes on polymerization occurs with acetylene and hydrogen forming. Similarly an equilibrium may be established involving acetylene, ethylene, hydrogen and ethane, as indicated in an experiment in which 100 volumes of acetylene gave 1.8 volumes of hydrogen, 0.8 volume of ethylene and 0.08 volume of ethane.

c. Electrolysis of Acetylene

The action of acetylene as a cathodic depolarizing agent in the electrolysis of acid and alkaline solutions has been investigated by Billitzer,[284] who finds this substance readily reacts as a depolarizer with a cathode of platinum and that the products of its action are ethylene and ethane and within certain limits of potential it is possible to obtain a quantitative yield. If the potential is gradually increased mixtures of ethylene and ethane are produced at the cathode and later hydrogen makes its appearance. In a sulphuric acid and mercury cathode small quantities of alcohol form. Thus the electrosynthesis of ethylene from acetylene may be accomplished.

5. Catalytic Oxidation of Ethylene

Catalytic oxidation of ethylene has been fairly neglected for the study of catalytic reduction.

Coquillon[285] reports that when a mixture of ethylene and air is passed over red-hot platinum wire some acetic acid is formed.

D. Campbell[286] determined the combustion point of ethylene with copper oxide and palladinized copper.

6. Hydrogenation

a. Direct Combination of Hydrogen and Ethylene

That a good many reactions of ethylene, furthered so to speak by catalysts, may be of purely thermal significance, seems to be brought out by the work of Berthelot[287] that at a dull red heat hydrogen combines directly with hydrocarbons, especially with ethylene, the combination being limited by the dissociation of the hydrides formed. This dissociation varies rapidly with the temperature, at the softening point of glass, about 550°, only 51 percent of the ethylene being converted into ethane. At a lower temperature, however, with longer time, as much as 70 percent of the ethylene is converted into ethane, and probably at a still lower temperature with sufficient time, the conversion would be complete. This incidentally indicates that a good many catalytic additions of hydrogen and ethylene are quite possibly pure thermal effects, at least to the extent of 70 percent.

b. Catalytic Hydrogenation of Ethylene

Various catalysts have been used for the classically notable hydrogenation of ethylene. Von Wilde[288] was the first to observe that when a mixture of ethylene and hydrogen is passed over platinum, even in the cold, ethane is formed. Working with platinum black he obtained the equi-volume reaction $C_2H_4 + H_2 = C_2H_6$ of 10.2 cc of analyzed gas: 8.3 cc were ethane and 1.9 cc hydrogen. He used excess hydrogen in ratio of 2 : 1.

Further work with platinum was done by Sabatier and Senderens.[289] The catalytic action of platinum black on mixtures of ethylene and hydrogen is only temporary at ordinary temperature; at 100°–120°, there is a slow combination, while at 185° the reaction is practically quantitative. Spongy platinum does not induce the hydrogenation of acetylene or ethylene at the ordinary temperature; at 180°, however, it behaves like platinum black.

Sabatier and Senderens[290,291] also pushed their investigation to other metals. Under circumstances similar to those for acetylene, nickel reduces it slowly in the cold, but the action soon stops. At higher temperatures it is more rapid but gradually diminishes in intensity through the carburation of the metal. Copper acts only above 180° C and slowly even then, but the action can be carried on indefinitely. Iron, too, acts above 180° C, and more slowly than copper, while its activity, like that of cobalt, diminishes as the metal gradually absorbs the carbon. This was an extension of some earlier work.

The effectiveness of palladium was investigated by C. Paal and W. Hartmann.[292] Ethylene is converted quantitatively into ethane by mixing it with an equal volume of hydrogen, adding a little palladium hydrosol and shaking at the ordinary temperature. Omission of the shaking causes the reaction to proceed more slowly. The time required for the complete conversion of ethylene into ethane varies from 70 min. upwards, according to the shaking and to the reactivity and concentration of the catalyst. A number of detailed measurements of the velocity of the reaction are given.

At a later date Paal and Schwartz[293] also investigated colloidal platinum. The following experiments were carried out with equal volumes of ethylene at room temperature under atmospheric pressure, with colloidal platinum, protected with sodium protalbinate as catalyst. Whereas it was previously found that with 0.05 g palladium, 25 cc ethylene are quantitatively reduced in a gas burette in 70 minutes, with 0.047 and 0.0915 g platinum in 10 cc of water, 160 and 88 minutes, respectively, are required. In experiments with a shaking apparatus, it was found that shaking increases the velocity of reduction and that with fresh colloidal platinum the reduction is also much faster than with platinum preparations which have already been used. The more concentrated the colloidal platinum solution the more rapid is the reduction with equal amounts of platinum but the velocities are not directly proportional to the concentrations, increasing much more slowly than the concentration and similarly with decreasing amounts of platinum in solutions of the same concentration. In other words, within certain limits both the quantity and the concentration of the catalyzer have but a slight influence on the course of the reduction. Palladium is somewhat more effective than an equi-atomic amount of platinum.

Detailed figures are given by Rather and Reid[294] (1915). The volatile substance to be hydrogenated, mixed with hydrogen, is passed through a non-volatile liquid containing the catalyst and kept thoroughly stirred. The catalyst used for the study of the reduction of ethylene was prepared by treating 100 g infusorial earth with 50 g $Ni(NO_3)_2.6H_2O$ in 150 cc water, adding the resulting moist mass to a concentrated solution of 60 g $Na_2CO_3.10H_2O$, washing, drying, reducing below red heat in hydrogen until no more water was formed and cooling in carbon dioxide; 1.0 g of this reduced the iodine number of 70 g cottonseed oil from 113.1 to 44.6 after 60 minutes' treatment in the hydrogenation apparatus at 180°, and its activity did not deteriorate appreciably during the period each portion of it was in use. Fifty percent ethylene was passed at the rate of 10–200 cc per min. into a mixture of 1 g catalyst plus 70 g paraffin kept at 180°–181°, the stirrer being run at the rate of 3300–3500 revolutions per min. and the amount of ethane in the issuing gases was determined when equilibrium was reached. For all mixtures of ethylene and hydrogen studied, about 70 percent of the ethylene was reduced when the rate of flow was 10 cc per min. All the results for the 10 percent mixtures are regular, while mixtures richer in ethylene gave irregular results, the determining factor doubtless being solubility and the reaction probably taking place between the gases dissolved in the paraffin. When the gas flow is rapid the gases are carried through before equilibrium can be established between the gas mixture and the solution. Plotting the volume of gases combined per min. against the rate of flow showed, as was to be expected, the volume combined, increased with the amount of the gas mixture exposed to the catalyst. In the 50 percent mixture 17 cc of hydrogen combined with 17 cc ethylene in 1 min., and since the 1 g of catalyst cannot contain more than 0.1 g or 0.01 cc or less of nickel, the latter can bring about the combination of 3400 times its own volume (calculated for 0°) of the gas mixture in 1 minute.

C. Ellis reports that with gases and catalyst of proper purity the hydrogenation is instantaneous wherever the gases are in the catalyst sphere.

The general theory of hydrogenation under pressure, of nickel and of aliphatic compounds with ethylene linkages other than ethylene itself, is discussed by A. Brochet and A. Cabaret.[295]

Grassi[296] studied the velocity of hydrogenation of ethylene at 150°-300° in contact with recently reduced copper. He found the average velocity of hydrogenation, taking into account the initial pressures of the components and time of contact, to be 0.25, 1:10, 1.19 and 1.21 at temperatures, respectively, of 150, 200, 250 and 275°. The fact that in his experiments the velocities of reaction were proportional to the concentration of hydrogen and ethylene shows them to be of the type due to adsorption.

F. MISCELLANEOUS ON ETHYLENE

1. Analytical

Haber and Oechelhauser,[297] Haber,[298] and Harbeck and Lunge[299] have published results on the separation and estimation of benzene and ethylene. Burrell and Robertson[300] have worked out a method for the preparation of ethane and ethylene by fractional distillation in a vacuum and low temperatures. (The boiling points are only 10° apart.) After eighteen fractionations at temperatures ranging between —155° and —170°, complete separation was effected, but the method is too long and tedious to be entirely satisfactory, constant temperatures being too difficult to maintain and the removal of the gas by the pump at any particular temperature too irregular to obtain a ratio between the quantity of gases removed at different temperatures. The less volatile gas, ethane, is not so difficult to obtain pure.

One of the best general methods for the estimation of ethylene in gaseous mixtures is given by P. Fritzsche.[301] He bases his method upon the absorption of ethylene by means of sulphuric acid, and the following mode of procedure is recommended. The gas, freed of tar, ammonia, and sulphuretted hydrogen, is made to fill a glass cylinder fitted at both ends with glass taps and of from 200–300 cc capacity. Sufficient concentrated sulphuric acid for easy agitation is now admitted into the tube and shaking continued until, on carefully opening one of the taps, no more air enters the apparatus. The acid is now drained out and the apparatus washed with a small quantity of water (not more than twice the weight of sulphuric acid used) and the acid and washings distilled. To this distillate a small quantity of soda is added and it is then redistilled till two-thirds of its bulk have passed over. The absolute weight and specific gravity of this second distillate are determined and the quantity of alcohol calculated from Mendeléef's figures. The best results are obtained when the alcoholic content lies between 1 and 2 per cent.

For coal-gas, and carbon monoxide, the method is not so simple, owing to the small quantity of ethylene present. To avoid the necessity of using larger volumes of sulphuric acid for absorption the author carried out an experiment at 100° C, at which temperature combination occurs more rapidly, and only employs sufficient acid to moisten the walls of the slowly rotating gas vessel. At 100° C the time required for complete absorption is about 4 hours, while working at ordinary temperature the reaction is not finished after 20 hours. The ethyl sulphuric acid obtained is diluted and distilled as before, and the successive distillation redistilled four or five times, until a final solution is obtained sufficiently rich in alcohol for correct specific gravity determination. For coal-gas the absorption vessel should be 500 mm long and 110 to 120 mm in diameter; the volume of concentrated acid used should be about 20 cc, and the wash-water about 40 cc. The butylene present may be removed from the gas before filling the tube by passing the gas through a wash-bottle moistened with 70 percent H_2SO_4, any propylene present is estimated as ethylene. Trials of volumetric method depended on the splitting up of barium ethyl suphate in concentrated solution into alcohol, barium sulphate, and free sulphuric acid did not lead to satisfactory results. The reason for this, according to the author, is that the ethylene absorbed exists partially as ethyl sulphuric acid, and also partially as alcohol in the sulphuric acid solution.

Elliott[302] and Uhlig[303] outline analysis of gases. Erdman and Stolzenberg[304] report interesting results of gas analysis by condensation.

2. Biological Data

(1) Ethylene in itself is not poisonous, though some of its halogen derivatives may be used as anesthetics.

(2) E. M. Harvey[305] reports that growing plants of Ricinus communis are sensitive to as little as 0.00001 percent of ethylene in the atmosphere. An amount of 1 : 1,000,000 causes the retioles of the leaves to droop or the laminae to fold down. Similar observations have been made with sweet pea seedlings.[306] D. Neljubow[307] found that a delicate test was indicated for ethylene due to seedlings stems becoming "transversally geotropisch." In general, he states that ethylene increases the amount of simple soluble substances. It retards carbon dioxide production and oxygen absorption. Neither the permeability nor the respiratory ratio is altered.

(3) As a gas works problem, Crocker and Knight[308] have some notes on the effect of illuminating gas and ethylene upon flowering carnations.

(4) J. L. Smith and A. P. Hoskins[309] state that a concentration of even 72 percent ethylene is not harmful for breathing. Any coal-gas present in poisonous air contains only

about 0.2 percent of ethylene and it is hardly conceivable that any toxic action is due to ethylene.

(5) Wanchot[310] states that ethylene combines with blood.

MISCELLANEOUS

Homfray[311] studied the absorption of ethylene in charcoal.

Giolloti and Tavanti,[312] Giolloti and Carnerali,[313] upon a series of cementation studies of nickel and chrome steel using ethylene and carbon monoxide, found homogeneity, but using ethylene alone the result was unhomogeneous.

H. Thiele[314] showed that when a mixture of ethylene and hydrogen was subjected to ultraviolet light for a period of six hours a contraction of one percent resulted in the volume.

D. Berthelot and H. Gaudechon,[315] using a mercury lamp 220 V. 4 cm dist. with ethylene, found an 11 percent contraction, leaving a residue of pure ethylene and a fluid formed having an odor of rancid fat and boiling a little above 100°. A mixture of ethylene and acetylene gave the above products and a contraction of 26 percent in volume.

Berthelot,[316] heating a mixture of 100 C_2H_4 + 100 N_2, gave 28.6 percent H_2; 0.4 percent C_2H_6; 62.2 percent N_2, and $C_{16}H_{32}N_4$.

Brooks,[317] upon distilling manila copal recovered ethylene as one of the products.

Several patents[318] have been taken out to purify ethylene for catalytic reactions, especially for the production of ethane.

Freeman[319] forms ethylene from the carbon arc by retaining hydrogen in the sphere of carbon particles sufficiently long, in an air-tight compartment.

Senderens[320] heats ethylene with hydrogen, forming ethane.

Frankland[321] finds that ethylene burns at the rate of 5 cu. ft. per hour with a 68.5 standard candle power. The illuminating power is increased by admixing hydrogen, carbon monoxide or methane, though the light given per cu. ft. of the mixture is less. The intrinsic illuminating power is reduced by nitrogen, carbon dioxide or water, but is increased by oxygen.

De Montmollin[322] analyzed an oil termed ethylene "petroleum," found as a by-product in the formation of ethylene from phosphoric acid and alcohol. The fluorescent brown oil upon fractional distillation yielded the following hydrocarbons:

	Boiling point	Density P
$(Me_2CH)_2$	58°–59°	
Me_2CEt_2	86°–87°	
Hexahydro-*m*-xylene	116°–117°	0.741
Hexahydro-*p*-xylene	137°–138°	0.719
Hexahydrocumene	150°–160°	0.798
Hexahydrocymene	160°–180°	0.794
Decanaphthene		
Tetradecanaphthene		

The highest boiling point fraction gave unidentified aromatic compounds.

The Commercial Research Company[323] patented the formation of chlorhydrins by the action of steam, chlorine and olefin (C_2H_4, C_3H_6, C_4H_8), etc., from cracked vapors of gas oil, kerosene, petroleum residues, etc., in a suitable apparatus.

McElroy[324] patents the formation of glycols by means of chlorinating the olefins in oil gas (ethylene, propylene, etc.) to dichlorides and hydrolyzing same under pressure by heating with water and calcium carbonate.

RESEARCH PROBLEMS OF ETHYLENE

The following demand further or new research:

1. Exact determination of ethylene constants.
2. Ethylene refrigeration system.
3. Ethylene storage.
4. Ethylene as a factor in luminosity of various flames.
5. The solubility of ethylene in various solvents and mixtures of solvents.
6. The solubility of various organic materials in ethylene.
7. Study of valence of carbon in olefines.
8. Ionization of ethylene and relation of ionization to reactivity.

9. Effect of various wave lengths on reactivity of ethylene.
10. Effect of various wave lengths and of other factors, as pressure, etc., on reactivity of ethylene.
11. Effect of X-rays.
12. Effects of radioactive material on ethylene.
13. A study of the radioactive properties of ethylene condensation products.
14. A reaction series of ethylene substitution products.
15. Studies on heat conductivity, velocity of flame, etc., and relations existing between them.
16. Variation of explosibility with introduction of foreign substances.
17. Compounds of ethylene with inorganic salts.
18. Compounds of ethylene with organic materials.
19. Ethylene in internal combustion engines.
20. Ethylene solvent mixtures for combustion engines.
21. Oxidation of ethylene.
22. Combination with straight chain hydrocarbons.
23. Combination with cyclic hydrocarbons.
24. Polymerization and condensation products of ethylene.
25. The nitration and sulphonation of ethylene.
26. The action of various organic and inorganic acids upon ethylene.
27. The occlusion of ethylene by metals.
28. The occlusion of ethylene by common substances (organic).
29. The catalytic production of alcohol.
30. Incomplete combustion of ethylene.
31. Development of incomplete and complete halogenation products of ethylene.
32. Carbon from ethylene (indirect).
33. Carbon from ethylene (direct).
34. Nitrifiable carbides from ethylene.
35. Ethylene to benzene.
36. Ethylene to toluene.
37. Fatty substances from ethylene.
38. Theoretics of ethylene equilibrium.
39. Surface effects on ethylene.
40. Carbohydrates from ethylene.
41. The action of heat and pressure upon C_2H_4 and N_2, CO, CO_2, NH_3, HCHO or $COCl_2$.
42. Electric nitrification of ethylene.
43. Effect of silent discharge on ethylene and ethylene mixtures of hydrocarbons.
44. Silent discharge on C_2H_4, N_2, CO, CO_2, NH_3, halogens.
45. Other types of discharge on C_2H_4, N_2, CO, CO_2, NH_3, halogens.
46. Oxidations (electrically).
47. Production of higher hydrocarbons.
48. Bacterial nitrification.
49. Bacterial oxidation.
50. Solidification of C_2H_4 (colloidally).

51. Cyanate from C_2H_4.
52. C_2H_4 generators.
53. C_2H_4 purifiers.
54. Analysis by condensation.

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NEW BOOKS

Color in Relation to Chemical Constitution. *By E. R. Watson. 14 × 23 cm; pp. xii + 197. New York: Longmans, Green & Co., 1918. Price, $4.00.*— The subject is treated in chapters entitled: early history of the subject; discussion of the quinonoid theory—modifications of the quinonoid theory; absorption spectra—methods of examining and recording; absorption spectra of typical organic substances and dye-stuffs; relationships between constitution and depth of color; theories on the nature of the vibrations causing absorption bands and color; infra-red absorption spectra of organic substances; fluorescence; the color and spectra of inorganic compounds; bibliography.

The author explains, p. 5, what is meant by depth of color. "It should be noted carefully that the term *depth* is used by color chemists in a very definite and limited way. In ordinary language the term depth of color has at least two meanings. Blue and red are said to be deeper colors than yellow and also one yellow is said to be deeper than another yellow if it is stronger or more intense, *i. e.*, less admixed with white. Color chemists restrict the use of the term and employ it for the first purpose only. Blue is deeper than red or yellow, and red is deeper than yellow. The ordinary colors arranged according to depth are: green, blue, violet, red, orange, yellow, *i. e.*, the complements to the ordinary colors of the spectrum taken in order from the red to the violet end."

One prerequisite to discussing the relation between color and chemical constitution is to agree as to the chemical constitution. The author points out, p. 91, that logwood, alizarin, fustic, and cochineal may be given as examples of polygenetic dyes. Alizarin is yellow in alcoholic solution, gives orange dyeings on tin, red on alum, maroon on chrome, and is purple in alkaline solutions. He adds that in the case of the mordant dyes the depth of color attained does not depend on the weight of the metal with which the dye has formed a salt, but rather on the electropositivity of the metal. The order is tin, alum, chrome, and sodium, or potassium. The first point to settle here is whether alizarin does form a salt with tin, alum, or chrome. The author is apparently not posted on colloid chemistry.

The book is admirable as a collection of facts and the matter is presented clearly. In a way it must have been an unsatisfactory book to write because the experimental data are so far ahead of the theory. Many of the theories of color explain a large number of the facts; but each one breaks down completely at some point or other and nobody as yet has formulated any definite theory out of the fragmentary ones which we now have. The author's views as to organic and inorganic compounds, p. 164, are distinctly interesting. "It is generally considered that the colors of organic and inorganic compounds are due to different causes. This is due to the fact that the simpler compounds of carbon are colorless under ordinary conditions, whereas even the simplest compounds of many other elements are colored. Most organic compounds consist of carbon and hydrogen; carbon, hydrogen and oxygen; carbon, hydrogen and nitrogen; or carbon, hydrogen, oxygen and nitrogen only. Hundreds of organic compounds are known which are colorless under ordinary conditions. This has led to the view that color when developed in organic compounds is due to some special arrangements of the atoms in the molecule, whereas the color of simple inorganic compounds is considered to be due to something inside the atoms for the elements forming those compounds—*i. e.*, some intra-atomic arrangement or vibration as distinguished from the inter-atomic arrangement or vibration which is supposed to cause the color of organic compounds.

"There are, however, facts which warn us against the unqualified acceptance of this view. On the one hand, we must recognize that even the elements—carbon, hydrogen, oxygen, nitrogen, and their simple compounds—can exhibit color under certain circumstances. The ordinary forms of solid carbon., *viz.*, charcoal, lamp-black, and graphite, are black or grey, which means that they absorb all the rays of the visible spectrum. Oxygen gas appears to be colorless, yet it absorbs rays in the red part of the spectrum and is responsible for a considerable number of bands seen in the ordinary solar spectrum. Liquid oxygen is of a pale blue color and liquid ozone is of a deep indigo-blue color which is so intense that a layer 2 mm thick is opaque. When stimulated by the electric current or discharge, all these elements emit light of characteristic vibration frequencies—*i. e.*, give emission spectra containing characteristic lines (or bands), and the light emitted is colored even to the naked eye. On the other hand, we must recognize that there are scarcely any elements, not even those which are generally regarded as colored elements *par excellence*, which are not colorless under certain conditions. Chromium, manganese, iron, nickel, cobalt, and copper are regarded as essentially colored elements, yet the first five of these are white in the metallic condition. This may be only because they reflect the greater portion of the incident light unchanged; but whatever the reason may be, they are apparently white. Nor are all the compounds colored, *e. g.*, anhydrous copper sulphate is white."

Since the reasons for copper salts giving blue and green flames have been worked out fairly definitely, the author should have included some reference to this matter under flame spectra. *Wilder D. Bancroft*

Gas and Flame in Modern Warfare. *By S. J. M. Auld. 19 × 13 cm; pp. ix + 201. New York: George H. Doran Company, 1918.*—Our point of view in regard to gas warfare has changed a good deal either because we are hardened to it or because we know more about it. At first, stress was laid on the brutality and ghastliness of it; but nowadays we hear it said that gas warfare is the most humane form of fighting. Both points of view may be right, depending whether we consider the men who die or those who recover. Those who are killed die in agony; but those who recover are not mutilated. They may be sensitive to pneumonia, but that danger is not so great as the one of developing tuberculosis in a German prison camp. The men who have been gassed do not go through life without eyes, arms, or legs, as may easily be the case when shrapnel or high explosive is used.

Gas warfare has been a contest of wits, with the Germans pretty well ahead most of the time so far as novelties were concerned; but with the Allies eventually making more of any gas than the Germans did. The general development has been from a volatile gas to a non-volatile solid. The Germans began with chlorine in a cloud attack. This was easily stopped by a bandage over the nose and mouth. The use of tear gases forced the use of a hood or mask. The introduction of phosgene made better protection necessary and this became still more imperative when chlorpicrin was used because this was not stopped by the early charcoal. After the mask had reached a high stage of development, two new lines of attack were worked out. Mustard gas is a high-boiling liquid which produces bad burns on the skin and consequently presents an entirely new problem, while diphenyl chlorarsine is a high-melting solid which is not stopped by the ordinary ingredients in the mask. A defense has been developed against both these substances and now it is usually considered that gas casualties are a sign of carelessness.

Colonel Auld is a chemist, who has had actual first-hand experience with gas warfare and who has followed the developments carefully from the beginning. He is probably better qualified to write on the subject than any man living. Since he also writes well, the combination is irresistible and the book is very well worth reading by everybody and will appeal to others besides chemists and soldiers.
Wilder D. Bancroft

Text-Book of Physical Chemistry. *By Azariah T. Lincoln. 21 × 15 cm; pp. viii + 547. New York: D. C. Heath and Company, 1918. Price: $3.50.* —In the preface the author says: "This text-book is intended primarily for the use of classes beginning the subject of Physical Chemistry. In the preparation of the text I have endeavored to keep in mind that the presentation is to students who meet the subject matter for the first time and that they are to acquire a broad foundation for their subsequent work. As some time intervenes between the elementary course in which the fundamental ideas of chemistry are presented and the time at which the work in Physical Chemistry is given, it is found that a short review of these fundamental concepts is necessary in order to have the student properly oriented as to the relationship of his elementary work and that which is usually incorporated in a course in Physical Chemistry. That this is absolutely necessary is the experience of most teachers, and the result can be attained more quickly by restating briefly this fundamental matter in a form in which it can subsequently be utilized. Hence there is given a résumé of some of the information which the student is assumed to have in order to place him in a position to correlate the new material with that which he already possesses."

The headings of the chapters are: introduction; laws of combination and chemical units; the gas law; determination of molecular and symbol weights; atomic and molecular theories; deviations from the gas law, and dissociation of gases; the periodic system; the kinetic theory of gases; specific heat of gases; van der Waals' equation; the physical properties of liquids; refraction of light; optical rotation; solutions; solution of liquid in liquids (2); phase rule; solutions of solids in liquids (4); application of the phase rule; osmotic pressure; lowering of vapor pressure; freezing-points and boiling-points of solution; thermodynamic considerations; electrical conductance; electrolytic dissociation; equilibrium between the dissociated and undissociated parts of an electrolyte in solution; concentrated solutions; hydration; hydrolysis; non-aqueous solutions; thermochemistry; colloid chemistry; rate of chemical reactions.

The book is a good one. It is written clearly and goes into a number of matters which are not to be found in other books. The one doubtful point about the book is its scope. There is nothing in the title or in the author's preface to show that this is an introductory volume or to show how much more physical chemistry the student is expected to take in college. Few people would be satisfied with thirty-two pages on reaction velocity or with no discussion on indicators. If the student is to take another lecture course, this is an admirable book. If he is not to do this, the first portion of the book should have been condensed enormously.

There are only a few changes that should be made in details. The word "consolute" is spelled wrongly throughout. The reviewer objects strongly to the term "disperse means," p. 441, and it is surely an exaggeration, p. 26, to say that "it is customary in Thermodynamics to express the terms in the Gas Law Equation in the English system and the Fahrenheit temperature scale."

Wilder D. Bancroft

Combinazioni chimiche fra metalli. *By Michele Guia and Clara Guia-Lollini. 24 × 17 cm; pp. xvi + 446. Milan: Ulrico Hoepli, 1917.*—In the preface the authors say: "The study of chemical compounds between metals is of great importance for general chemistry. When one thinks of the recent development of the chemistry of the metals, one is amazed at the enormous progress made in less than two decades. This progress has become possible through the rapid and continuous improvements in modern metallography." In the first chapter are given the equilibrium diagrams for the binary alloys which have been studied. Then follows a chapter on thermal analysis, one on the nature of metallic compounds, and one on the physical properties of these compounds. Where neither constituent is an acid-forming the compounds are called homopolar; while the borides, carbides, phosphides, arsenides, silicides, phosphides, sulphides, selenides, and tellurides are classed as heteropolar metallic compounds, in so far as they have any metallic properties. In this group are included the carbides of boron, aluminum, titanium, vanadium, chromium, molybdenum, tungsten, uranium, manganese, iron, and nickel. After the chapters on homopolar and heteropolar compounds, there is one on ternary metallic compounds, in which the systems which have been studied experimentally are sodium-potassium-mercury, sodium-cadmium-mercury, magnesium-aluminum-zinc, and silver-gold-tellurium. At the end of the volume are tables showing the melting-points and atomic weights of the more important metals and metalloids, the binary systems which have been studied by the method of thermal analysis, and a list of the binary systems in which no chemical compounds occur. There is also an index of all the binary systems referred to in the book.

The volume seems to be a very interesting and satisfactory compilation giving a great deal of information in a compact and accessible form. The reviewer has not been sufficiently in touch with alloy work recently to be able to say definitely that there are no omissions; but he has not noticed any.

Wilder D. Bancroft

Outline of Theoretical Chemistry. *By Frederick H. Getman. Second revised edition. 21 × 15 cm; pp. xiv + 539. New York: John Wiley and Sons, 1918. Price: $3.50.*—The first edition was reviewed some years ago (18, 183). The features which distinguish the second edition from the preceding one have been summarized briefly by the author as follows:

1. The necessity of introducing a short chapter on the modern conception of the atom and its structure involved the further necessity of including a preliminary chapter treating of those radioactive phenomena upon which the greater part of our present atomic theory is based.

2. The chapter on solids has been practically rewritten: the space formerly devoted to an outline of crystallography being devoted in the present edition to a discussion of the absorption of heat by crystalline solids and the bearing of X-ray spectra on crystalline form.

3. The increasing importance of colloidal phenomena, not only to the chemist but also to the biologist, to the physician and to the technologist, has made it seem desirable to rewrite the entire chapter devoted to the chemistry of colloids.

4. The Brownian movement and its bearing upon the existence of molecules has been presented briefly in a separate chapter in order to emphasize the importance of the brilliant experimental work of Perrin and others in confirming the kinetic theory.

5. The chapter treating of electromotive force has been enlarged so as to include a discussion of some of the more valuable methods which have been proposed for determining junction potentials and also to point out several useful applications of concentration cells.

6. An entirely new chapter, in which an attempt has been made to present the salient facts and more important theories of photochemistry in succinct form, replaces the former chapter treating of the relations between radiant and chemical energy.

The present arrangement of chapters is: fundamental principles; classification of the elements; the electron theory; radio-activity; atomic structure; gases; liquids; solids; solutions; dilute solutions and osmotic pressure; association, dissociation, and solvation; colloids; molecular reality; thermochemistry; homogeneous equilibrium; heterogeneous equilibrium; chemical kinetics; electrical conductance; electrolytic equilibrium and hydrolysis; electrolysis and polarization; photochemistry. *Wilder D. Bancroft*

The Chemical Analysis of Iron. *By A. A. Blair. Eighth edition. 23 × 17 cm; pp. 318. Philadelphia: J. B. Lippincott Company, 1918. Price, $5.00.* —The first edition was published in 1888 and the eighth in 1918, thirty years later. In the preface to this edition the author says: "Since the last edition of this book was issued, there have been so many improvements in the method for the determination of the usual elements in iron and steel; and the so-called alloy metals have become so important that is was found necessary to recast the work and to rewrite the greater part of it. The various methods employed in the analysis of the alloy steels have been placed together, and a separate part has been arranged for the alloy metals. The methods for the analysis of furnace and other gases have been omitted. The table of atomic weights has been corrected to correspond with the values recommended by the Committee for 1918, and the table of factors corrected to correspond with the new values."

Doubtless the author knows his public; but one always looks for the things that interest oneself and the reviewer wonders whether it would not be helpful to explain why one cannot determine total carbon by dissolving iron in hydrochloric acid. It might take a few lines more; but one could cut out the statement, p. 126, that Karsten first showed that graphite was not a hydrocarbon, and the picture of a tripod, p. 19, and the paragraph about the gasolene lamp, p. 20. A word of explanation as to the effect of silicon in changing the form of iron globules, p. 73, would not be amiss, and many young chemists would like to know what impurity is removed by redistilling iodine with great care, p. 37. It seems a pity not to do a little more here and there. *Wilder D. Bancroft*

The Chemist's Pocket Manual. *By Richard K. Meade. Third edition. 16 × 11 cm; pp. v + 530. Easton: The Chemical Publishing Company, 1918. Price: $3.50.*—In the preface the author says: "In getting out the third edition, that portion of the manual devoted to chemical engineering, as well as that to analytical chemistry, has been materially enlarged so that, while still serving the analyst, it is believed that the chemical engineer will find in this edition much of use also. The book is now over two and a half times as large as when it originally appeared and the third edition has been enlarged over the second by 87 pages. Included in this new material and of interest to the chemical engineer are data and tables on fuels, boilers, engines and chimneys, drying and evaporation, fire-brick and refractories, heat-conductivity and resistivity, tanks, piping and pumps, belts, pulleys and shafting, elevators and conveyors; and the table on the heats of formation of chemical compounds has been extended and arranged alphabetically....

"The author's aim throughout has been to present in as condensed form as possible such information as would seem to him to be of service to the plant chemist and the chemical engineer. The chemist whose lines of work lie in the field of pure chemistry has at his command many valuable works of reference, and this little book has, therefore, been designed for the former rather than the latter." *Wilder D. Bancroft*

SOME STUDIES ON CASEIN

BY L. A. MAYNARD

In 1906, Plimmer and Bayliss[1] showed that when casein was digested with one percent caustic soda for 24 hours at 37° all the phosphorus was changed to a soluble inorganic form. During this period no soluble nitrogen was formed. The fact that so weak a solution of alkali rendered the phosphorus soluble, but with no corresponding production of soluble nitrogen raised the question as to the state of union between the phosphorus and the rest of the casein molecule. It seemed possible that instead of being in chemical combination the phosphorus might be merely adsorbed. The experimental work to be described in this paper was undertaken in the hope of throwing some light on this question.

The casein used in our experiments was prepared from skim milk according to the method described by Osborne[2] (1911). A product free from calcium was obtained.

The Separation of Phosphorus from Casein

In order to check up the results obtained by Plimmer and Bayliss their work on the digestion of casein by caustic soda was repeated. According to the procedure followed by them casein in the concentration of one gram in 500 cc solution was allowed to digest at 37° with one percent sodium hydroxide solution.[3] To determine the amount of soluble phosphorus formed at a certain period, an aliquot of the digest was withdrawn and added to an equal volume of tannic acid solutions. The phosphorus remaining in the filtrate from this precipitation was considered soluble phosphorus. A similar method was used in the case of soluble nitrogen. The inorganic phosphorus was determined in the caustic soda digest by direct

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[1] Jour. Physiology, 33, 439 (1906).

[2] Jour. Biol. Chem., 9, 333 (1911).

[3] This solution was prepared according to Cathcart's formula half-strength, Jour. Physiology, 21, 497.

precipitation with magnesium citrate solution after acidification to get rid of albuminous matter.

In our experiments determinations of total and inorganic phosphorus were made after 24 hours digestion, the period at which total digestion was obtained according to Plimmer and Bayliss. In determining the soluble phosphorus an aliquot of the caustic soda digest was precipitated with tannic acid solution. The filtrate obtained was concentrated and the organic matter was oxidized with nitric and sulfuric acids. The resulting solution was treated according to the official gravimetric method described in Bull. 107, Bur. of Chem., U. S. D. A. The total phosphorus was determined by the same procedure, using an aliquot of the caustic soda digest, but omitting the precipitation with tannic acid solution. In determining the inorganic phosphorus the magnesium citrate method was used and the phosphorus was weighed as magnesium pyrophosphate.

The results obtained from the analysis for phosphorus checked those reported by Plimmer and Bayliss. These results are listed in Table I. The figures tabulated show the amounts of the different kinds of phosphorus present in equal amounts of the caustic soda digest.

TABLE I—DIGESTION OF CASEIN BY ONE PERCENT SODIUM HYDROXIDE SOLUTION. 24 HOURS AT 37°

Experiment	Total P_2O_5 mgms	Soluble P_2O_5 mgms	Inorganic P_2O_5 mgms
1	16.31	16.40	16.81
2	17.22	16.97	17.10

The question arose as to whether the phosphorus would be totally split off at a lower temperature provided a longer time was allowed for the alkali to act. Accordingly a one percent solution of the latter was allowed to act on the casein for two weeks at room temperature. It was found that all the phosphorus was thus changed to a soluble inorganic form. The results of these experiments are shown in Table II.

Table II—Digestion of Casein by One Percent Sodium Hydroxide Solution. Two Weeks at 25°

Experiment	Total P_2O_5 mgms	Soluble P_2O_5 mgms	Inorganic P_2O_5 mgms
1	17.22	17.10	16.68
2	17.15	17.22	16.84

Experiments were next run to ascertain how much of the phosphorus could be split off during 24 hours at room temperature. The results are shown in Table III.

Table III—Digestion of Casein by One Percent Sodium Hydroxide Solution. 24 Hours at 25°

Experiment	Total P_2O_5 mgms	Soluble P_2O_5 mgms	Inorganic P_2O_5 mgms
1	16.58	13.01	12.76
2	16.96	12.75	12.75

It is shown in Table II that one percent caustic soda will completely change the phosphorus of the casein molecule to an inorganic soluble form at room temperature, provided sufficient time is allowed. No attempt was made to ascertain the minimum time requirement. Two weeks is evidently longer than necessary inasmuch as Table III shows that over 75 percent of the phosphorus is changed in 24 hours.

The Substance Precipitated from the Caustic Soda Digest by Acids

Plimmer and Bayliss reported that a white precipitate was obtained on addition of sulfuric acid to the caustic soda digest. This precipitate was studied by us. Inasmuch as its chemical nature was not determined it will be designated as substance A. It was found to be precipitated by sulfuric acid, hydrochloric acid and acetic acid similar to the precipitation of casein dissolved in caustic soda. However, considerably more care was required to obtain a rapidly settling precipitate and a clear supernatant liquid. The caustic soda digest was used in different dilutions together with various strengths of acid in an endeavor to determine the conditions most favorable to precipitation. It was found desirable not to dilute the digest. No marked differences were obtained with the different acids used. The use of dilute acid gave the best results because a slight excess of acid carried some of the precipitate back into solution. This resulted in a cloudy supernatant liquid. After several trials a five percent hydrochloric acid solution was chosen as the precipitating agent. It was found desirable to add it drop by drop from a burette.

In the precipitation of casein by acids a slight excess did not result in peptization of the precipitate formed. That this consequence occurred in the case of substance A was considered due to salts present, resulting from the neutralization of the one percent sodium hydroxide in which the casein was digested. The presence of salts hinders the precipitation of casein and the same cause was considered operative in the case of substance A. To test this idea some of the digest was nearly neutralized with hydrochloric acid and then dialyzed. After salts had been removed from the digest in this manner, the precipitation process was not as sensitive to a slight excess of the precipitating agent.

From the above work it seemed possible that precipitation was not complete when acid was added directly to the sodium hydroxide digest even though a clear supernatant liquid was obtained. To test this point some of this clear supernatant liquid in which the addition of more acid produced no precipitate was dialyzed. After dialysis the addition of acid produced a white precipitate similar in all respects to that thrown down by the acid in the original digest. Thus it was shown that the sodium chloride present in the latter prevented the complete precipitation of substance A.

Although it was easier to precipitate substance A after dialysis, most of the product used in later experiments was precipitated without previous dialysis because the procedure was thus shortened. As previously indicated, with proper care a satisfactory product was obtained, and no differences could be noticed in products prepared by the different processes.

The precipitate formed on the addition of acid to the caustic soda was purified by reprecipitation. The supernatant liquid was decanted off and the precipitate dissolved in just sufficient dilute caustic soda. The resulting solution was made up to the volume of the original digest and reprecipitated by acid. This process was repeated three times. The final caustic soda solution was filtered through pulp to clarify it. The final precipitate was washed with water, dilute alcohol, 95 percent alcohol and ether. On adding the dilute alcohol the precipitate which was always previously white and flocculent, resembling in every respect the casein precipitate, became gummy and turned brown. When this gummy mass was worked up in a mortar with 95 percent alcohol it gradually lost its gumminess and its brown color, becoming a white precipitate, much more finely divided than the casein precipitate ever was at that stage. After washing with ether the precipitate was allowed to dry in air and was finally obtained as a white powder. No matter how carefully the precipitate was previously purified the addition of dilute alcohol always resulted in the formation of a brown gum. When ether was added to the precipitate no brown gum was formed. When the precipitate was repeatedly washed with water it gradually went back into colloidal solution due to the washing out of the precipitating agent.

Properties of Substance A

The properties of substance A were studied to determine how it differed from casein. In this connection several of the characteristic reactions of the latter were tried with the former. The results of this study will next be given.

Substance A is very slightly soluble in water but tends to form a gummy mass which is colorless. It is insoluble in 95 percent alcohol and ether. It forms a gummy mass in dilute alcohol and is somewhat soluble. Casein is insoluble in all these reagents and no gumminess results with any of them.

Substance A is easily soluble in alkalies. It is precipitated by a very little acid but this precipitation is hindered by neutral salts. An excess acid causes pectization. These properties are also shown by casein. In common with casein substance A gives the Biuret test, the Hopkins-Cole reaction, the xanthoproteic reaction, and may be precipitated from solution by magnesium sulfate and sodium chloride without change of properties.

Substance A becomes gummy in limewater and finally dissolves to form a clear solution. Casein, on the other hand, swells in limewater and forms a white solution similar in appearance to milk. When the latter is heated coagulation does not occur but a skin forms over the surface. No change was observed on heating a limewater solution of substance A. Casein in limewater is coagulated by rennin. The solution of substance A in limewater shows no evident change when digested with rennin.

Several experiments were conducted to determine whether substance A would adsorb the phosphoric acid radical. As pointed out earlier it seemed possible that such a state of union existed in consideration of the ease with which the phosphorus is split off. Samples of substance A were dissolved in varying concentrations of phosphoric acid. Another sample was dissolved in caustic soda and phosphoric acid added until the resulting precipitate was pectized. Other samples were left in contact with various acid salts of phosphoric acid. At the end of a few days the acid solutions were neutralized by alkali to the point where a precipitate was formed. These precipitates were filtered and purified by dissolving in alkali and reprecipitating by hydrochloric acid and repeating the process. The final precipitate was washed with water, alcohol and ether. During the washing with dilute alcohol the precipitate went through the brown gum stage similar to the behavior exhibited by substance A. The final product was a white powder which resembled substance A rather than casein in its reactions. The trials were repeated allowing a considerably longer period for the absorption to take place. In one case a sample of substance A was dissolved in alkali and phosphoric acid added nearly to the point of precipitation thus leaving the solution alkaline. All the trials failed to result in a product containing adsorbed phosphoric acid.

It has been stated that substance A is peptized by either limewater or phosphoric acid forming a clear solution. In this connection the following experiments were made. To a clear solution of substance A in limewater very dilute phosphoric acid was added drop by drop. A milky solution formed and no precipitate settled out. Addition of excess acid caused, of course, precipitation. Reversing the procedure, limewater was added to a solution of substance A in phosphoric acid. Again a milky solution was formed. In both the above cases it must be considered that tricalcium phosphate was formed but did not settle out because it was peptized by substance A.

The Filtrate Obtained from the Precipitation of Substance A

It was stated by Plimmer and Bayliss that the filtrate obtained after the precipitation of the white substance from the caustic soda digest contained albumoses precipitated on half saturation and complete saturation with ammonium sulfate. It was shown by us that the clear filtrate from the precipitation of substance A still contained some of that substance held in solution by sodium chloride present. The question therefore arose whether the precipitate obtained by Plimmer and Bayliss with ammonium sulfate might not have been due at least in part to incomplete precipitation by acid in the original digest. Accordingly some of the filtrate from the precipitation of substance A was saturated with ammonium sulfate. The resulting precipitate was filtered off, washed with alcohol and ether, and dried. It was a white powder resembling substance A in appearance. However, it differed markedly from the latter in that it was quite soluble in water. This indicated that the ammonium sulfate precipitate consisted chiefly at least of albumoses. It seemed probable, however, that a certain amount of substance A was also present due to incomplete precipitation in the original digest. To test this point, some of the ammonium sulfate precipitate was dissolved in just sufficient dilute caustic soda. This solution was diluted with five volumes of water and dilute hydrochloric acid drop by drop. A precipitate was obtained which was found to resemble substance A in all its reactions. The filtrate from the above was saturated with ammonium sulfate and another precipitate was obtained. The latter was completely soluble in water and was much larger than the one obtained on the addition of acid. Thus it was shown that the precipitate obtained on saturation with ammonium sulfate contained some of substance A but consisted principally of albumoses as stated by Plimmer and Bayliss.

The Splitting Off of Sulphur by One Percent Caustic Soda

Sulfur is believed to be present in the protein molecule in two forms—loosely combined sulfur and oxidized sulfur. The former is present in the greatest amount and is easily split off by alkali. In this connection it seemed worth while to note the effect of the caustic soda digestion on the sulfur of the casein molecule. Loosely combined sulfur was found present in casein before digestion but neither substance A or the albumoses precipitated by ammonium sulfate gave a test for it. Thus this sulfur must have been split off in a soluble form by the one percent caustic soda. Tests for sulfate showed that this was not the form into which the loosely combined sulfur was changed by the caustic soda digestion. Both substance A and the albumoses gave tests for oxidized sulfur.

Summary

The phosphorus of the casein molecule is split off and changed to a soluble inorganic form by the action of one percent caustic soda at room temperature. During this digestion the loosely combined sulfur is also split off.

On addition of acids to the caustic soda digest at the end of the digestion a white precipitate is obtained which was studied in some detail and designated for convenience,—substance A. The properties of this substance were determined with special reference to its difference from casein. The substance exhibited colloidal properties similar to casein as regards its behavior with acids and alkalies. A similarity was also noted in connection with its response to protein tests and its precipitation by salt solutions. However, marked differences were shown as regards solubility in different reagents. A limewater solution of substance A showed none of the characteristic properties of a similar solution of casein. However, when phosphoric acid was introduced into the former in such a way as not to destroy the colloidal solution a milky solution was obtained which on heating behaved similar to a limewater solution of casein. Evidence is here furnished for the supposition that the white color of milk is due to the peptization of tricalcium phosphate by the colloids in the milk.

Attempts to cause substance A to adsorb the phosphoric acid radical were unsuccessful. This experimental work, however, furnishes no proof that such a state of union is not present. Inasmuch as sulfur and albumoses are also split off from the casein molecule by caustic soda these substances are probably closely associated with the phosphorus and therefore, assuming that phosphorus is adsorbed, their presence may be essential to the union.

The author wishes to acknowledge his indebtedness to Prof. Wilder D. Bancroft for valuable suggestions and advice in carrying out the above study.

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THE COLORS OF COLLOIDS. III

BY WILDER D. BANCROFT

Reflection and Visibility

When light is reflected from a practically smooth surface, we get only images of external substances which are either self-luminous or reflect diffusely, while the reflecting surface, which is often called a mirror, is more completely invisible the smoother it is.[1] "If the only source of light in a room is a tiny flame and if one places on a table in the room a piece of white paper and close beside it a very good mirror, preferably a black mirror or a dish filled to the brim with pure mercury, the paper surface and the mirror surface behave quite differently. The paper can be seen from any point where one can look down upon the table but the mirror can be seen only when there are definite relative positions for the observer and the mirror, when one can see the mirrored image of the flame. Both substances reflect light; but the mirror sends out light only in definite directions, whereas the paper reflects the incident light in all directions. We say that the mirror reflects light regularly and the paper irregularly. All smooth substances reflect light regularly and all rough ones irregularly. Usually both types of reflection occur simultaneously but with one or the other predominating. Any particle of dust on the mirror reflects light in all directions and so does any impurity on the surface of the mirror. It is almost as difficult to make an absolutely matt surface. Almost all of them show some lustre, reflecting part of the incident light regularly. Plaster of Paris is one of the least lustrous of the white substances." As Chwolson[2] puts it: "On the retina of the eye there are formed only images of objects reflected by the mirror, or, to be very exact, images of the images given by the mirror. If the surface of the mirror has little inequalities or is covered by small foreign substances, the surfaces of the elementary waves

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[1] Von Bezold: "Die Farbenlehre," 58 (1874).

[2] "Traité de Physique," 2, 206 (1906).

formed round each point on the mirror, where the rays from a luminous source strike it, do not, in accordance with Huygens' principle, form a wave surface of which one can consider a finite portion as spherical. There is, instead, a superficial dispersion of radiant energy and the mirror becomes visible. For the diffusion to be perceptible, the height, h, of the inequalities of the mirror must be very small compared with the wave-length, λ of the radiant energy in question, relatively small with respect to 0.5 μ in case of the visible rays. Rays making an angle of φ with the normal at the point of incidence may be reflected regularly if $h \cos \varphi$ is small with reference to λ, which explains why a smooth paper may almost act like a mirror and give images when rays fall upon it at a very small angle of incidence. Such images have a reddish color because the rays which are reflected most regularly, are those with a large wave-length, in other words, the red rays."

Rayleigh[1] has discussed the whole question of polish. "The fineness necessary, in order that a surface may reflect and refract regularly without diffusion, *viz.*, in order that it may appear *polished*, depends upon the wave-length of the light and upon the angle of incidence. At a grazing incidence all surfaces behave as if polished, and a surface which reflects red light pretty well may fail signally when tested with blue light at the same angle. If we consider incidences not too far removed from the perpendicular, the theory of gratings teaches that a regularly corrugated surface behaves as if absolutely plane, provided that the *wave-length* of the corrugations is less than the wave-length of the light, and this without regard to the *depth* of the corrugations. . . Finely-ground surfaces are still too coarse for perpendicular specular reflection of the longest visible waves of light. Here the material may be metal, or glass silvered chemically on the face subsequent to grinding. But experiment is not limited by the capabilities of the eye; and it seems certain that a finely ground surface would be smooth enough to reflect without sensible diffusion

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[1] Proc. Roy. Inst., 16, 563 (1901).

the longest waves, such as those found by Rubens to be nearly 100 times as long as the waves of red light. . . .

"In view of these phenomena we recognize that it is something of an accident that polishing processes, as distinct from grinding, are needed at all; and we may be tempted to infer that there is no essential difference between the operations. This appears to have been the opinion of Herschel,[1] whom we may regard as one of the first authorities on such a subject. But although, perhaps, no sure conclusion can be demonstrated, the balance of evidence appears to point in the opposite direction. It is true that the same powders may be employed in both cases. In one experiment a glass surface was polished with the same emery as had been used effectively a little earlier in grinding. The difference is in the character of the backing. In grinding, the emery is backed by a hard surface, *e. g.*, of glass, while during polishing the powder (mostly rouge in these experiments) is embedded in a comparatively yielding substance, such as pitch. Under these conditions, which preclude more than a moderate pressure, it seems probable that no pits are formed by the breaking out of fragments, but that the material is worn away (at first, of course, on the eminences) almost molecularly.

"The progress of the operation is easily watched with a microscope, provided, say, with a 1/4 inch object-glass. The first few minutes suffice to effect a very visible change. Under the microscope it is seen that little facets, parallel to the general

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[1] "Enc. Met. Art. Light," 447 (1830). The intensity and regularity of reflection at the external surface of a medium is found to depend not merely on the nature of the medium, but very essentially on the degree of smoothness and polish of the surface. But it may reasonably be asked, how any regular reflection can take place on a surface polished by art, when we reflect that the process of polishing is, in fact, nothing more than grinding down large asperities into smaller ones by the use of hard gritty powders, which, whatever degree of mechanical comminution we may give them, are yet vast masses, in comparison with the ultimate molecules of matter, and their action can only be considered as an irregular tearing up by the roots of every projection that may occur in the surface. So that, in fact, a surface artificially polished must bear somewhat of the same kind of relation to a liquid or a crystal that a ploughed field does to the most delicately polished mirror, the work of human hands.

plane of the surface, have been formed on all the more prominent eminences.[1] The facets, although at this stage but a very small fraction of the whole area, are adequate to give a sensible specular reflection, even at perpendicular incidence. On one occasion five minutes polishing of a rather finely ground glass surface was enough to qualify it for the formation of interference bands, when brought into juxtaposition with another polished surface, the light being either white or from a soda flame; so that in this way an optical test can be applied almost before the polishing has begun.[2]

"As the polishing proceeds, the facets are seen under the microscope to increase both in number and size, until they occupy much the larger part of the area. Somewhat later the parts as yet untouched by the polisher appear as pits or spots upon a surface otherwise invisible. The continuation of the process consists in rubbing away the whole surface down to the level of the deepest pits. The last part of the operation, while it occupies a great deal of time, and entails further risk of losing the 'truth' of the surface, adds very little to the effective area, or to the intensity of the light regularly reflected or refracted.

"Perhaps the most important thing taught by the microscope is that the polish of individual parts of the surface does not improve during the process. As soon as they can be observed at all, the facets appear absolutely structureless. In its subsequent action the polishing tool, bearing only upon the parts already polished, extends the boundary of these parts but does not enhance their quality. Of course, the mere fact that no structure can be perceived, does not of itself prove that pittings may not be taking place of a character too fine to be shown by a particular microscope or by any possible microscope. But so much discontinuity, as compared with the

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[1] The interpretation is facilitated by a thin coating of aniline dye, which attaches itself mainly to the hollows.

[2] With oblique incidence, as in Talbot's experiments (see Phil. Mag., (5) 28, 191 (1889)), achromatic bands may be observed from a surface absolutely unpolished but this disposition would not be favorable for testing purposes.

grinding action, has to be admitted in any case, that one is inevitably led to the conclusion that in all probability the operation is a molecular one, and that no coherent fragments are broken out. If this be so, there would be much less difference than Herschel thought between the surfaces of a polished solid and of a liquid.

"Several trials have been made to determine how much material is actually removed during the polishing of glass. In one experiment a piece six inches in diameter, very finely ground, was carefully weighed at intervals during the process. Losses of 0.070, 0.032, 0.045, 0.026, 0.032 gram were successively registered, amounting in all to 0.205 gram. Taking the specific gravity of the glass as 3, this corresponds to a thickness of 3.6×10^{-4} cm, or to about 6 wave-lengths of mean light, and it expresses the difference between the original *mean* surface and the final plane. But the polish of this glass, though sufficient for most practical purposes, was by no means perfect. Probably the 6 wave-lengths would have needed to be raised to 10 in order to satisfy a critical eye. It may be interesting to note for comparison that, in the grinding, one charge of emery, such as had remained suspended in water for seven or eight minutes, removed a thickness of glass corresponding to 2 wave-lengths.

"In other experiments the thickness removed in polishing was determined optically. A very finely ground disc was mounted in the lathe and polished locally in rings. Much care was needed to obtain the desired effect of a ring showing a continuously increasing polish from the edges inwards. To this end it was necessary to keep the polisher (a piece of wood covered with resin and rouge) in constant motion, otherwise a number of narrow grooves developed themselves. The best ring was about half an inch wide. When brought into contact with a polished flat and examined at perpendicular incidence with light from a soda flame, the depression at its deepest part gave a displacement of three bands, corresponding to a depth of 1.5 λ. On a casual inspection, this central part appeared well polished, but examination under the microscope revealed a fair number of small pits. Further working increased the maximum depth to 2.5 λ, when but very few pits remained. In this case, then, polish was effected during a lowering of the mean surface through 2–3 wave-lengths; but the grinding had been exceptionally fine.

"It may be well to emphasize that the observations here recorded relate to a hard substance. In the polishing of a soft substance, such as copper, it is possible that material may be loosened from its original position, without being detached. In such a case pits may actually be filled in, by which the operation would become much quickened. Nothing suggestive of this effect has been observed in experiments upon glass."

While every sufficiently smooth surface gives rise to regular reflection, we do not notice this unless the light reflected from it is not interfered with too much by transmitted light. At night, especially in the country, the windows of a street-car are practically opaque and act as mirrors because relatively little light comes through from outside. If the light inside the car is extinguished owing to the power going off, the glass panes cease to be mirrors and become windows because the light transmitted through the glass is all that one sees, though it has not increased absolutely in amount. If one drives a motor toward the sun, the increased illumination of the people on the front seat may give rise to such strong reflections from the wind-shield as to interfere a good deal with one's view of the road. This is an especially interesting case because the disturbing light has passed through the wind-shield and has then undergone two reflections. Everybody is familiar with the fact that an electric fan is practically transparent if there is a bright light behind it and a dim one in front, whereas it is practically opaque if these conditions are reversed. So far as our eyes are concerned, transparency and opacity depend on the illumination as well as on the nature of the substance illuminated. The terms are therefore relative and not absolute.

The question of reflection from matt surfaces has been discussed by Wood.[1] "One of the most interesting and instruc-

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[1] "Physical Optics," 42 (1911).

tive applications of the Fresnel construction is to the diffuse reflection and refraction which occur when light strikes unpolished or matt surfaces, such as paper, plaster of Paris, or ground glass. We have explained regular reflection by showing that there is destructive interference between the wavelets arriving at any point from the surface of the mirror, and that the illumination is practically due to the disturbances coming from a small region surrounding the point so situated that straight lines joining it to the source of light and the illuminated point make equal angles with the normal. An unpolished surface destroys all phase relation between the elements on the wave-front. The secondary wavelets start from the elevated portions of the surface first, since these portions are struck first by the incident wave, and the wave-front, instead of being plane, is pitted and corrugated in an irregular manner. It is impossible to arrange any zone system on such a surface, for there are all possible phase differences irregularly distributed over the reflected wave-front, consequently each point on the surface acts as an independent luminous source sending light out in all directions."

This paragraph will probably not be any more helpful to most people than it is to me. The substance of it can be put more simply, though perhaps less accurately. If we have a perfectly polished surface, the image of any given illuminated point will be seen reflected from only one place on the surface and will therefore not interfere with the image of any other illuminated point. If the surface is rough, the light from the first point will be reflected to the eye from a number of different points on the reflecting surface and one will get a blur instead of an image. With a very smooth sea, one sees a single image of the moon at night; but, if there is a slight breeze, the images run together to form a bright path. The only night I ever crossed from Lübeck to Copenhagen, there was no breeze and there was a slight, long swell, and I saw half a dozen images of the moon, one from each swell, but enough apart not to conflict in any way. It would, of course, be easy to duplicate this on a small scale. Von Bezold[1] points out that "in order to change regular reflection into irregular reflection, it is sufficient to change the surface of the substance. The moment the regularity of the surface disappears, the substance appears matt. If one looks at a lake surrounded with trees from a distance on a very calm day, one may be deceived by the mirrored image of the trees, but a breath of air is sufficient to destroy the illusion, and one sees at once the rippled surface of the water."

It has already been mentioned that a reflecting surface is invisible if absolutely smooth.[2] Actually this invisibility is not absolute[3] because of scratches, cracks, dust, etc. This brings us to the general question of visibility as discussed by Wood.[4] "Opaque substances are seen by the light reflected from their surfaces; transparent substances in part by reflected light and in part by transmitted light. If we analyze carefully the appearance of a cut-glass decanter stopper we shall find it to be extremely complicated. Each facet reflects the image of some object in the room from its surface, and in addition to this shows some other object by refracted rays which have entered some other facet, these latter being in general more or less spread out into a spectrum by dispersion. If the stopper is wholly or in part made of colored glass, the refracted rays passing through the colored portions are modified by absorption, and affect the appearance. This remarkable complex, we say, looks like a stopper, and unless we try to paint a picture of it, or have our attention drawn to the details, we are apt to regard its appearance as quite simple.

"We thus see that reflection, refraction, and absorption, all play a part in making objects visible. It is interesting to examine into the conditions under which objects are invisible. If they are immersed in a medium of the same refractive index and dispersion, reflection and refraction disappear; and they

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[1] "Die Farbenlehre," 58 (1874).

[2] Chwolson: "Traité de Physique," 2, 206 (1906).

[3] Winkelmann: "Handbuch der Physik.," 2, I, 18 (1894).

[4] "Physical Optics," 98 (1911).

possess in addition the qualities of perfect transparency, they will be absolutely invisible, the light rays passing through them without any modification either in intensity or direction. Could a transparent solid be found whose refractive index was the same as that of air, objects made of it would be invisible. The effect of immersing a transparent solid in a medium of similar optical properties is usually illustrated by dipping a glass rod into Canada balsam or oil of cedar, the immersed portion being practically invisible. A still better medium can be made by dissolving chloral hydrate in glycerine by the aid of heat. Only a little glycerine should be taken, as it is necessary to dissolve some eight or ten times its volume of the chloral before the solution acquires the right optical density. A glass rod, if free from bubbles or striae, becomes absolutely invisible when dipped in the liquid, and if withdrawn presents a curious appearance, the end appearing to melt and run freely in drops. As a matter of fact, transparent objects are only visible by virtue of non-uniform illumination, as is pointed out by Lord Rayleigh in his article on optics in the Encyclopedia Britannica. If the illumination were the same on all sides they would be invisible, even if immersed in a medium of very different optical index. A condition approaching uniform illumination might, he says, be attained on the top of a monument in a dense fog. The author has devised a very simple method of showing this curious phenomenon, which, in brief, is to place the object within a hollow globe, the interior surface of which is painted with Balmain's luminous paint, and view the interior through a small hole.

"The apparatus can be made in a few minutes in the following manner: A quantity of Canada balsam is boiled down, until a drop placed on cold glass solidifies. The Balmain paint, in the form of dry powder, is stirred into the hot balsam until the whole has the consistency of thick paint. Two glass evaporating dishes of equal size are carefully cleaned and warmed, and coated on the outside with the hot mixture, which can be flowed over the glass, and by the dextrous manipulation of a small Bunsen flame made to cover the entire outer surface. Probably two perfectly plain hemispherical finger-bowls could be used instead of the evaporating dishes. As soon as the coating has become hard a small hole is cut through it through which the interior is to be viewed. If the lips of the dishes are placed together the interior can be seen through the small opening, but in this case the line of junction, which is always more or less dark, comes opposite the aperture, which is a disadvantageous arrangement.

"If the inner surfaces be exposed to bright daylight, sun or electric light, and the apparatus taken into a darkened room, a crystal ball or the cut-glass stopper of a decanter placed inside, will be found to be quite invisible when viewed through the small aperture. A uniform blue glow fills the interior of the ball and only the most careful scrutiny reveals the presence of a solid object within it. One or two of the side facets of the stopper may appear if they happen to reflect or show by refraction any portion of the line of junction of the two hemispheres.

"The apparatus would give better results if it were made on a larger scale, as the eye would not have to be brought so near the object. Two large wooden bowls would answer the purpose admirably. It is of the utmost importance to have a very thick and uniform coating of the paint, as otherwise the illumination is not uniform."

Tyndall[1] points out that "reflection always accompanies refraction; and if one of these disappear, the other will disappear also. A solid body immersed in a liquid having the same refractive index as the solid, vanishes; it is no more seen than a portion of the liquid of the same size would be seen." This has been discussed more in detail by von Bezold.[2] "If one fills a test-tube partly full with coarse glass powder, the powder appears white and it is impossible to see through it. If one pours water into the test-tube, the latter becomes somewhat transparent. This is more marked if one substitutes turpentine for water. Carbon bisulphide is a liquid having

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[1] "Light and Electricity," 39 (1895).

[2] "Die Farbenlehre," 62 (1874).

about the same refractive index as glass. If this liquid is poured on the powder, the powder becomes practically invisible, and one can see through the test-tube as though it contained only the clear liquid and no glass powder at all. If one dips a glass rod into a mixture of olive oil and cassia oil, it looks as though the glass rod reached only to the surface of the liquid, for it cannot be detected in the liquid, which is completely transparent. Instead of the glass powder one can substitute small beads of transparent colorless glass. These also become invisible as soon as the liquid displaces the air between them. This shows that the presence of one transparent substance in another can be detected by the eye only when the two refract light differently. If that is not the case the light goes through the mixture unchanged."

Actually, the matter is not always as simple as this because Christiansen has shown that there may also be an effect due to the difference between the dispersions of the liquid and the immersed solid.[1] "Powdered glass, all from one piece and free from dirt, is placed in a bottle with parallel flat sides. In this state it is quite opaque; but if the interstices between the fragments are filled up with a liquid mixture of bisulphide of carbon and benzene, carefully adjusted so as to be of equal refractivity with the glass, the mass becomes optically homogeneous and therefore transparent. In consequence, however, of the different dispersive powers of the two substances, the adjustment is good for one part only of the spectrum, other parts being scattered in transmission much as if no liquid were employed, though, of course, in a less degree. The consequence is that a small source of light, backed preferably by a dark ground, is seen in its natural outlines but strongly colored. The color depends upon the precise composition of the liquid, and further varies with the temperature, a few degrees of warmth sufficing to cause a transition from red through yellow to green.

"The author had long been aware that the light regularly transmitted through a few strata from fifteen to twenty

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[1] Rayleigh: Proc. Roy. Inst., 16, 116 (1899).

millimeters thick was of a high degree of purity, and it was only recently that he found to his astonishment, as the result of a more particular observation, that the range of refrangibility included was but two and a half times that embraced by the two D-lines. The poverty of general effect, when the darkness of the background is not attended to, was thus explained; for the highly monochromatic and accordingly attenuated light from the special source is then overlaid by diffused light of other colors. . . As regards the size of the grains of glass, as great or a greater degree of purity may be obtained in a given thickness from coarse grains as from fine ones, but the light not regularly transmitted is dispersed through smaller angles."

The same subject has been discussed in more detail by Wood.[1] "While engaged upon some determinations of the refractive indices of white powders by the method of immersing them in liquid mixture of the same refractive index, Christiansen[2] observed some very remarkable and interesting effects. Owing to the different dispersive powers of the liquid and powder, complete transparency could only be obtained for monochromatic light. If white light was employed the transmitted light was highly colored, the transmitted color corresponding to the particular wave-length for which the two substances happened to have the same refractive index. Finely powdered glass immersed in a mixture of benzol and bisulphide of carbon was found to exhibit the colors well. The powder must be quite free from dirt, the elimination of which is sometimes difficult. The author has obtained the best results with powdered quartz, which can be procured from the large chemical houses. The powder is boiled in nitro-muriatic acid to free it from impurities and thoroughly washed in clean water. It is then dried and placed in a small flask with enough bisulphide of carbon to wet it thoroughly. Benzol is then added a little at the time until the mixture begins to get transparent. It will be found that red light is transmitted first, then yellow,

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[1] "Physical Optics," 110 (1911).

[2] Wied. Ann., 23, 289 (1884).

green, and blue in succession as more benzol is added. It is best to stop when the transmitted light is yellow. In the general illumination of a brightly lighted room the colors are not very pronounced, and it is best to employ a distant lamp in a fairly dark room as a source of light. If a permanent preparation is desired, the following method gives good results. A quantity of the quartz powder is introduced into a 100 cc flask (not more than $^1/_{10}$ of the volume of the flask) the neck of which is then drawn down in a blast until it has a diameter of only a few mms. The liquid previously adjusted in the manner described is then introduced in sufficient quantity to form a rather thick pasty mass, which will stick in a thick layer to the walls of the flask if it is shaken. The flask is then packed in powdered ice and salt and the neck closed by fusion in the flame. The freezing mixture is necessary on account of the inflammability of the vapor and its tension, and it is a good plan to wrap a towel around the beaker containing the flask and cooling mixture in case of explosion. On removing the flask from the ice it will be found to be quite opaque, owing to the change in the refractive index of the liquid. As the temperature rises red light is transmitted first and by lightly warming the flask in spots by momentary contact with a flame or even with the fingers all colors of the rainbow may be made to appear simultaneously, the whole appearing like a great opal. The reason of these beautiful temperature changes will be readily understood" if we consider "a linear source of light which is deviated to the right and spread out into two spectra by prisms of the same angle, the one composed of quartz, the other of the liquid mixture. The refractive indices having the same value for yellow light, the yellow of one spectrum will fall immediately above the yellow of the other. Since, however, the liquid has a much higher dispersion it will yield a longer spectrum and the other colors will not be in coincidence, or in other words, the refractive indices are different for all the other colors. The color transmitted will obviously be the one for which we have coincidence. The other colors will be more or less scattered by irregular refractions. Suppose now we heat the mixture, the increase of temperature will cause the liquid to expand and its refractive index to decrease, while the effect upon the quartz is comparatively slight. This will mean a shift of the lower spectrum in the diagram towards the left, the green regions of the two spectra coming into coincidence, while a further increase of temperature will bring the blue regions together. The effect of the warming is thus to shift the region of transmission down the spectrum towards the blue.

"In general, unless the thickness of the heterogeneous medium is considerable, the light which is not directly transmitted emerges to some extent as diffused light. The color of this diffused light is complementary to the transmitted, and the green image of a lamp flame seen through a thin layer of the paste is surrounded by a purple halo. The colors seen when equal volumes of glycerine and turpentine are shaken together into an emulsion are of similar nature, though erroneously attributed to interference in some text-books. The opalescent precipitate obtained by the addition of hydrofluosilicic acid to a solution of potassium chloride has been found by the author to be another case, the color of the transmitted light changing in a most beautiful manner upon the addition of water, which diminishes the refractive index of the liquid, precisely as the rise of temperature did in the case of the benzol mixture. Fuller particulars regarding these curious mixtures will be found in the original papers of Christiansen, and in an interesting paper by Lord Rayleigh."[1]

If conditions are suitable for multiple reflections, a number of new phenomena occur. By this means it is possible, for instance, to distinguish between the superficial and the true colors of metals.[2] "When the luminous rays fall on the surface of a substance, part of them are reflected, while others penetrate some distance into the substance. Of these latter rays, some are absorbed and their radiant energy changed into other forms of energy, usually heat energy, while others are

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[1] Phil. Mag., 20, 358 (1885).

[2] Chwolson: "Traité de Physique," 2, 353 (1906).

sent back in all directions from the substance and mingle with the rays reflected regularly. The superficial color depends on all the rays thus sent back. The fact that a perfectly polished substance, reflecting rays like a mirror, is not visible in itself and has no color, shows that the superficial color is not due to the rays reflected regularly. When a surface is lighted in the ordinary way and part of the rays are reflected, we do not see the true color of the substance, but that color weakened by an admixture of white light. By arranging two parallel sheets of metal with the polished surfaces turned inwards, so that the incident light is reflected a number of times, Prévost has determined the true color of the metals. At each reflection the rays which do not correspond to the true color of the metal are absorbed. After a number of reflections, these rays are all stopped and there remain only those rays sent back from the superficial layer and which determine the true color of the metal. In this way Prévost found that gold was red-orange, silver was orange, and copper a brilliant purple. W. L. Rosenberg has pointed out that the superficial color varies with the angle of coincidence of the luminous rays, and he has constructed an apparatus which permits one to study this variation conveniently. Margot has noticed that several alloys have a characteristic color: an alloy of 72 percent Al and 28 percent Pt is yellow like gold; and alloy of 20–25 percent Al and of 80–75 percent Co is yellowish; an alloy of 18 percent Al and 82 percent nickel is reddish yellow, while an alloy of aluminum and palladium is pink." A ground glass surface appears opaque and gray; but a matt surface may appear nearly white if it reflects a large proportion of the incident light. Electrolytically precipitated silver is a striking instance of this. On the other hand, a special state of things may occur at porous surfaces.[1] "The absorption of light at surfaces formed of lamp-black or finely divided metals such as platinum black is accompanied by very little reflection. The question naturally arises as to why a metal with a high reflecting power can, under certain conditions, appear nearly

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[1] Wood: "Physical Optics," 449 (1911).

dead black. The surfaces of electrolytically deposited silver appear as white as plaster. Chemically precipitated silver, on the other hand, appears black. The phenomenon is to be referred to the conditions of the surface. Consider a bunch of polished steel needles, turned with their points towards the light. Rays falling upon the surface formed by the points will be reflected down into the interstices between the needles, and practically none of them will escape or be reflected back. A portion is absorbed at each reflection, and the large number of reflections reduces the intensity rapidly to zero. Surfaces of lamp-black (soot) and platinum black can be considered as porous, the pores acting as light 'traps.' The energy penetrates into the spongy mass by multiple reflection, and is speedily transformed into heat by absorption. If the pores are closed up by compressing the mass, its reflecting power is increased or wholly restored. If, too, the angle of incidence is too large to admit of downward reflection into the mass, the light is more or less completely reflected. A surface of smoked glass reflects very perfectly at large angles of incidence, and at the same time yields a sharply defined image of the source of light."

If the index of refraction of a dispersed phase is quite different from that of the dispersing medium, and if the dispersed phase consists of small particles, very little light will get through and the appearance of the system will depend on the amount and the nature of the reflected light. We have just seen that silver may seem quite white or very black under different conditions. If the dispersed phase is fairly transparent, the absorption of the internally reflected light is negligible and the color of the reflected light is white if the incident light is white.[1] Emulsions may be white and so may masses of fine crystals even though the massive crystal is quite colored. The blue color of copper sulphate, for instance, disappears practically completely when a large crystal is ground to a powder.

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[1] Burton: "The Physical Properties of Colloidal Solutions," 94 (1916).

As von Bezold[1] puts it, "if one crushes into powder a substance whose surfaces reflect regularly, each little fragment will reflect regularly; but the positions of the reflecting surfaces are so numerous that the incident light is scattered in all directions. Every ice-crystal in a falling snow-flake has a perfectly reflecting surface, is colorless, and is transparent; but a snow-covered field appears matt and white. Glass powder behaves the same way and so does the powder of any transparent colorless crystals. For the same reason a spray of water appears white and so does effervescing soda-water."

Chwolson says that the powders of colorless substances, such as different crystals and glass, and the foam of colorless liquids, such as water, appear white. In the powders and in the foam there are produced a multiple refraction and a total reflection which makes them less transparent. A considerable number of the rays which have penetrated into powders or a foam are scattered in all directions which makes the powder and the foam appear white. If a colored mass is sufficiently transparent, it will appear practically colorless when powdered.[2] "The nature of pigments can be well studied by preparing a number of beads of fused borax, colored with varying amounts of cobalt. If we powder a bead which appeared bright blue by transmitted light, we shall find that the powder is white, the reason being that the light in this case does not penetrate a sufficient thickness of the absorbing medium. A bead colored so dense as to appear black will, however, furnish us with a blue pigment when it is reduced to powder. Pigments, then, are very powerful absorbing media and would be intensely opaque even in fairly thin sheets, if they could be obtained in homogeneous masses."

Tyndall[3] says: "In the passage from one medium to another of a different refractive index, light is always reflected; and this reflection may be so often repeated as to render the mixture of two transparent substances practically impervious

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[1] "Die Farbenlehre," 58 (1874).

[2] Wood: "Physical Optics," 440 (1911).

[3] "Light and Electricity," 59 (1895).

to light. It is the frequency of the reflections at the limiting surfaces of air and water that renders *foam* opaque. The blackest clouds owe their gloom to this repeated reflection which diminishes their *transmitted* light. Hence also their whiteness by *reflected* light. To a similar cause is due the whiteness and imperviousness of common salt and of transparent bodies generally when crushed to powder. The individual particles transmit light freely; but the reflections at their surfaces are so numerous that the light is wasted in echoes before it can reach to any depth in the powder. The whiteness and opacity of writing paper are due mainly to the same cause. It is a web of transparent fibers, not in optical contact, which intercept the light by repeatedly reflecting it. But if the interstices of the fibers be filled by a body of the same refractive index as the fibers themselves, the reflection of their limiting surfaces is destroyed, and the paper is rendered transparent. This is the philosophy of the tracing-paper used by engineers. It is saturated with some kind of oil, the lines of maps and drawings easily copied *through* it afterward. Water augments the transparency of paper, as it darkens a white towel; but its refractive index is too low to confer any high degree of transparency. It however, renders certain minerals translucent which are opaque when dry."

An interesting phenomenon of a similar type has been observed by Krukenberg.[1] "The great difference in color among flamingoes is very striking. The color of the plumage may vary from the palest pink to a uniform, deep rose-red, such as is found otherwise only on the Central American red ibis (*Ibis rubra*). It has often been asserted that the color of the plumage was due to the flamingo living on fish. Since we now know that the feathers of the flamingo are dyed with zooerythrin, this view seems rather superfluous, more especially since flamingoes have been kept for years on a diet containing no fish without any decrease in the original red being noticeable. The most probable explanation seems to be that of Fatio, that the varying intensity of red among the

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[1] "Vergleichend-physiologische Studien," 1, V, 90 (1881).

flamingoes is due to individual variations in the natural fat content of the feathers, for the feathers seem much redder when soaked in oil than when in an air-dry state."

Von Bezold[1] has discussed the behavior of fabrics. "The fibres from which the threads of textile fabrics are made are colorless. When dyed they take up the color in such a way as to appear colored throughout, like threads of colored glass; but between these threads there is air and the light which falls on such a fabric is converted at the surface of each thread partly into reflected and partly into transmitted light. According to the method of weaving, one can vary the amount of reflected light within fairly wide limits and can make the reflection more or less regular; in other words one can produce matt or glossy fabrics and, in the case of the matt fabrics, can reduce the amount of reflected white light to a minimum, as is done with velvet. The regular reflection with these fabrics differs considerably from that at a plane glass surface. Through the arrangement of the threads, the reflection may be intensified in certain directions. With taffeta or linen the reflection is strongest in two directions at right angles to each other. With a twill the reflection is usually very marked in only one direction. The effect is still greater with satin, which really belongs to the twill class. Here the warp passes very many times over the woof and the latter is visible only at very irregular intervals in order to avoid the diagonal lines peculiar to the ordinary twill. In this way the whole effect is due to the parallel threads of the woof and the direction of these threads acquires a special significance. When one looks from the side one sees the shaded grooves, which appear to be separated from one another only by narrow lustrous lines. When looking perpendicularly, these lustrous lines are the things which catch the eye. If the warp and woof change places within definitely limited spaces, the fabric is damask, the two parts of which differ only in the relative amounts of white light reflected from the surface and colored light coming from the depths.

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[1] "Die Farbenlehre," 68 (1874).

"Quite a different state of things occurs with velvet, which has a structure like a brush. Here every effort is made to keep the light reflected from the surface down to a minimum, to eliminate it as completely as possible. Regular reflection and the actual lustre is avoided almost completely with velvet, since only the tips of the threads reflect the uncolored light and these reflect irregularly. By far the greatest portion of the incident light comes to the eye only after a long and broken path among the threads. The color is therefore highly saturated but has lost a good deal in brightness. For this reason velvet shows the color of the threads with a very slight admixture of white even when illuminated and looked at from a very sharp angle. When looked at perpendicularly it has a depth of color (saturation) such as no other fabric can show. The phenomena are the same as are shown, though to a lesser extent, by a cloth arranged in very many and very deep folds. For this reason one also gets, even with velvet, the same gradation of tints between the absorption color and the faint lustre which can be noticed in hangings of other materials which fall in many folds. Satin and velvet are the two extremes among textiles. One admires the first for its lustre and the second for its color. Certain very definite colors are better adapted for one kind of effect or for the other."

The scattering of reflected white light at a surface can be overcome by introducing regular reflection.[1] "This is done in oil paintings by varnish. Varnish gives the painting a reflecting surface which reflects a great deal of white light in certain directions and this may be very disturbing; but this light is reflected only in definite directions and if one stands away from the line to the source of light, one gets the real color relatively intense because not admixed with much white. If the oil dries while the painter is working at a picture in oils, the brilliant surface and the regular reflection disappear. The white light is then reflected in all directions from the surface and the colors of the picture appear dull and opaque from any place in the room. . . .

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[1] Von Bezold: "Die Farbenlehre," 66 (1874).

"The opaque colors act quite differently from the transparent ones, even though they are transparent in very thin films and even though it is the transmitted light which gives them their characteristic color The great difference in the optical properties of the pigment and the vehicle makes it impossible for the light to penetrate deeply and consequently at each surface of the pigment particles there is a splitting into reflected and transmitted light, the latter becoming negligible only a little way below the surface. The same is of course true for the light sent out from the lower layers and consequently such pigments are opaque when put on in moderately thick layers. Since the light is not changed materially by reflection at the surface of the pigment grains, the amount of white light reflected from the opaque colors always contains more white than that reflected from the transparent colors. One, therefore, never gets the fire and depth, or saturation, with opaque colors that we do with transparent colors. For this reason varnish brings out the glazing colors pre-eminently, because with them elimination of the light reflected at the surface takes out all the disturbing light, whereas some white light comes from the deeper layers in the case of the opaque pigments. . . . .

"The proper understanding of the part which the medium plays in painting led von Pettenkofer to the important discovery of the regeneration process. He recognized that the clouding of old oil paintings is not due to fungus growth as people had supposed; but is the result of very fine cracks in the vehicle, whereby the transparency is destroyed and the amount of white light scattered at the surface becomes relatively large. The vapor of cold alcohol is sufficient to soften the resins or the resinified oils used in oil paintings sufficiently to close the pores and to bring back the colors in their original force and freshness."

The general question of varnish has been discussed by Livache and McIntosh.[1] "In addition to a preservative

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[1] "The Manufacture of Varnishes and Kindred Industries," 2, 3, 121, 120, 28 (1908).

action, varnishes have a decorative effect. The application of a coat of varnish to any porous surface, dressed and smoothed in an appropriate manner, enhances its appearance by imparting thereto a uniform, polished, glassy lustre. Should the object to which it is applied consist of previously dressed wood, it not only brings into bolder relief the more prominent structural features of the wood, by filling up the pores thereof with a transparent medium, but by a light and shade contrast (produced by the harder and denser fibers as against the softer and less compact) it brings prominently into view all the characteristic modifications and ramifications of the woody fiber of different timbers included under the term 'grain.' The whole structure of the wood is, as it were, brought to the same level by actual contact with a glassy surface. By coloring the varnish, artificially, by coloring principles, soluble in varnish, like that of alkanet root, a stained glassy surface is produced, by which poorer quality timber may be made to pass for better quality; the same result may also be arrived at by using aniline dyes, colored resins, gamboge, dragon's-blood, grass-tree gum, etc. The coloring principle by being fixed more intensively on certain portions of the grain of the wood than upon others, still further brings the grain into more bold relief and still further accentuates the beautifying effect of the varnish."

"Brilliancy and lustre depend on the nature of the resin. The greater the ratio of resin to oil the greater is the brilliancy and lustre of the varnish. As a matter of fact the brilliancy of a varnish is a property dependent on its index of refraction. As the index of refraction of a resin is greater than that of linseed oil, a varnish is more lustrous the more resin is in it. Hence the reason why spirit varnishes after drying are more lustrous than oil varnishes. Each unit percent of oil in a dried coating of an oil varnish diminishes its lustre *pro rata*. On the other hand, even if it increases the lustre proportionately, each unit percent of resin in varnish after a certain amount diminishes its durability *pro rata*. A compromise has therefore to be made according to the object in view in designing a varnish for any given purpose. Where brilliancy is a desideratum, the resin must not be less than $^1/_3$ to $^1/_4$ by weight of the dried coat. But where brilliancy leaves off, durability is only beginning, and, where great elasticity is demanded, varnishes are used in which the resin forms only $^1/_6$ of the dried coat. In the case of piano varnish, for instance, durability is sacrificed to lustre to a certain extent, and the percentage of resin to oil preponderates in such a varnish. The harder the resin the greater the brilliancy. A Manila varnish made with the same number of gallons of linseed per 100 lbs. of Manila is less lustrous than one made in the same ratio of oil to resin from Zanzibar copal. It is asserted that the index of refraction of a varnish is greater than that calculated from its composition; but this may be due to a turpentine residuum left out of the calculation. Be this as it may, the skill and care with which varnishes are made are factors which cannot be lost sight of in any investigation into the cause of the brilliancy of the varnish."

"The color of the varnish will be paler the greater the amount of care that has been taken in the selection and cleansing of the resins and in the selection and preparation of the oil made from well-matured pure linseed, and in the refining and bleaching of such oil, and careful as well as prolonged tanking of the same, and the greater the amount of attention with which the exact temperature necessary for the fusion of the resins in the most appropriate vessels as regards size and shape has been regulated. Lead driers tend to darken varnish. But pale varnishes are not always appropriate. Dark-colored varnishes accentuate the beauty of dark wood, and, to enhance this effect still further, dyes are often dissolved in varnish to still further accentuate the color of the wood, so that one imagines that he is looking through colored glass on to a smooth polished opaque matrix of the same color. But lead driers have a marked action on delicate colors, especially vegetable colors."

"For many purposes varnishes drying with a dull surface are preferred; such varnishes are termed *matt* varnishes by the photographer and *flatting* varnishes by the decorative painter. On the other hand, where the special lustre and brilliancy and smoothness of surface, so much better appreciated when seen than when described, are requisite, the result is attained by the application of certain spirit varnishes which are applied by means of a pad, with a peculiar circular turn of the wrist, and by lubricating the pad with a little linseed oil to aid the development of the characteristic lustre, massive smoothness and homogeneity, and uniformity of such varnished surfaces. Varnishes of this class are termed polishes, for instance French polish, in which shellac should be the chief ingredient. Furniture polish is an ephemeral extemporaneous product in which beeswax should predominate."

Some quantitative determinations on the multiple reflection of light have been made by Stokes,[1] who points out that "the frequent employment of a pile of plates in experiments relating to polarization suggests, as a mathematical problem of some interest the determination of the mode in which the intensity of the reflected light, and the intensity and degree of polarization of the transmitted light, are related to the number of the plates, and to their defect of transparency in case they be not perfectly transparent. The plates are supposed to be bounded by parallel surfaces, and to be placed parallel to one another. They will also be supposed to be formed of the same material, and to be of equal thickness except in the case of perfect transparency, in which case their thickness does not come into account. The plates themselves and the interposed plates of air will be supposed, as is usually the case, to be sufficiently thick to prevent the occurrence of the colors of thin plates, so that we shall have to deal with intensities only."

"The following table gives the intensity of the light reflected from or transmitted through a pile of m plates for the values 1, 2, 4, 8, 16, 32 and ∞ of m, for three degrees of transparency, and for certain selected angles of incidence. The assumed refractive index μ is 1.52. $\delta = 1 - e^{-qT}$ is the loss by absorption in a single transit of a plate at a perpendicular

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[1] "Mathematical and Physical Papers," 4, 144, 151 (1904).

incidence, so that $\delta = 0$ corresponds to perfect transparency. The most interesting angles of incidence to select appeared to be zero and the polarizing angle $\omega = \tan^{-1} \mu$; but in the case of perfect transparency the result has also been calculated for an angle of incidence a little (2°) greater than the polarizing angle. ϕ denotes the intensity of the reflected and ψ that of the transmitted light, the intensity of the incident light being taken at 1000. For oblique incidences it was necessary to distinguish between light polarized in and light polarized perpendicularly to the plane of incidence; the suffixes 1, 2, refer to these two kinds respectively. For oblique incidences a column is added giving the ratio of ψ_1, to ψ_2, which may be taken as a measure of the defect of polarization of the transmitted light. No such column was required for $\delta = 0$ and $i = \omega$, because this in $\psi_2 = 1000$.

$\delta = 0$

	$i = 0$		$I = \omega$		$i = \omega + 2°$				
m	ϕ	ψ	ϕ_1	ψ_1	ϕ_1	ψ_1	ϕ_2	ψ_2	$\frac{\psi_1}{\psi_2}$
1	82	918	271	729	300	700	1	999	0.701
2	151	849	426	574	459	541	2	998	0.542
4	262	738	598	402	628	372	4	996	0.373
8	416	584	749	251	771	229	8	992	0.231
16	587	413	856	144	870	130	16	984	0.132
32	740	260	922	78	931	69	32	968	0.071
∞	1000	0	1000	0	1000	0	1000	0	0.000

$\delta = 1/50$

	$i = 0$		$i = \omega$			
m	ϕ	ψ	ϕ_1	ψ_1	ψ_2	$\frac{\psi_1}{\psi_2}$
1	80	900	265	711	976	0.728
2	145	815	410	544	953	0.571
4	244	679	555	355	908	0.391
8	364	490	656	182	824	0.221
16	464	276	695	58	679	0.086
32	509	97	699	7	461	0.014
	516	0	699	0	0	0.000

$\delta = 1/10$

	$i = 0$		$i = \omega$			
m	ϕ	ψ	ϕ_1	ψ_1	ψ_2	$\frac{\psi_1}{\psi_2}$
1	74	826	245	639	881	0.725
2	125	686	351	435	777	0.559
4	185	479	427	215	604	0.357
8	229	237	451	57	365	0.156
16	243	59	453	4	133	0.030
32	244	4	453	0	18	0.001
	244	0	453	0	0	0.000

"The intensity of the light reflected from an infinite number of plates is a^{-1}; and since a is changed into a^{-1} by changing the sign of α or of Δ,

$$a^{-1} = \frac{1}{2r}(1 + 2^r - t^2 - \Delta) \ldots\ldots\ldots\ldots (21),$$

which is equal to 1 in the case of perfect transparency. Accordingly a substance which is at the same time finely divided, so as to present numerous reflecting surfaces, and which is of such nature as to be transparent in mass, is brilliantly white by reflected light,—for example snow, and colourless substances thrown down as precipitates in chemical processes.

"The intensity of the light reflected from a pile consisting of an infinite number of similar plates falls off rapidly with the transparency of the material of which the plates are composed, especially at small incidence. Thus at a perpendicular incidence we see from the above table that the reflected light is reduced to little more than one half when 2 percent is absorbed in a single transit, and to less than a quarter when 10 percent is absorbed.

"With perfectly transparent plates, little is gained by multiplying the plates beyond a very limited number, if the object be to obtain light, as bright as may be, polarized by reflexion. Thus the table shows that 4 plates of the less defective kind reflect 79 percent, and 4 plates of the more defective as much as 94 percent, of the light that could be reflected by a greater number, whereas 4 plates of the perfectly transparent kind reflect only 60 percent.

"The table shows that while the amount of light transmitted at the polarizing angle by a pile of a considerable number of plates is materially reduced by a defect of transparency, its state of polarization is somewhat improved. This result might be seen without calculation. For while no part of the transmitted light which is polarized perpendicularly to the place of incidence underwent reflexion, a large part of the transmitted light polarized the other way was reflected an even number of times; and since the length of path of the light within the absorbing medium is necessarily increased by reflexion, it follows that a defect of transparency must operate more powerfully in reducing the intensity of light polarized in, than of light polarized perpendicularly to the plane of polarization. But the table also shows that a far better result can be obtained, as to the perfection of the polarization of the transmitted light, without any greater loss of illumination, by employing a larger number of plates of a more transparent kind."

Gadow[1] goes so far as to say that "there is no white pigment or white objective color in natural objects; and whenever we have a white object, its color is due to there being an innumerable number of interstices between its molecules, or air-cells in its substance. The whole substance of a white feather, the ceratinine, is colorless; but its texture forms a fine network." As will be shown later, white pigments do occur; but it is probably true that no white pigment occurs in the feather of any bird. The white color of the lily is due to air-bubbles and the same explanation holds for white hair.[2] "Albino varieties occur occasionally as a sport, especially under domestication; but many mammals are natually white. As is well known, certain Arctic animals, *e. g.*, the polar bear, are always white; others only turn white in winter, *e. g.*, the Arctic fox. The change of color in these cases is associated with the devel-

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[1] Proc. Zool. Soc., London, 1882, 410.

[2] Newbigin: "Color in Nature," 287 (1898).

opment of numerous air-bubbles in the hair. It would seem that in some cases this is not accompanied by a destruction of the pigment, which is merely concealed by the air-bubbles."

The question of the white winter coating of many mammals has been discussed by Poulton.[1] "It is now necessary to inquire into the actual physical cause of the development of white hairs. It has already been explained that the dark color depends upon absorption, while the whiteness depends upon scattering of light. The former is occasioned by pigment granules, the latter by included gas bubbles. When the latter are sufficiently abundant, the hair becomes white in spite of the pigment; if then the gas were absorbed the dark color would be restored.[2] It appears to be well authenticated that in certain cases patches of human hair have become white during some nervous attack, again becoming dark at its cessation. Such changes can be explained by the evolution of gas (probably carbon dixoide) at the base of the hair, and its subsequent absorption (probably by some alkaline fluid). It is therefore probable that the nervous system can so modify the processes taking place in the cells at the base of the hair as to cause the formation of gas bubbles. The many recorded cases of hair turning white in a few hours as the result of some strong nervous shock are to be explained in the same manner.

"That the change in the long autumnal hairs of Lepus Americanus is due to the appearance of large numbers of bubbles is rendered probable by an examination of Welch's figures and descriptions. He speaks of the white part of a hair being much broader than the colored part, and containing additional rows of 'cells.' His 'cells' appear to be bubbles of gas, and he draws them with characteristic dark borders. It must be

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[1] "The Color of Animals," 98 (1890).

[2] This explanation only applies to the existing dark hairs which become white. It is very improbable that any pigment exists in the new hairs which make up the great part of the winter coat. Hence, in testing the explanation offered above, the hairs must be selected with the greatest care, and the investigation should be conducted in connection with an experiment like that of Sir J. Ross: "Appendix to Second Voyage, Nat. Hist.," 14 (1835).

remembered that the dark parts of a hair also contain bubbles, although in smaller amount.

"The experiment of Sir J. Ross to which reference was made in the foot note was made with a Hudson's Bay Lemming, which had been kept in the cabin and thus shielded from the low temperature, and which had retained its summer coat through the winter.[1] 'It was accordingly placed on deck in a cage on February 1, and next morning, after having been exposed to a temperature of 30° below zero, the fur on the cheeks and a patch on each shoulder had become perfectly white. On the following day the patches on each shoulder had extended considerably, and the posterior part of the body and flanks had turned to a dirty white; during the next four days the change continued but slowly, and at the end of a week it was entirely white, with the exception of a dark band across the shoulders, prolonged posteriorly down the middle of the back. No further change took place and the lemming died of the cold on February 18, the thermometer having been between 30° and 40° below zero every night. On examining the skin it appeared that all the white parts of the fur were longer than the unchanged portions, and that the ends of the fur only were white so far as they exceeded in length the dark-colored fur; and by removing these white tips with a pair of scissors it again appeared in its dark summer dress, but slightly changed in color, and precisely the same length as before the experiment.' "

Poulton points out[2] that "this experiment proves conclusively: (1) that the external condition itself provides the cause which brings the appropriate change in color, for the animal did not change until subjected to the condition; (2) that in all probability the cause is a lowered temperature acting upon the skin; (3) that the existing dark hairs become white at the tips, for we cannot well believe that a fresh growth

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[1] This conclusion is also supported by the fact that such changes occur earlier when the winter is exceptionally early. Concerning the Alpine Hare, see Tschudi: "Thierleben der Alpenwelt," 300.

[2] E. B. Poulton: "The Colors of Animals," 94 (1890).

could have overtopped the existing hair in a single night; (4) that the whitening hairs grow suddenly and rapidly."

In view of the fact that albinism is an abnormal state, it is rather interesting to read[1] that "there is certainly evidence that coloration has some relation to the distribution of the underlying nerves. Mr. Allen[2] has stated that the white marks on the head of the tiger correspond to the areas of distribution of the infra-orbital nerves. The nerves terminate in or near the skin; and it is clear that there must be some connection between nerve-supply and coloration, from the fact that in a hedgehog whose spines were white, the nerves in connection with the muscles for contraction of the skin were greatly diseased.[3] There are plenty of other pathological facts of a like nature."

Hopkins[4] takes direct issue with Gadow, though without mentioning his name. "It has frequently been stated that white animal pigments do not exist. It is certain, however, that the scales of many white *Lepidoptera* contain substances which give opacity and 'body' to the more transparent whiteness which the chitinous structures otherwise possess. Whether these are to be dignified with the name of pigments is perhaps a matter of words. The wing of the common cabbage butterfly, for instance, when the scale contents are extracted, loses its characteristic opaque, chalky-white color, and shows rather the appearance common to translucent structures containing air. In this and in other white *Pieridae*, the substance which lends this opaque character to the chitinous scale is none other than uric acid. . . The scales of allied yellow insects (*Pieridae*) are pigmented with a substance closely related to uric acid, the yellow pigment being in all probability identical with a product obtained when uric acid is heated with water under pressure."

In the case of fishes there is no question but that we have

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[1] Beddard: "Animal Coloration," 19 (1892).

[2] Science, 9, 36.

[3] Zoologist, 9, 3022.

[4] Phil. Trans., 186B, 661 (1895).

guanin functioning as a pigment.[1] "A substance, which is widely utilized as a coloring agent among fishes, is guanin. This substance, used in the manufacture of artificial or Roman pearls, is colorless or chalk-like; but it occurs in the skins of fishes as small crystals which frequently display a beautiful iridescence and a pearly lustre. It is to these crystals, mingled with pigments, that the soles, the cod family, and numerous others owe their frequently beautiful color. The crystals occur in the scales, and also in the deep layers of the skin, in peritoneum and in the air-bladder, as well as elsewhere. It is interesting to note that in Elasmobranchs, which are ancient fishes, although guanin is present in the skin it has no metallic lustre, such as it exhibits in many of the modern bony fishes. Guanin is not of course a pigment in the strict sense of the word, but it is of much importance in producing coloration in fishes."

"As to the detailed characters of the coloration of fishes, there are several points of great interest. We have already mentioned the occurrence of crystals of guanin in the skin, which are important factors in the production of the iridescence and the silvery appearance of many fishes. The exact effect of these crystals on the coloration has not, however, been sufficiently determined, and it remains uncertain how far they are instrumental in producing the gorgeous colors of many tropical fishes. There is every reason to believe that these are optical in nature; but the exact investigations into the mechanism of production are still required. Owing to the fugitive nature of the colors, the investigation would need to be conducted on the spot where the fishes are found, so we must look to some tropical biological station of the future for the complete solution of the question. . .

"According to Cunningham and M'Munn, the elements important in coloration [in the skin of fishes] occur in two layers in the skin, and the two layers differ considerably in the upper and lower surfaces of the fish. In most cases the outer layer occurs in relation to the scales, while the inner layer lies close

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[1] Newbigin: "Color in Nature," 37, 219 (1898).

to the surface of the muscles; but in the mackerel the loose scales contain no coloring elements. The outer layer consists of often branched and contractile chromophores, containing different pigments, and of polygonal cells of peculiarly silvery appearance called by Pouchet iridocytes. The silvery iridescent appearance is due to the presence of crystals of guanin. The inner layer consists of the same elements. On the lower surface of the skin the outer layer contains iridocytes but no chromatophores, the inner consists of argenteum—that dead-white layer which clings to the surface of the muscles and is familiar to all who have examined fishes. Though no histological elements can be found in the argenteum in the adult, development shows, as might be expected, that it is formed from the fusion of the iridocytes. The silvery or dead-white appearance is again due to crystals of guanin. The distribution of the coloring elements of the skin may be summarized in the following table:

	Upper surface	Lower surface
Outer layer	Iridocytes and Chromatophores	Iridocytes only
Inner layer	Iridocytes and Chromatophores	Argenteum

"This table is true for the flounder and, *mutato mutandis* for other kinds of fishes as well. The points of importance are the presence of a large amount of reflecting tissue, especially on the lower surface, and the absence of pigment cells on that surface. The relative development of the parts varies of course greatly in different fishes, but the distribution appears to be fairly constant. The two layers of reflecting tissue seem to have different functions in some cases at least, for while the outer layer may exhibit a brilliant iridescence, the inner layer presents either a chalk-white opaque surface or an evenly bright silvery surface."

I have not found any statement whether the whiteness of the bark of the birch, the silver poplar and the sycamore is due to pigment or to air bubbles.

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THE OCCLUSION OF HYDROGEN BY THE METALLIC ELEMENTS AND ITS RELATION TO MAGNETIC PROPERTIES

BY DONALD P. SMITH

Although the literature of the subject is large and fairly comprehensive, no recent general survey of the comportment of the metallic elements toward hydrogen appears to exist. As a basis for the discussion of a parallel which obtains between the occlusion of hydrogen and the magnetic character of the occluding metal, it will therefore be necessary to consider briefly the three types of metal-hydrogen combination which may readily be distinguished, and to review the empirical material so far as it is of direct bearing upon the confines of these classes.

Types of Combination

The three types of combination, which seem to be generally, although as a rule tacitly, distinguished by recent investigators, may be characterized as follows:

The compounds of the first type, represented by H_3Sb, are non-metallic in character, and are further distinguished by extreme volatility, being gaseous at the ordinary temperature and pressure. They are formed only by elements which display metalloidal as well as metallic characters, and may probably be regarded as compounds in which hydrogen acts as a *positive* univalent element while its associate plays a negative or non-metallic role. These substances belong, therefore, rather to the compounds of hydrogen with the non-metallic elements, and since they are nearly all of them well known, no justification need be offered for placing them as a class apart. From their close analogy to the hydrocarbons they might well be called hydro-compounds, in distinction from the substances of the next paragraph.

The compounds of the second type are also non-metallic in character as is shown by their optical and electrical properties. They include KH, CaH_2, and analogous compounds with all of the alkali and alkaline earth metals. They are transparent, crystalline substances, volatile without decomposition in an atmosphere of hydrogen at comparatively low temperatures. Since they resemble in various respects the corresponding chlorides and nitrides, they may most simply be regarded as binary salts in which hydrogen plays the part of a *negative* univalent element, while the metal has its customary saline valence. These substances were studied extensively by Moissan, who also distinguished them from those of the type which follows.[1,2] They might be termed the hydrides proper.

The combinations of the third type, of which palladium-hydrogen is the classical example, differ from both of the preceding primarily in that they are metallic. They also exhibit in a peculiar degree the property of forming solid phases of compositions variable with the external conditions. Other general characteristics, more or less distinctive, are their relatively high dissociation pressures, and great involatility. To these substances, or perhaps rather to their solid solutions in excess of the metallic component, may appropriately be applied the name hydrogen alloy, which was used by Troost and Hautefeuille,[3] although in a less restricted sense. It is the process of formation of these alloys which is known as occlusion.

Although the distinction of the classes which have just been enumerated is not an innovation, it remains for the review of the literature, given below, to show that the three are probably sharply separated, and to fix the positions of the lines which divide them. For the sake of clarity, however, these points are anticipated, and the comportment of the elements toward hydrogen is displayed in Table I, in which the periodic arrangement of Werner[4] has been followed, as affording a particularly clear oversight of the relations in question. In this table the metals which form compounds of Type 1 appear with the non-metals at the extreme right, and are marked off from the others by heavy lines. In a similar manner the metals which form compounds of Type 2 are set apart at the left of the table. To avoid crowding, the right half of the table has been placed above the left half.

In the two end classes the typical character of the hydrogen compounds is so readily apparent that further discussion does not seem to be required; whence the review of the experimental evidence may be confined to that which relates to the central elements, included between the heavy lines. The metals of the central group may be subdivided into: (1) those which have been shown to take up hydrogen in amounts measurable by the ordinary volumetric method,—represented in Table I by *bold-faced type;* (2) those which have been shown not to absorb in the same degree,—represented in *small Roman;* and (3) those which have not been investigated,—indicated in *italics*. Marks of interrogation signify that doubtful or contradictory data render the indicated behavior in some measure uncertain.

The data to be found are extremely numerous, but of very uneven quality. For most of the commoner elements the extensive investigations published by Sieverts and his fellow-workers since 1907 afford adequate and reliable information, which has accordingly been treated as final, except where still later studies exist. All the earlier work, so far as known, has been compared; but, in cases of conflicting statements, has appeared to deserve little weight. For the rarer elements, and a few others, dependence has had to be placed upon observations which are frequently very inadequate, but which nevertheless present a not inconsistent body of results. Citations have for the most part been limited to papers which contain observations upon the occlusion of hydrogen from the gas phase, since data regarding cathodic occlusion are not directly comparable. Space has also been saved by referring to partial compilations, wherever these exist. While mention of most of the older literature, and of the many studies relating to the effects of occluded hydrogen upon the physical and electrochemical properties of the metals, has thus been omitted, this material has not been ignored.

As may be seen from Table I, the occluding metals of the central group appear to consist of a right-central (upper) and of a left-central (lower) sub-group. This division is not improbably

TABLE I—COMPORTMENT OF THE METALS WITH HYDROGEN

In Central Group: **Bold-faced Type** = Occluding; Ordinary Type = Non-occluding; *Italics* = Uninvestigated

	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	He
	—	—	—	—	—	—	—	—	—	Gl ?	B	C	N	O	F	Ne
	—	—	—	—	—	—	—	—	—	Mg ?	Al	Si	P	S	Cl	A
	Sc	*Ti*	**V**	**Cr** ?	**Mn** ?	**Fe**	**Co**	**Ni**	**Cu**	Zn	*Ga*	Ge	As	Se	Br	Kr
	Y ?	**Zr** ?	**Cb**	Mo	—	*Ru*	Rh	**Pd**	Ag	Cd	*In*	Sn	Sb	Te	I	X
	—	—	**Ta**	W	—	*Os*	Ir ?	**Pt**	Au	Hg	Tl	Pb	Bi	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Li	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Na	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
K	Ca	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rb	Sr	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cs	Ba	**La**	**Ce**	**Nd** ?	**Pr** ?	—	—	**Sa** ?	*Eu*	*Gd*	*Tb*	*Ho*	*Er*	—	*Tu*	*Yb*
—	Ra ? !	—	**Th** ?	—	—	—	—	—	**U**	—	—	—	—	—	—	—

the result merely of the incompleteness of our present information, but the fact that all of the thoroughly investigated elements are included within one of these sub-groups makes it convenient to separate them in the following review.

The Empirical Evidence for Occlusion

In the right-central sub-group the elements tantalum,[5] palladium,[6] nickel,[7] iron,[8] cobalt,[9] copper[10] and platinum[11] have been thoroughly investigated. All form compounds of Type 3, although the degrees of occlusion which are exhibited vary within wide limits, apparently diminishing in the order given, at least for temperatures in the neighborhood of 1000° C.

Absorption of hydrogen in considerable amounts seems also to have been established for vanadium[12] and columbium,[13] if the published results are to be judged merely from internal evidence. Both elements are therefore entered as occluding in Table I, although no proof of the variable composition of the products has been given.

With regard to chromium[14] and manganese[15] the data are surprisingly scanty. For chromium it has been shown that when deposited electrolytically with high current density it may retain as much as 250 volumes of hydrogen (its own volume reckoned as unity). This, in spite of the experimental conditions, seems to be too large a quantity to attribute wholly to mechanical enclosure. As to manganese, there exist the observations that it increases the solubility of hydrogen in iron, and that highly carboniferous manganese takes up more hydrogen than does iron of like carbon content. Both of these findings seem to indicate a large occlusive capacity on the part of manganese. For this, it must be said, there is little support in the later results of Wedekind and Veit.[15] But the observation of the last-named experimenters that manganese which had been heated in hydrogen displayed altered magnetic properties may be regarded as doubtful indication of the occurrence of some occlusion, and their inability to find more than traces of dissolved hydrogen has little weight as contrary evidence, since their gas had confessedly a considerable admixture of oxygen. Upon the ground of their position between the occluding elements vanadium and iron, quite as much as for such dubious experimental reasons, chromium and manganese are listed in Table I as occluding. Both must be marked doubtful.

The metals glucinum, magnesium, yttrium and zirconium appear to be unstudied, save for a single investigation,[16] in which all were reported to take up hydrogen when the oxides, intimately mixed with magnesium, were heated in a current of the gas. These data have been rejected in Table I for two reasons: in the first place, because an absorption of hydrogen was reported to occur upon heating magnesium oxide with metallic magnesium, although none was observed when magnesium alone was heated in hydrogen; and in the second place, because the experimental arrangements appear to have been of a kind open to serious objections. Since this rejection is undeniably arbitrary, however, these four elements are provided with marks of interrogation.

The elements molybdenum,[17] tungsten,[18] rhodium,[19] silver,[20] gold,[21] zinc,[22] cadmium,[23] aluminum,[24] thallium,[24] tin,[24] lead,[24] and bismuth[24] may be said, upon excellent authority, not to combine with hydrogen in a degree measurable by volumetric methods, although tungsten and thallium at least, probably absorb in quantities just detectable. Indications, electrochemical and other, that some of these metals occlude in lesser degrees might be cited in considerable number, but are without bearing in the present connection.

Mercury also may doubtless be classed among the non-occluders, on the strength of general experience, although it does not appear that any investigator has concerned himself with the demonstration of the fact. A very small occlusion by this metal is evidenced by numerous observations.

Iridium appears not to absorb in its ordinary condition, although after prolonged cathode bombardment it attains a state in which it is capable of taking up as much as 800 volumes of hydrogen.[25] An earlier investigation, in which occlusion was reported to occur under ordinary circumstances, may be disregarded with little hesitation, since, from the description available, it seems to have been carried out under conditions which were not well defined, and by the method of complete combustion; while this method, in the form employed, is open to serious criticism,[26] and has several times yielded values for the absorption of hydrogen by finely-divided metals which proved later to be far too high.

Titanium must be regarded as uninvestigated, since the only reported experiment which appears to have any bearing, was so conducted that, according to the statement of the investigator himself,[10] it is unlikely that elementary titanium was subjected to the action of hydrogen.

The remaining elements of this sub-group, namely, scandium, ruthenium, osmium, gallium and indium, are entirely unstudied with respect to their conduct toward hydrogen, unless indications are to be found in the statement[27] that ruthenium is capable of taking up gases during electrolysis, or in the observation[28] that an osmium-iridium alloy absorbed no hydrogen upon being heated in the gas.

The conduct of the elements of the right-central subgroup may be summed up by saying that, in all of the nearly twenty cases which have been investigated with an approach to adequacy, these metals either do not absorb hydrogen in measurable amounts, or else occlude to form alloys of Type 3. The probability is therefore great that, in the cases in which a considerable absorption has been found, but in which its character has not been sufficiently determined, we have to do with an occlusion of this same sort.

Turning now to the left-central elements of Table I, we encounter rarer metals, which have been relatively little investigated.

Uranium alone [29] has been studied by the methods which have given the most reliable information as to the common metals already considered. While the uranium employed was not pure, there seems to be no ground for attributing to this circumstance the observation of a small absorption of the usual type. This element may therefore be counted among those which occlude.

Cerium and lanthanum have been several times investigated.[16, 30, 31] Of the most recent study of cerium,[32] in which the most suitable method seems also to have been employed, only a brief abstract has been accessible. As a result of the earlier work it appears that, while there is no unquestionable evidence of the metallic character of the products, there is excellent proof that Ce-H and La-H form phases of variable composition, in which hydrogen may reach high concentrations. While the later paper seems to confirm these indications that cerium and lanthanum occlude to form alloys of the usual Type 3, certain of the earlier observations suggest analogies to the alkali and alkaline earth hydrides, and therefore require mention.

In the first place, the combination of hydrogen with cerium or lanthanum is a strongly exothermic reaction, accompanied by evolution of light,[31] resembling in this respect the formation of CaH_2;[33] whereas most of the common hydrogen alloys, such as Fe-H, are produced by feeble reactions, which, as is shown by the positive temperature coefficients of absorption,[34] are endothermic in character. That this does not differentiate Ce-H and La-H from the alloys, and relegate them to the hydrides proper, becomes evident only when it is noted that exothermal substances are to be found also among the unquestionable compounds of Type 3, and that, too, in precisely the cases in which hydrogen is occluded in largest amounts. The temperature coefficients of the solubility of hydrogen in tantalum and palladium are negative.[34]

In the second place, the lanthanum and cerium compounds share with the hydrides of Type 2[2] their ready oxidizability which, under suitable conditions, causes them to take fire spontaneously.[31] This analogy also loses its apparent significance when it is recalled that finely-divided palladium, if highly charged with hydrogen, is likewise pyrophoric.[35]

Finally, it should be pointed out that the gradual increase of dissociation pressures exhibited by Ce-H and La-H, which led their observers to conclude[31] (p. 291), that these substances cannot be regarded as simple solutions of hydrogen in metal, do not necessarily, or indeed probably, imply any essential difference from the other substances of Type 3; for while changes of dissociation pressure, at a given temperature, have not, apparently, been observed to occur in other instances, during the actual course of experiment, great differences in the occlusive behavior of palladium, produced by heating and cooling, have been repeatedly noted; and many facts point to the dependence of the occlusive capacities (and hence dissociation pressures), of various of the metals upon their "thermal histories." It appears, moreover, from the abstract cited,[32] that these gradual changes of dissociation pressure have not been confirmed in the more recent study of cerium.

Regarding the hydrogen compounds of cerium and lanthanum it may therefore be said that they share the general characteristics which have been described for Type 3, although they may display some of the divergence of properties often found in the end members of a series.

The metals thorium,[16, 30] neodymium,[30] praseodynium[30] and samarium[30] appear to absorb measurable quantities of hydrogen, and the products exhibit at least one of the characteristics of Type 3 in their relatively high dissociation pressures, which are noticeable at temperatures below 1000° C. They are, however, so little studied that their assignment to the alloy-forming compounds must be made chiefly upon general considerations of analogy, and they are consequently marked as uncertain in Table I.

With respect to the behavior toward hydrogen of the remaining elements of the left-central group, all of which are extremely rare, nothing whatever seems to be known.

The empirical material available with regard to the entire sub-group may be summed up by saying that all of the indications which it affords point to the formation of hydrogen compounds of the same type as those given by the better-studied elements of the right-central group. The indications which amount, apparently, to proofs in the case of uranium, are very strong for lanthanum and cerium, and slight for the remaining metals. Quantitatively, cerium and lanthanum absorb large amounts of hydrogen, and uranium very little, while as to the other elements, it can only be said that those which have been investigated fall within the limit set, taking up quantities measurable by volumetric means.

The foregoing discussion has sought to make clear that the division of the elements into a great central class, within which alone occlusion occurs, and into two other classes, is justified upon purely chemical grounds. It is the aim of the paragraphs which follow to show further that the capacity to occlude hydrogen has a very close parallel in the magnetic character of the metals.

Magnetic Character and Occlusion

The magnetic properties of the elements, as shown by his own experiments and by those of previous investigators, were the subject of an exhaustive review by Honda.[36] Among other regularities, he showed that the specific magnetic susceptibility of the metals is a periodic function of the atomic weights. His graph of this function, except for the lettering, is reproduced in Fig. 1, and an auxiliary figure is placed below in which a broken line indicates the character of the metals with respect to occlusion. Where this line is on the higher level, the corresponding elements are among those which have been found to occlude in a measurable degree; the lower level marks metals which, although belonging to the central group of Table I, have been shown not to occlude measurably; dotted portions of the line correspond to metals uninvestigated; and intervals are left wherever an element forms a compound of Types 1 or 2.

Honda's work was extended and revised by Owen,[37] but the changes to which this revision gave rise are without significance for the present discussion, except for a modification of the position of columbium (shown by the dotted curve in Fig. 1), and for certain questions which it raises regarding the conduct of the alkaline earths. These points are taken up in later paragraphs. A continuation of his work by Honda, together with T. Soné,[37] also adds nothing of importance to the present discussion.

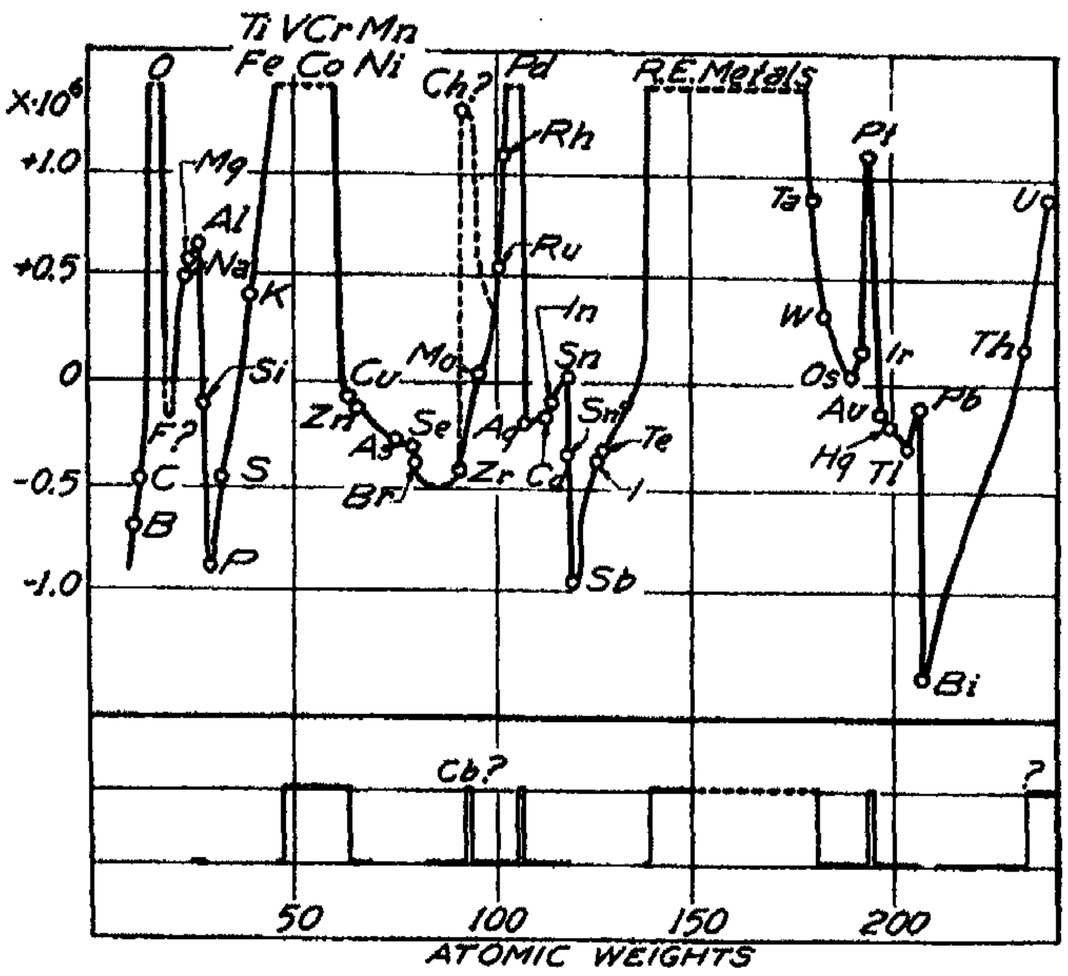

Fig. 1
Upper figure, specific magnetic susceptibility (Honda)
Lower figure, occurrence of occlusion of hydrogen

Upon regarding Fig. 1 it will be noticed that the elements having specific susceptibilities greater than about $x = + 0.9 . 10^{-6}$ are, with the single exception of rhodium, among those which occlude hydrogen in large measure.

Conversely, all the elements which have been shown to occlude in a measurable degree have susceptibilities which exceed the limit just named, with two apparent exceptions presented by copper and thorium.

The exceptional conduct of thorium rests upon experimental evidence of somewhat doubtful credibility, as has been mentioned in reviewing the literature.

The fact that rhodium does not occlude measurably, in spite of its high susceptibility, must be taken as established, although the first of the three investigators cited[19] reported a considerable occlusion.

The behavior of copper is established by so much excellent evidence, with respect to both of the properties involved, that it cannot be called in question. It is true of this metal, however, that while feebly diamagnetic in the elementary state, it exhibits strongly magnetic character in some of its compounds, so that Wedekind[38] has termed it "latently ferromagnetic." Hence it is probable that if the fundamental magnetic characters of the elements could be compared, instead of the magnetic susceptibilities observed for the metals in the free state, copper would no longer offer an exception

Assuming the correctness of Table I, and of Fig. 1, it may be said, that in the entire central group of elements, large occlusive capacity and strongly magnetic character accompany each other, save for two exceptions in the cases of rhodium and thorium.

The question which naturally presents itself as to the reliability of the Table, and hence of the conclusion just drawn, has in large part been answered already in the discussion of the literature, but a concise statement of the evidence is in order.

Of the 49 elements shown in the central group, 13 are uninvestigated with regard to occlusion, and so have had to be omitted from the comparison. The 36 which remain appear to divide equally between the occluding and the nonoccluding classes.

Of the 18 metals which have been considered to show high degrees both of occlusion and of magnetic susceptibility, chromium, manganese, thorium, neodymium, praeseodymium and samarium are to be considered doubtful, having regard to the chemical evidence alone; while of the 18 exhibiting both properties in small degree, if at all, yttrium, zirconium, glucinum, magnesium and iridium may be said to be more or less uncertain. While there are thus some 11 among the 36 elements considered, with regard to which the data are not altogether adequate, the probable number of exceptions to the rule is evidently small, and the entire absence of exceptions among the best studied cases can hardly be accidental.

It is to be noted, however, that the comparison has been between susceptibilities measured at or near 18° and occlusive capacities observed at considerably higher temperatures. An examination of the diagrams in which Honda[36] and Owen[37] present their results respecting the dependence of susceptibility upon temperature, will show that, while there are numerous instances of intersection among the curves which represent the function $\chi = f(T)$, none of them involves one of the highly occluding elements, within a range of temperature for which the degrees of occlusion have been measured. On considering the literature already cited it will also be found that reversals in the order of occlusive capacity have been observed only at high temperatures, the lowest being apparently that at about 1140° in the case of copper and iron. Thus the rough divisions into occluding and non-occluding elements, and into those of large and those of small susceptibility, upon which the comparison has been based, are unaffected by the differences between the various temperatures of observation.

The existence of the reversals of order just mentioned makes it evident, however, that if the data were sufficient to make possible an extension of the comparison to wider ranges of temperature and of occlusion, the parallel between occlusion and susceptibility would fail. In this there may doubtless be seen further evidence for the conclusion, already drawn from the anomalous behavior of copper, that the parallel is in reality not with the susceptibility itself, but with the magnetic character of the element, which is usually, but not without exception, reflected in the susceptibility of the metal in the uncombined state. It is only upon this conception, moreover, that the conduct of the ferromagnetic metals ceases to present a difficulty in the continued increase of occlusive capacity which they exhibit at temperatures above their magnetic transition points.

The outcome of the foregoing discussion may perhaps be most concisely stated by saying that the capacity of the metals to occlude hydrogen appears to present a complete(?) parallel to their magnetic characters. Of the many properties which have been found to be periodic functions of the atomic weights, these two are therefore exceptional in that their periods are coincident.

It need scarcely be said that an attempt to compare the two properties quantitatively would be premature. For this, data would be needed regarding the small degrees of occlusion which are doubtless to be found among the elements hitherto classed as non-occluding; and while a considerable literature already relates to this subject, it is so extraordinarily contradictory and inconclusive as to make certain that the methods thus far employed are unsuited to the measurement of very small absorptions.

The regularity which has been pointed out relates only to occlusion by the central elements of Table I. While there is a general parallel between the magnetic characters of the elements and their ability to form hydrogen compounds of Types 1 and 2, the compounds of the former type being usually associated with pronounced diamagnetism, and those of the latter with weak paramagnetism, this regularity does not appear to be well carried through, and the number of elements involved is too small to afford a good basis for comparison. In this connection it may be remarked that Owen's values for barium and calcium give these elements positions in Fig. 1 (not shown) above the limit at which occlusion apparently becomes measurable, the susceptibilities being respectively +0.9 and +1.10. This may indicate either that the formation of compounds of Type 3 is not an accompaniment of high susceptibility in the cases of elements of the end groups of Table I, or that barium and strontium possess the power of occluding in addition to that of forming compounds having the distinctive physical properties of Type 2. From the very inadequate data the former indication seems perhaps the more likely, but the possibility that these elements represent a transitional group is present.

Summary

From a review of the literature relating to the occlusion of hydrogen by the metallic elements it is shown that the resulting alloys are clearly to be distinguished from other types of binary hydrogen compounds, and that the metals which form the alloys probably occupy a definite region in the periodic table of Werner.

The metals of this region are classified into those which do and those which do not, occlude in a degree measurable by the ordinary volumetric method.

From a comparison with magnetic data it is shown that the occluding and non-occluding elements, excepting copper rhodium and thorium, are identical with those for which the specific magnetic susceptibility possess a value respectively greater or less than about $+0.9 \cdot 10^{-6}$ at room temperature.

It is concluded that the capacity of a metal to occlude hydrogen in large degree is an accompaniment of strongly magnetic character.

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NEW BOOKS

The Theory and Use of Indicators. *By E. B. R. Prideaux. 22 × 15 cm; pp. ix + 375. New York: D. Van Nostrand Company, 1917. Price: $5.00.*—In the preface the author says: "It is the purpose of the present work to present to the student a connected survey in which it may appear that different views of the subject are not necessarily inconsistent with one another, and that, taken together, they form a body of theory which has already given a great power in dealing with, *e. g.*, the problems of physiology, the fermentation industries, and chemical geology. The book is also addressed to the technical chemist who appreciates the value of working hypotheses. On this account there have been included a selection of the most important formulas and constants (in excess of those required to illustrate the theories) in order that the hydrion and hydroxylion concentrations of all common aqueous solutions at various temperatures might be calculated with the greatest ease."

The titles of the chapters are: the equilibria of acids, bases, and salts, and the physical methods of determining acidity and alkalinity; light absorption in the visible spectrum and colorimetry; theories of color in their relation to the ionic theory, chemical constitution, and the formation of salts; the color of indicators as a function of hydrion concentration—the determination and use of indicator constants; the preparation and use of solutions of standard hydrion concentration; the course of neutralization and the theory of titration; the solution equilibrium and titration of some acids; a summarized list of the principal indicators, with absorption spectra.

It is admitted, p. 73, that there is no necessary, simple relation between the color of an aqueous solution and the degree of ionization. "More recent researches, *e. g.*, those of Hantzsch and Hilscher, and Bjerrum, have proved that in most cases of inorganic colored salts the color is to a considerable extent independent of the degree of ionization. This has been shown particularly well in the case of chromic acid and its salts by Hantzsch, although in some more recent work it appeared that the specific absorption of more concentrated solution of chromates does vary somewhat with the concentration, as well as with the nature of the alkali metal. The extinction coefficient of the hexaquochrom salts was found by Bjerrum to be quite constant over a considerable range of concentration. The nature and amount of the acid which was added to prevent hydrolysis also appears to have no effect on the extinction........ It was possible to be sure in this case that all the Cr was present as ions $Cr(aq)_6^{\cdot\cdot\cdot}$.or salt $Cr(aq)_6X_3$, since the formation of other complexes is slow and can easily be followed by the analytical estimation of the amount of anion. When this changes and other complexes are formed, the color of the solution and the extinction coefficient also change.

"In the case of copper sulphate not only is the absorption ratio nearly constant in solutions of the most different concentrations and degrees of dissociation, but this constancy also extends to the solid crystal hydrate. Plates of $CuSO_4\cdot5H_2O$ were cut perpendicularly to the optical axis and polished. The molecular extinction was compared with that of acid $CuSO_4$ solutions.

MOLECULAR EXTINCTION FOR

λ Color	0.579 μ Yellow	0.546 μ Green	0.436 μ Blue
Solid.............	4.75	2.07	0.381
Solution..........	4.53	1.83	0.405

The experimental error is unavoidably large in the case of the solid; but the results suggest distinctly identity of absorbing power. The absorption is ascribed to the complex $Cu(H_2O)_4$ whether present as ion or sulphate. As soon as the H_2O is replaced by NH_3 as in copper-ammonia solutions, the absorption changes its character. The molecular extinction curves at different concentrations of H_2PtCl_6 and Na_2PtCl_6 were found to fall almost together. For the blue Hg line $\gamma = 0.436\mu$, the molecular extinction only varies between 39.2 and 41.5 in the case of three compounds of this type present at dilutions of $v = 10$ to $v = 500$. Here also the absorption is to be ascribed to $PtCl_6$, not as ion only but equally as compound. When an alteration in the nature of the complex is to be assumed on other grounds, there is an alteration in the color and the converse also holds. Thus $CuCl_2.2H_2O$ is blue, $Cu(CuCl_4.2H_2O)$ is green. Abundant examples are furnished by the metal amines. The change in the complex $(Co.6NH_3)X_3$ to $(Co.5NH_3.H_2O)X_3$ results in a change from yellow to red."

It is recognized, p. 210, that colloidal substances may affect the readings of indicators though the author seems to think that this is something distinct from adsorption. "The hydrolyzed salts of some metals such as aluminum exert a specific action upon indicators such as alkannin. Organic colloids, such as gelatine, albumin, etc., affect most indicators, but less seriously those of a relatively simple structure such as paranitrophenol. Congo red, which itself has a great tendency to assume the colloidal state, may in the presence of other colloids yield results which are absolutely erroneous. The indicators in Sorenson's list have been chosen specially as suitable for physiological solutions, which generally contain more or less protein. The disturbance in the results is more serious in the presence of true proteins than in that of other organic colloids. Thus a solution of glue falsifies the results on the average by 0.1 in log $[H^{\cdot}]$, while white of egg may make a difference of 1.0 and even more."

It is interesting to note, p. 224, that "in the open sea the hydrogen exponent was found to vary between the limits 7.95 and 8.35. Only in an exceptional case, the depths of the Black Sea, was the acidity as high as 7.26, and this was due to hydrogen sulphide. The exponent found almost everywhere below the surface was 8.07 to 8.09. Thus sea-water may be said to be always alkaline by virtue of its bicarbonate. In shallow water near the land and in presence of abundant life, there are much greater variations, both on the acid and the alkaline side."

The book is a valuable one and contains a vast amount of interesting and useful information. The covers have been spotted by water in transit, but this has not affected the printed matter. *Wilder D. Bancroft*

ADSORPTION BY PRECIPITATES. I

BY HARRY B. WEISER AND J. L. SHERRICK

Adsorption of Anions by Precipitated Barium Sulphate[1]

A great deal of work has been done on the contamination of precipitated barium sulphate by the adsorption of substances dissolved in the solution from which the salt separates. For the most part, these investigations have dealt with the influence of different metallic ions on the purity of the precipitated salt. However, as early as 1842, Mendelejeff[2] carried out experiments which would seem to indicate that nitrate ion is adsorbed more readily than chloride ion. "In a few precipitations, a part of one of the dissolved salts is so attracted that it comes down with the precipitate. The author dissolved barium nitrate in ten parts of water, precipitated approximately one half of it with sulphuric acid and allowed the barium sulphate to settle. The clear supernatant liquid was poured off and evaporated and the barium nitrate content was determined. The precipitate and the remaining liquid was weighed and finally the weight of the precipitate was determined. The latter was filtered, washed and ignited and hence consisted of pure barium sulphate. The solution obtained by filtering and washing the precipitate was evaporated and the barium nitrate obtained was weighed. If the weight of the barium nitrate and of the barium sulphate is subtracted from the weight of the precipitate and the solution contained in it, one obtains the weight of the water which was present in the solution. If one calculates from these experiments how much barium nitrate there was present in the supernatant solution and from this how much there was in the solution which was mixed with the precipitate, one finds that this contains only two thirds as much barium nitrate as was obtained by the

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[1] A portion of a thesis presented by J. L. Sherrick to the Faculty of the Rice Institute in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Pogg. Ann., 55, 214 (1842).

evaporation of the wash water; so that one third of this adheres to the barium sulphate on account of the surface attraction of the barium sulphate for the barium nitrate. If barium chloride is precipitated in the same way with sulphuric acid no barium chloride is carried down with the barium sulphate. If, on the other hand, a solution of nitric acid and sodium sulphate is precipitated with barium nitrate and the precipitate washed until a drop on a platinum foil leaves no residue, the barium sulphate contains as much as two percent of sodium nitrate. If this is ignited so that the sodium nitrate is decomposed, it can then be extracted with water. Barium sulphate has such a slight attraction for barium chloride that it can not take it up from an aqueous solution of the same; for the barium nitrate the attraction is so great that a great deal of water is necessary in order to wash it out; for the sodium nitrate the attraction is so great that it can not be removed even though the water possesses a marked solvent power for sodium nitrate."

In 1871, Teschemacher and Smith[1] mention the contamination of barium sulphate by barium chloride used in the precipitation and even at that time they recognized the fact that the chloride contamination depended in amount on whether the sulphate or the barium chloride was present in excess. Various other investigators observed this chloride contamination from time to time and it was made the subject for rather extended investigations by Richards and Parker[2] and by Hulett and Duschak.[3]

The various text books of Quantitative Analysis have much to say as to the necessity for the absence of certain ions from the solution in which sulphates are to be determined as barium sulphate. Thus Fresenius[4] states: "It (barium sulphate) has a great tendency, upon precipitation, to carry down

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[1] Chem. News, 24, 61–64, 66–69 (1871).

[2] Zeit. anorg. Chem., 8, 413 (1895).

[3] Ibid., 40, 196 (1904).

[4] Fresenius: "Quantitative Chemical Analysis," 1, 169 (1908); Compare Treadwell-Hall: "Analytical Chemistry," 2, 464 (1907).

with it other substances contained in the solution from which it separates, more particularly barium nitrate, nitrates and chlorates of the alkali metals, ferric oxide, etc. Even the precipitate obtained from the solution of barium chloride, by means of sulphuric acid in excess contains traces of barium chloride, which it is impossible to remove, even by washing with boiling water, but which are dissolved by nitric acid (Siegle). If a fluid contains metaphosphoric acid, barium can not be completely precipitated out of it by means of sulphuric acid: the resulting precipitate too, contains phosphoric acid (Scheerer, Rube)."

As regards the mechanism of the contamination of barium sulphate by foreign substances, the views are many and divergent. Hulett and Duschak[1] consider as a possible explanation of chloride contamination the formation of such complex salts as $BaCl.HSO_4$ and $(BaCl_2)SO_4$. Silberberger[2] for the contamination by potassium nitrate claims the formation of a complex $NO_3.BaSO_4.BaSO_4.K$; and for potassium chloride $Cl.BaSO_4.BaSO_4.BaSO_4.K$. He states further that sodium salts are not retained by barium sulphate in the form of complexes. Johnson and Adams[3] conclude that it is a phenomenon of adsorption. Richards[4] compares the contamination with ferric sulphate[5] to the occlusion of hydrogen by palladium which probably involves both solid solution and adsorption. Schneider[6] looks upon it as a case of solid solution; but Küster and Thiel[7] and also Korte[8] conclude that the contamination is an adsorption phenomenon. Smith[9] states that it is neither a case of solid solution nor adsorption; but is the result of the

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[1] Loc. cit.

[2] Monatshefte Chemie, 25, 220 (1904).

[3] Jour. Am. Chem. Soc., 32, 588 (1910).

[4] Zeit. anorg. Chem., 23, 383 (1900).

[5] Glendenning and Edgar: Chem. News, 24, 140 (1871); Sloane: Ibid., 44, 221 (1882); Gladding: Jour. Am. Chem. Soc., 16, 398 (1894).

[6] Zeit. phys. Chem., 10, 425 (1893).

[7] Zeit. anorg. Chem., 19, 97 (1898); 22, 424 (1899).

[8] Jour. Chem. Soc., 81, 1503 (1905).

[9] Jour. Am. Chem. Soc., 39, 1152 (1917).

formation of a complex of the composition $Ba(Fe(SO_4)_2)_2$. Weiser[1] attributes the contamination to adsorption and has shown the influence of the preferential adsorption of ions on the size of the crystals of barium sulphate.

The adsorption theory offers the only explanation of the well-known fact that barium sulphate takes up all manner of substances. Thus, not only do we have records of the contamination of barium sulphate by the sulphates of iron, chromium, aluminium, calcium and the alkali metals and by the chlorides of sodium, potassium and barium, but barium sulphate when added to both true and colloidal solutions, has been found to serve as an excellent adsorbing agent. Vanino and Hartl[2] find that when barium sulphate is added to a colloidal gold solution, the solution is decolorized and destroyed. Patten[2] finds that, when barium sulphate is boiled with solutions of the chlorides of iron, manganese, and chromium, some of the metal passes into the solid in each case. Hulett and Duschak[3] find that pure barium sulphate takes up chlorides upon standing in contact with a chloride solution.

Since a systematic study of the adsorption of different anions by barium sulphate has not been made, it was thought desirable to conduct a series of experiments along these lines for the purpose of determining the order of adsorption of ions under identical conditions of precipitation. In the first place it was hoped that such an order of adsorption of ions might enable us to trace out some of the factors influencing adsorption in general. Furthermore, it was thought that such a series of experiments would enable us to determine the validity of conclusions previously reached concerning the relative effect of the presence of certain anions on the purity of precipitated barium sulphate.

Two general methods have been used for determining the relative adsorption of ions. One method consists in determining the effect of various ions of one charge on the precipi-

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[1] Jour. Phys. Chem., 21, 315 (1917).

[2] Jour. Am. Chem. Soc., 25, 186 (1903).

[3] Loc. cit.

tation of a colloid that owes its stability to preferential adsorption of an ion of opposite charge. The precipitating power in such cases depends on the degree of adsorption. This method was first used by Schulze;[1] and from the results of his experiments we have what is known as Schulze's law, namely, that the power of an active ion to precipitate colloidal solutions is a function of its valence or of the number of electrical charges which it carries. There are two general methods of conducting experiments on the precipitating power of electrolytes. One method consists in allowing a drop of the colloid to flow into a large volume of the salt solution. In this way a series of determinations are made until that concentration of salt solution is found that will just cause a coagulation of the drop. A second method consists in adding the salt solution a drop at a time to a given amount of the colloidal solution until precipitation takes place.

Many determinations made in this way are of doubtful accuracy because of the experimental difficulties involved. The time factor may influence these determinations to quite a large extent since the adsorption of the different ions may require different lengths of time for attaining equilibrium. Furthermore, although agitation usually has very little effect on the most stable colloidal solutions, nevertheless, when electrolytes are added in amount slightly less than that necessary to cause precipitation, the stability of the colloid is interfered with to such an extent that agitation will cause precipitation.[2] In view of these facts it is hard to see how the solutions may be mixed uniformly so as to give true measures of concentration effects and prevent local effects, without at the same time affecting the precipitation by agitation. These and other sources of error were recognized by Schulze:[3] "The beginning of precipitation is dependent on a few factors other than the degree of dilution of the solution and the influence of these must be kept constant if strictly comparable results are to

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[1] Jour. prakt. Chem., (2) **25**, 43 (1882); **27**, 320 (1884).

[2] Hardy: Zeit. phys. Chem., **33**, 385 (1900).

[3] Loc. cit.

be obtained. The effect of these factors may be shown best by an example. Dilute sulphuric acid (9.8 grams per liter of H_2SO_4) immediately precipitates arsenic sulphide solution dropped into it. On the other hand a solution one-third as strong, that is, with 3.267 grams per liter of H_2SO_4, remains clear after the addition of the yellow solution even on long standing. By very vigorous shaking, however, it becomes slightly turbid and a like change is brought about by boiling. If the hot liquid is thoroughly shaken, the turbidity increases until finally the sulphide agglomerates and sinks to the bottom, the solution becoming clear as water. If, however, the solution is nearer the critical dilution, namely, 3.6 grams of H_2SO_4 per liter, the resulting solution which is clear yellow at the start becomes turbid on standing. The phenomenon takes place in such a way that the yellow color changes into a reddish yellow and this in turn into a yellowish red while the solution which was quite transparent at the start decreases in clearness and finally becomes quite cloudy. By shaking this solution which is on the verge of the change, insoluble sulphide very quickly precipitates."

"In the precipitation of soluble arsenious sulphide therefore temperature, mechanical agitation and time are of very great importance even if of lesser influence than the dilution of the liquid which effects the precipitation. In order to keep all these factors constant in the observations it is necessary to work under the same external conditions."

Kato[1] found that the usual difficulties in determining the concentration of electrolyte that would just cause coagulation, were magnified in the case of colloidal barium sulphate. The degree of turbidity of the colloidal solution caused by adding an electrolyte varied continuously with the concentration of the latter, within certain limits. This made it difficult to determine at what concentration the turbidity really took place. The attempt to use Richards'[2] nephelometer for determining the critical concentration failed and viscosity meas-

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[1] Mem. Coll. Sci. Eng. Kyoto Imp. Univ., 2, 187 (1909–10).

[2] Richards and Wells: Am. Chem. Jour., 31, 235 (1904).

urements[1] proved valueless. The concentration of electrolyte necessary for coagulation that was finally adopted, was the concentration in which the colloid settled within 24 hours. "In this way quite definite results were obtained since there was no difficulty in judging whether the settling was complete. . . . It must be added here, however, that by complete settling it is not meant that the colloid was completely coagulated. But the concentration determined by measuring the time required for the settling will serve safely as a measure for comparison of the coagulative power of electrolytes."

The results of Kato's investigation are of doubtful value for deducing the order of adsorption of anions. Thus he finds little difference in the precipitating concentration for potassium chloride, potassium bromide, potassium iodide, potassium chlorate and potassium nitrate; as nearly as can be determined, hydrochloric acid and nitric acid behave alike, as do barium chloride and barium nitrate. This would mean that the anions concerned are adsorbed by positively charged colloidal barium sulphate to approximately the same degree, which can not be true, particularly in view of the results reported in this paper. The difficulty lies in the experimental method which is necessarily limited in accuracy and hence, figures representing the relative amounts of the various ions adsorbed are only approximate.

It is usually assumed, as Hardy did, that the effect of the cation is negligible in the precipitation of a positive colloid, and the anion in the precipitation of a negative colloid;[2] but this can not be strictly true. For example, if a positive colloid is precipitated by means of a representative series of sodium salts, it will be found that the critical concentration of the electrolytes necessary to produce precipitation will vary within wide limits. Now, if the concentration of the anion is the only thing that counts it must be assumed either that the sodium ions are not adsorbed at all by the disperse phase or that the adsorption is the same at all concentrations. In view

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[1] Kawamura: Jour. Coll. Sci. Tokyo Imp. Univ., 25, Art. 8 (1908).

[2] Hardy: Loc. cit.; Cf. Bancroft: Jour. Phys. Chem., 19, 363 (1915).

of what is known of the specific nature of adsorption it is questionable whether this is strictly true with any disperse phase; and it certainly would not be true with all. It seems more probable that the relatively slight effect of the ion with the same charge as the colloid under consideration may in certain cases, be lost sight of altogether because of the errors inherent in the experimental method.

Kato found a wide variation from Hardy's rule in a number of cases. Among others he found that sodium tetraborate, mercuric chloride, acetic acid, sodium citrate, phosphoric acid, barium chloride, barium nitrate, ferrous chloride, ferric sulphate, calcium chloride and aluminum sulphate have a particularly weak coagulative power; while sodium thiosulphate, citric acid and sodium and potassium hydroxide have a particularly strong coagulative power. Even in the light of all these exceptions, he considers that his results are in accord with Hardy's rule. However, he rightly attributes the abnormally weak coagulative power of certain electrolytes to the protective action of the cation.

A second method of determining adsorption consists in shaking a solution of known concentration with a known weight of solid and pipetting off some of the supernatant liquid which is subsequently analyzed. The amount of adsorption is then calculated from the change in concentration. Leighton,[1] working in Bancroft's laboratory, on the adsorption of alkali and acids by cellulose, pointed out that such a calculation was accurate only in case no liquid was taken up by the solid. Since cotton does take up water, results for cotton obtained by the above method are wrong. The method of determination adopted by Leighton consisted in centrifuging the cotton and then analyzing the cotton direct. This method would give too high results unless the treatment with the centrifuge removes all the liquid. It seems to us that the latter is altogether improbable, particularly in view of the difficulty experienced by Leighton in getting cotton even approximately free from water.

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[1] Jour. Phys. Chem., 20, 32, 188 (1916).

In the case of a crystalline precipitate, for example barium sulphate precipitated from chloride solution, it is possible by washing to remove the solution held among the crystals so that the wash water gives no test for chlorides. Adsorbed chloride is not removed by this process. It would be interesting to know in Leighton's experiments to what extent the alkali would be removed by washing with water.

Osaka[1] carried out some experiments on the adsorption of salts by charcoal, analyzing the solution before and after the treatment. He recognized, as did Leighton, that correct results could not be obtained without taking into account the amount of solution taken up by the solid adsorbing agent: "Since the amount of salt in a given quantity of solution has been determined, the total amount of salt remaining in solution after adsorption may easily be found if the total amount of solution after adsorption or that of water in it be known. In order to obtain the amount of water remaining in solution after adsorption that adsorbed by charcoal must be estimated, but as there is no direct means for its determination, the following procedure was taken: Some water was put in the bottom of a small glass vessel of desiccator form about 9 centimeters high, a small glass basin with a given quantity of blood charcoal was placed over it and the cover was water-tightly sealed with picetin. The whole apparatus was dipped completely into a thermostat at 25° and the basin with charcoal was weighed, at intervals of about a week until it became constant in weight, being kept during the weighing between a pair of watch glasses. This required about one month and as a mean of five determinations it was ascertained that animal charcoal, treated as above stated, adsorbed water to 85 percent of its weight. As the solutions used in the experiments were about one-normal or less, it was assumed that the amount of water adsorbed by charcoal from solution does not differ much from that adsorbed from pure water."

These results were obtained under the assumption that charcoal takes up the same amount of water from the saturated

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[1] Mem. Coll. Sci. Kyoto, 1, 267 (1915).

vapors as it does when placed in the liquid. It is a question whether this is true[1] and if not, Osaka's results are necessarily incorrect, so far as absolute amounts adsorbed are concerned.

It is evident that the determination of the order of adsorption of ions is open to considerable experimental difficulty. From what has been said it is probable that the most accurate results may be obtained by choosing a suitable adsorbing material and analyzing for the adsorbed ions direct. It so happens that precipitated barium sulphate furnishes a very satisfatory adsorbing medium for the determination of a number of adsorbed anions. In the first place, it has a marked tendency to adsorb most ions; in the next place, it may be precipitated directly in the presence of anions that do not form insoluble barium salts and the adhering solution may be removed by washing the crystals; finally, it has been found possible to analyze the precipitated salt for a number of adsorbed anions without unduly complicated and time-consuming procedures.

It was, of course, particularly important to maintain uniform conditions in the experiments if comparable results were to be obtained. The general method of procedure was to precipitate a constant amount of barium sulphate by mixing a solution of a given sulphate with a solution of barium salt. By this procedure three ions were kept constant throughout the series of experiments and the fourth was varied. The concentrations of the ions were maintained as uniform as possible by working with fairly dilute solutions. The adsorbed ion was determined directly in the precipitated salt.

It was found necessary to devote considerable attention to the determination of conditions which would yield uniform results since small variations in the conditions of precipitation and the subsequent treatment of the salt had a marked influence on the amount of a given anion adsorbed. The conditions of precipitation and treatment finally adopted were followed throughout all the experiments.

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[1] See Von Schroeder: "Uber Erstarrungs und Quellungserscheinungen von Gelatin," Zeit. phys. Chem., 45, 109 (1903); Cf. Bancroft: Jour. Phys. Chem., 16, 1395 (1912).

Special methods of analysis were required to determine the ions adsorbed by barium sulphate since such small quantities of material were involved. Hulett and Duschak[1] determined the adsorbed chloride in barium sulphate by dissolving the latter in sulphuric acid and estimating the hydrochloric acid evolved. With this as a start, methods were applied or evolved for the determination of a number of ions. In making determinations which involve the estimation of such small quantities of the various elements, it was realized that volumetric analysis should be used as far as possible if the procedures were not to be excessively time-consuming and complicated. Although some of the methods used for the determination of the ions adsorbed were not brought to such a degree of accuracy as might be possible we felt that they were sufficient for our purposes and we did not wish to become involved in tedious analytical work and lose sight of our main purpose by attempting to refine methods beyond our immediate needs. We are certain that some of the methods used were capable of much greater accuracy than was indicated by the preliminary applications of them to the estimation of known weights of material; and we expect at some later date to take them up systematically for the purpose of determining their limitations. However, *there was manifestly no use in our trying at this time to refine a method of analysis beyond the point where the error of the determination fell within the variation in adsorption incident to our inability to control conditions affecting adsorption itself.* Furthermore, the determinations of ions adsorbed by barium sulphate were made under particularly favorable conditions and were in most cases unquestionably more accurate than the determinations made on known weights of material. The reason for this will be pointed out in the subsequent experiments.

Determinations were made on the following anions adsorbed by barium sulphate: chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, sulphocyanate, ferricyanide and ferrocyanide. In the interest of accuracy a number of determinations were made in every case and the

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[1] Loc. cit.

average taken. The determinations of the various ions will be taken up separately.

The Adsorption of Chlorine Ion

As before mentioned Hulett and Duschak determined directly the amount of chloride ion taken up by barium sulphate under widely varying conditions of precipitation. The method was essentially as follows: The precipitated salt contained in a closed vessel was dissolved in concentrated sulphuric acid. In this process any chloride was converted into hydrochloric acid which was carried into a standard silver nitrate solution by aspirating air through the system. The rate of the solution of barium sulphate was hastened by heating in a hot water bath. Allen and Johnston[1] shortened the process of solution of the salt by direct heating with a small flame. Futhermore they determined the silver chloride gravimetrically instead of by the more accurate volumetric method.

Apparatus and General Method.—In our experiments on adsorbed chloride ion an apparatus was employed similar to

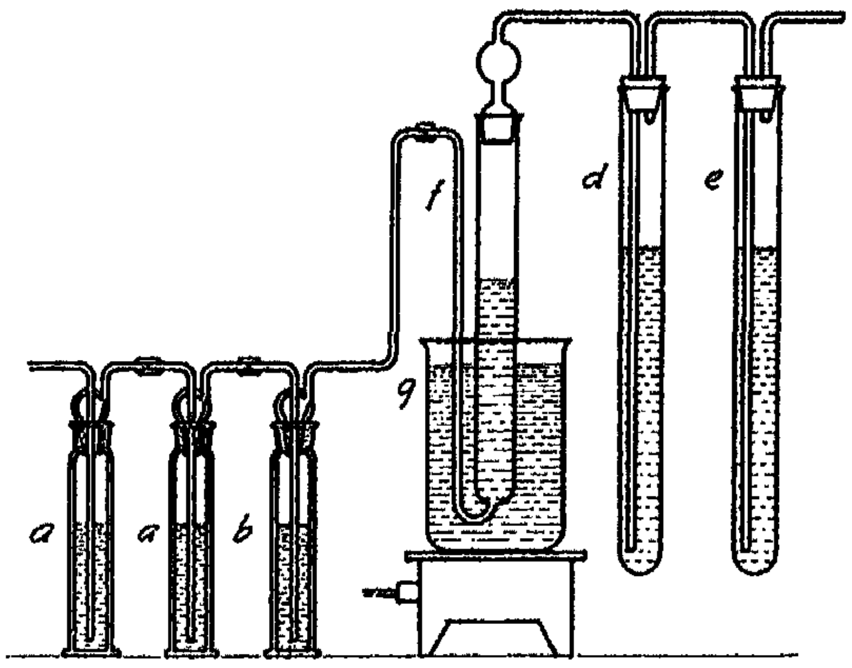

Fig. I

that recommended by Hulett and Duschak. The apparatus is shown in Figure I. The precipitate, together with the as-

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[1] Jour. Am. Chem. Soc., 32, 594 (1918).

bestos mat from the Gooch crucible into which it was filtered, was placed in the reaction vessel of approximately 100 cc capacity; and 50 cc of concentrated sulphuric acid was poured onto it. The ground-glass stopper with the delivery tube *c* was attached as quickly as possible and air was aspirated slowly through the apparatus. The wash bottle *a* contained 20 percent solution of potassium hydroxide and *b* contained concentrated sulphuric acid. In addition to these precautions for obtaining pure air the source of supply was outside the laboratory. The two tubes *d* and *e* contained $N/100$ silver nitrate solution. To prevent leaking, the ground-glass joint was moistened with concentrated sulphuric acid. After the aspiration of the air had been started the water in the beaker *g* was heated to boiling. Under these conditions the barium sulphate dissolved slowly in the acid and any adsorbed chloride was converted into hydrochloric acid which was carried along in the stream of air and reacted with the silver nitrate in tube *d*. Under the conditions of our experiments no hydrochloric acid escaped the first tube but the tube *e* was always retained as a safeguard against loss. When all of the hydrochloric acid had been evolved—usually four hours were sufficient—the excess of silver nitrate was determined by titration and the adsorption computed from this data.

The titrations were made under carefully controlled conditions using potassium chromate as indicator. The process was carried out in a dark room lighted by an electric light; the solution was contained in a porcelain dish and yellow glasses were worn. Using these precautions a sharp end-point was possible and check results were readily obtained.

Determination of "Blank."—As we were not sure of the purity of the sulphuric acid and as chlorides might be adsorbed by the asbestos mat during the filtration process, a number of "blank" determinations were run. The mat was prepared and through it was filtered a solution corresponding to the mother liquor resulting from the precipitation of barium sulphate from barium chloride solution in the regular determination of adsorbed chloride ion. After washing until the wash water gave no test for chlorides, the asbestos was placed in the apparatus and the determinations were made as before described. The results of a series of determinations are given in Table I. The correction was applied in subsequent determinations.

TABLE I

Time aspirated Hours	Conc. H_2SO_4 cc	N/100 $AgNO_3$ cc	N/100 NaCl cc	Blank, N/100 solution cc	Average
6	50	50	49.5	0.5	
6	50	50	49.6	0.4	
10	40	50	49.7	0.4	
24	50	50	49.5	0.5	
24	50	50	49.5	0.5	
24	40	50	49.6	0.5	
24	40	50	49.6	0.5	
24	50	50	49.5	0.5	0.5

Determinations of Chlorine in $BaCl_2.2H_2O$.—In order to test the accuracy of the method a determination was made on a known weight of barium chloride. A sample of the pure salt labeled "For Analysis" was weighed in a weighing bottle. From this was removed a crystal, the weight of which was determined by difference. The crystal was placed in the apparatus and the chlorine content determined as before described. The crystal disappeared slowly in the concentrated acid due to the immediate formation around it of a film of barium sulphate which dissolves but slowly. The result of the determination given in Table II shows that the method is very accurate indeed.

TABLE II

Determination of Chlorine in $BaCl_2.2H_2O$

Weight of $BaCl_2.2H_2O$		Percent chlorine		Difference expressed in cc N/100 solution
Taken	Found	Theoretical	Found	
0.03580	0.03573	29.03	28.97	0.05

In order to get some idea as to the best conditions for obtaining comparable data, a number of determinations were made of chloride ion adsorbed in barium sulphate, precipitated under different conditions.

It is a well-known fact that barium sulphate precipitated from sodium sulphate solution by an excess of barium chloride is in a finer state of subdivision than that precipitated by an excess of sodium sulphate. This is due to the fact that, other conditions being the same, barium ion is much more strongly adsorbed than is sulphate ion, and hence peptization is greater in the former case than in the latter.[1] It was of interest to know to what extent the adsorption of chloride ion was affected by the two conditions. Accordingly a series of experiments were carried out as follows:

Adsorption of Chloride Ion in Presence of an Excess of Sodium Sulphate.—On account of the great amount of work already done on barium sulphate it was thought best to take such concentrations of solutions and amounts of materials as would correspond with usual analytical procedures for the determination of barium or sulphate. Our results might then serve for application to analytical methods and would throw some light on the various statements found as to the contamination of barium sulphate precipitates by different materials in solution. In these experiments 50 cc of $M/10$ sodium sulphate were added to 160 cc of water in a 400 cc beaker; and the solution brought to boiling. While stirring the solution vigorously with a platinum gauze stirrer driven by an electric motor, 40 cc of an $M/10$ solution of barium chloride were added from a burette, thus precipitating 4 millimols of barium sulphate. The time of addition was 30 seconds; the total time of stirring, 4 minutes. The precipitate was allowed to stand in its mother liquor on a hot plate at 60° for 23 hours, after which it was filtered through a Gooch crucible and washed six times with hot water, the 30 cc crucible being filled each time. After this treatment tests showed the absence of chlorides in the wash water. The precipitate together with the asbestos mat was transferred to the apparatus above described and the amount of adsorbed chloride ion was deter-

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[1] Weiser: Jour. Phys. Chem., 21, 315 (1917).

mined. The results of a series of determinations are given in Table III. In the first column is given the number of cubic centimeters of $N/100$ $AgNO_3$ corresponding to the amount of hydrochloric acid evolved from the precipitate. From this the other values given in the table were calculated.

TABLE III
Adsorption of Chloride Ion
(Na_2SO_4 in excess)

$N/100$ $AgNO_3$ cc	Chloride ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
0.50	0.00018	4.44	0.125	
0.60	0.00021	5.33	0.150	
0.50	0.00018	4.44	0.125	
0.43	0.00015	3.82	0.108	
0.48	0.00017	4.26	0.120	
0.48	0.00017	4.26	0.120	0.125

Adsorption of Chloride Ion in the Presence of Excess Barium Chloride.—The same procedure was followed in this series of experiments as in the preceding, except that 40 cc of $M/10$ sodium sulphate were added to 50 cc of $M/10$ barium chloride diluted with 160 cc of water. Thus the same excess of barium chloride was employed as there was excess sodium sulphate in the preceding experiments. The results are given in Table IV.

TABLE IV
Adsorption of Chloride Ion
($BaCl_2$ in excess)

$N/100$ $AgNO_3$ cc	Chloride ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
5.48	0.00195	48.64	1.370	
5.68	0.00202	50.04	1.420	
6.19	0.00230	57.43	1.547	
6.89	0.00245	61.20	1.722	
6.79	0.00241	60.26	1.697	
6.84	0.00244	60.96	1.710	1.578

As was to be expected, the amount of chloride ion adsorbed in the presence of excess barium chloride was more than 12 times greater than with sodium sulphate in excess. Since the absolute amount of adsorbed material is very small in any case, if a convenient quantity of precipitated material is used, it was decided to adopt for all subsequent determinations that condition in which the adsorption would be the larger, that is, the precipitation in the presence of an excess of barium salt.

In the previous determination of the adsorbed chloride ion in barium sulphate precipitated in the presence of an excess of barium chloride, the variation in the individual results was rather large, amounting to the equivalent of 1.4 cc of *N*/100 solution for the four millimols of barium sulphate precipitated. Since the method used was much more accurate than this, it was evident that we were not controlling sufficiently the conditions under which the precipitation and consequently the adsorption took place. The greatest chance for variation of conditions seemed to be in the digestion of the precipitate on the hot plate as there was no regulating device on the plate and hence its temperature probably fluctuated considerably. Hulett and Duschak have shown that the amount of adsorption changes during prolonged standing of the precipitate in contact with its mother liquor. A further chance for variation seemed to exist in the local temperature effects which might result from the addition of a cold (25° C) solution of sodium sulphate to a boiling solution of barium chloride. Further determinations were accordingly made in order to determine whether a change in conditions of precipitation along the lines indicated would result in more constant values for the adsorption.

Adsorption of Chloride Ion in Barium Sulphate Precipitated from Sodium Sulphate Solution.—The method of precipitation and treatment of the salt was modified in the following respects: Instead of adding a cold solution of sodium sulphate to the boiling hot solution of the barium salt, the following procedure was adopted. A 100 cc burette was filled to the 40 cc mark with a *M*/10 solution of sodium sulphate; this solution was then allowed to run from the burette into a clean beaker until the burette had emptied itself down to the glass stop-cock; the solution in the beaker was then brought to boiling and evaporated to about one-half its original volume; the boiling hot solution was now poured back into the burette and, after washing in any of the solution that was clinging to the side of the beaker, the liquid in the burette was made up to the 40 cc mark by the addition of boiling water. This solution was now mixed thoroughly by turning the burette over and over after it had been stoppered. Forty cubic centimeters of this solution were then used for precipitating the barium sulphate. As a further change instead of allowing the precipitate to stand for twenty-three hours on the hot plate, as previously, it was filtered immediately after precipitation. The time of stirring was decreased from four minutes to one minute. These changes in procedure should tend to increase the total amount of adsorption. The results of a series of determinations are given in Table V.

TABLE V
Adsorption of Chloride Ion
($BaSO_4$ from Na_2SO_4 with excess $BaCl_2$)

N/100 $AgNO_3$ cc	Chloride ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
7.00	0.00249	62.13	1.750	
6.80	0.00241	60.35	1.700	
7.20	0.00256	63.93	1.800	
7.10	0.00252	63.01	1.775	
7.10	0.00252	63.01	1.775	1.760

Adsorption of Chloride Ion in Barium Sulphate Precipitated from Sulphuric Acid Solution.—Since barium ion is strongly adsorbed by barium sulphate and since hydrogen ion is much more strongly adsorbed than most univalent[1] cations, it follows that greater peptization of barium sulphate should

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[1] Freundlich: "Kapillarchemie," 354 (1909).

result when the precipitation was effected from sulfuric acid solution than from sodium sulphate solution.[1] It follows further that, other conditions remaining constant, one would expect to get a greater anion adsorption when the precipitation was effected in the presence of hydrogen ion than in the presence of sodium ion. A series of experiments were carried out to verify this point. The conditions of precipitation and the procedure followed are the same as given in the preceding paragraph with the exception that an $M/10$ solution of sulphuric acid was used instead of an $M/10$ solution of sodium sulphate. The results are given in Table VI.

Table VI
Adsorption of Chloride Ion
($BaSO_4$ from H_2SO_4 with excess $BaCl_2$)

$N/100$ $AgNO_3$ cc	Chloride ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
9.0	0.00319	79.88	2.250	
9.0	0.00319	79.88	2.250	
9.4	0.00333	83.43	2.350	
9.3	0.00330	83.54	2.325	2.294

By comparing the results in Table V with those in Table VI it will be seen that the conclusion was correct, namely, that greater chloride ion adsorption results in the presence of hydrogen ion than in the presence of sodium ion.

Since in both sets of experiments the results of the different determinations agreed closely enough among themselves it was felt that the conditions of precipitation, filtration and washing were controlled sufficiently; hence these same conditions were used in all subsequent determinations. In all cases hereafter the precipitation was effected from sodium sulphate solution as dilute sulphuric acid would have an undesirable effect on certain of the salts, for instance the cyanides. In

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[1] Weiser: Loc. cit.

every case was used the barium salt of the ion whose adsorption was to be determined. These conditions will hereafter be alluded to as regular.

Adsorption of Bromide Ion

Determination of Bromine in Bromides.—It seemed probable that the same general method of procedure could be used for the determination of bromide ion adsorbed in barium sulphate as was used for chloride ion. It was planned to treat the precipitate with 50 cc of concentrated sulphuric acid to which had been added a small amount of potassium dichromate. The bromine liberated could then be swept along in the air stream; adsorbed in a solution of potassium iodide; and finally titrated with an $N/10$ solution of sodium thiosulphate. In order to test this method, small weighed portions of bromides were placed in the apparatus and subjected to the procedure. The results are given in Table VII.

TABLE VII
Determination of Bromine in Bromides
(Fine powder)

Salt	Weight		Percent Found	Cc of $N/100$ solution		
	Taken	Found		Required	Taken	Difference
$BaBr_2.2H_2O$	0.0509	0.0468	91.9	30.55	28.10	2.45
$BaBr_2.2H_2O$	0.0400	0.0353	88.0	24.01	21.19	2.82
$BaBr_2.2H_2O$	0.0842	0.0775	92.0	50.54	46.52	4.02
$BaBr_2.2H_2O$	0.0386	0.0349	90.4	23.17	20.97	2.20
$BaBr_2.2H_2O$	0.0439	0.0404	92.0	26.35	24.25	2.10
$BaBr_2.2H_2O$	0.0644	0.0595	92.3	38.72	35.70	3.02
KBr	0.0134	0.0114	85.1	11.26	9.56	1.70

The results were disappointing, to say the least, as in no case did we obtain more than 92.3 percent of the theoretical amount of bromine. It was noticed, however, that there was a brisk evolution of gas when the acid was first thrown upon the bromide and, as in the first few cases, the acid was added through the ground-glass joint at the top of the apparatus, it was thought that some of the gas may have escaped before the apparatus could be closed. In the last four determinations of the series the bromide was placed in the apparatus and, after closing the ground-glass joint and disconnecting the two wash bottles, the acid was run in through the tube *c*, Fig. I, while a stream of air was being aspirated through the system. In this way there would be no chance of losing any of the gas evolved. The results, however, were no better than before. In the last case, where potassium bromide was used instead of barium bromide, only 85 percent of the theoretical amount of bromine was obtained. It seemed altogether probable that the low values resulted from one or both of the following causes: In the first place a very rapid reaction resulted at the moment the acid struck the crystals and it is altogether likely that some of the hydrobromic acid formed escaped oxidation by the chromic acid and hence escaped detection. In the last few determinations which were run in order to find out, if possible, the reason for the low results, it was noted that the gas first evolved was not colored and fumed; while the gas evolved after the crystals were completely covered with the acid mixture, was the color of bromine and was given off slowly. The slow evolution of bromine following the first reaction was due to the fact, that the particles of barium bromide were coated with a layer of barium sulphate which dissolved slowly and hence slowed down the action on the crystal to such an extent that no hydrobromic acid escaped oxidation. In the experiment with potassium bromide on which the action was rapid from the start to finish the result was lower than with barium bromide. This would be expected since more hydrobromic acid would escape oxidation in the former case than in the latter. A second factor is the following: In so far as the hydrobromic acid formed was oxidized by the sulphuric acid, sulphur dioxide was produced which might escape oxidation and be carried along with the bromine into the potassium iodide solution. There it would act on the iodine liberated by the bromine reducing it to hydriodic acid. This would give low results. In order to get accurate results by this method it would seem that it was necessary to have the action on the bromide proceed very slowly so that sufficient time was allowed for complete oxidation by the chromic acid mixture. Since the samples used in the above experiments had been ground in an agate mortar, they were in a rather fine state of division and hence were acted on more rapidly than larger particles would be. Accordingly a number of determinations were made on $BaBr_2.2H_2O$ in which the weighed sample consisted of a single crystal of the salt. As the samples were of the same average weight as in the previous experiments, the surface of contact and hence the rate at which they were attacked was correspondingly decreased. The results of the experiments are given in Table VIII.

TABLE VIII
Determination of Bromine in $BaBr_2.2H_2O$
(Single Crystal)

Weight $BaBr_2.2H_2O$		Percent Found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0350	0.0341	97.4	21.01	20.47	0.54
0.0435	0.0424	97.6	26.11	25.47	0.64
0.0502	0.0484	96.4	30.13	29.05	1.08
0.0313	0.0307	98.0	18.85	18.41	0.44

In the above series of experiments the lowest result obtained was 96.4 percent of the theoretical, while the highest was 98 percent. These values were much more satisfactory than those previously obtained because of the slower action. On account of the slow rate at which precipitated barium sulphate dissolves in sulphuric acid, the method is entirely satisfactory for the quantitative estimation of bromide ion adsorbed in barium sulphate.

Adsorption of Bromide Ion.—Four millimols of barium sulphate were precipitated in the regular way by adding 40 cc of an *M*/10 solution of sodium sulphate to 50 cc of *M*/10 barium bromide diluted with 160 cc of water. The precipitate was treated as previously described and the amount of bromide ion adsorbed was determined. The results of a series of determinations are given in Table IX.

TABLE IX
Adsorption of Bromide Ion

N/100 $Na_2S_2O_3$ cc	Bromide ion absorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
3.68	0.00294	73.51	0.920	
3.07	0.00245	61.32	0.768	
3.27	0.00261	65.32	0.818	
3.17	0.00243	60.82	0.793	
3.27	0.00261	65.32	0.818	
3.48	0.00278	69.52	0.870	0.831

Adsorption of Iodide Ion

Determination of Iodine in Potassium Iodide.—It was thought that the same method used for determining adsorbed bromide ion might be applied to the determination of adsorbed iodide. In order to test this, weighed amounts of potassium iodide were taken and subjected to the same treatment as the barium bromide in the preceding experiments. The use of barium iodide was impracticable for the preliminary tests because of the highly deliquescent nature of the salt. The first difficulty encountered was that the iodine liberated from the sulphuric acid-dichromate mixture condensed in the upper part of the reaction chamber around the ground-glass joint; and after aspirating air through the system for twenty-four hours only 21 percent of the theoretical amount of iodine was obtained, although all color of the element had disappeared. It was thought that the low results might be due to loss of iodine through the ground-glass joint. To determine whether or not this was the case experiments were carried out in an apparatus without the ground-glass joint. The weighed sample was placed in a reaction vessel the same size at that previously used, after which the exit tube was sealed on. This apparatus was surrounded by a steam jacket to facilitate the sweeping over of the iodine into the potassium iodide solution. The experiments with this apparatus were as unsatisfactory as those preceding. It was noted, however, that a considerable quantity of iodine vapor was swept into the potassium iodide solution but relatively little of it remained as such, indicating that reduction had taken place. In view of our experiments with the bromides these results might be expected. Since hydriodic acid is a much stronger reducing agent than is hydrobromic acid, it reduces sulphuric acid very rapidly with the formation of sulphur dioxide and hydrogen sulphide. Under the conditions of the experiment these gases were in part swept over into the potassium iodide solution and subsequently reduced the iodine that was carried over. It is altogether probable that the method would work much more satisfactorily with barium iodide than with potassium iodide for the action would be slower under these conditions and the oxidation by the chromic acid would be more nearly complete. However, it was decided to adopt a different method altogether. The sample of iodide was placed in the reaction vessel to which the outlet tube was subsequently sealed. This was surrounded by a steam jacket as in the previous experiments. Instead of catching the gases liberated by the chromic acid mixture in potassium iodide solution they were absorbed in a 10 percent solution of sodium hydroxide. Under these conditions the iodine would exist as iodide and iodate while sulphur dioxide and hydrogen sulphide would go to sulphite and sulphide, respectively. After aspirating air through the system for 24 hours in order to make sure that all the iodine was washed over, the sodium hydroxide solution was placed in a distilling flask; acidified with sulphuric acid; and an excess of ferric ammonium alum solution added.[1] It was then distilled, and the distillate caught in a solution of potassium iodide. All the iodine was obtained in this way and it was subsequently titrated with *N*/100 sodium thiosulphate in the usual way. The results are given in Table X.

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[1] Scott: "Standard Methods of Chemical Analysis," 205 (1917).

TABLE X

Weight of KI		Percent Found	Cc of $N/100$ solution		
Taken	Found		Theoretical	Taken	Difference
0.0147	0.0143	97.3	8.85	8.62	0.23
0.0130	0.0126	97.0	7.83	7.57	0.25
0.0250	0.0252	100.9	15.06	15.20	0.14

It may be seen from the above table that the method as finally modified gives quite satisfactory results.

Adsorption of Iodide Ion.—Four millimols of barium sulphate were precipitated in the regular way and the amount of adsorbed iodide ion determined. On dissolving the sulphate in acid no color of iodine vapor was observed at any time, whereas in the case of known weights of iodides the violet vapor of iodine could be distinguished for a full hour while air was being aspirated through the system. When the final titrations were made they showed that but very little iodide ion had been adsorbed. The results of a series of experiments are given in Table XI.

TABLE XI

Adsorption of Iodide Ion

$N/100$ $Na_2S_2O_3$ cc	Iodide ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
0.3	0.00038	9.52	0.075	
0.2	0.00025	6.35	0.050	
0.1	0.00013	3.17	0.025	
0.3	0.00038	9.52	0.075	0.056

Indeed the quantity adsorbed was so minute that the values can be only approximately accurate. The results show conclusively that iodide ion is adsorbed by barium sulphate the least of any of the ions considered.

Adsorption of Chlorate Ion

Determinations on Known Weights of $Ba(ClO_3)_2.H_2O$.—The attempt was made to use a method for the determination of chlorate ion which depends on the oxidizing power to liberate chlorine from hydrochloric acid, so that advantage could be taken of the accurate iodine-thiosulphate titration. The procedure was as follows: A weighed amount of barium chlorate was mixed with 0.2 gram of barium chloride and placed in the reaction vessel. Onto this was poured fifty cubic centimeters of concentrated sulphuric acid to which had been added 3 drops of concentrated hydrochloric acid. The evolved gas was drawn through potassium iodide solution as previously and the liberated iodine was titrated with *N*/100 sodium thiosulphate. The following reaction was expected to take place between the chloric and hydrochloric acids:

$$Ba(ClO_3)_2 + 5BaCl_2 + 6H_2SO_4 = 6BaSO_4 + 6H_2O + 6Cl_2$$

The results are given in Table XII.

Table XII
Determinations on $Ba(ClO_3)_2.H_2O$
(In light)

Weight of $Ba(ClO_3)_2.H_2O$		Percent found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0105	0.0079	75.2	39.08	29.36	9.72
0.0110	0.0086	77.9	40.94	31.92	9.02
0.0114	0.0099	87.0	42.43	36.93	5.50
0.0135	0.0111	82.5	50.25	41.43	8.82
0.0139	0.0104	75.1	51.74	38.83	12.91

The results obtained show only from 75 percent to 87 percent of the theoretical and are evidently unsatisfactory from any point of view. In the previous experiments with bromides and iodides, tests were made to determine whether it was possible to pour in the sulphuric acid at the ground-glass joint or whether the gas evolution was so rapid that some gas escaped before the joint could be closed. It was found

that in no case was there any loss in this way since the results were the same whether the acid was poured into the inlet tube after the joint had been connected or whether it was added at the joint. Since the latter procedure was much more convenient, the above experiments were carried out in this manner. Furthermore since we had been mistaken in attributing the low results in previous experiments to losses at the joint we were inclined to look for some other explanation. In view of our previous experiments the most probable source of error seemed to be the escape of some ClO_2 before it had a chance to be reduced by the hydrochloric acid. This would cause no error providing the ClO_2 reached the acidified solution or potassium iodide as such, for the following reaction would then take place[1]: $5KI+ClO_2+4HCl=5I+5KCl+2H_2O$.
On the other hand if some of this ClO_2 were decomposed by the light before reaching the potassium iodide solutions, low results would be expected. To test this point a series of experiments were carried out in the dark room. The results are given in Table XIII.

TABLE XIII
Determinations on $Ba(ClO_3)_2.H_2O$
(In dark)

Weight of $Ba(ClO_3)_2.H_2O$		Percent found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0114	0.0092	80.2	42.43	34.07	8.36
0.0130	0.0079	60.9	48.39	29.46	18.93
0.0108	0.0074	69.0	40.20	27.72	12.48

As may be seen the results were not so good as those previously obtained in the light. The wide variation in the values pointed to a loss of gas which must have happened before the joint was fitted in place after the addition of the acid. This seemed not unlikely, for the conditions were quite different than in the experiments with bromides and iodides. Not only was the total amount of gas liberated in the experi-

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[1] Luther and McDougall: Zeit. phys. Chem., 62, 199, 242 (1908).

ments with chlorates very much greater but the gases were lighter. Accordingly a series of determinations were made in the dark, adding the acid through the inlet tube after the ground-glass joint was closed tightly and sealed with concentrated sulphuric acid. A blank was run with each experiment in order to make sure that the quantity of hydrochloric acid evolved and passing into the potassium iodide solution did not itself liberate iodine from the solution due to the presence of iodates. The results are given in Table XIV.

TABLE XIV

Determinations on $Ba(ClO_3)_2.H_2O$

Weight of $Ba(ClO_3)_2.H_2O$		Percent found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0130	0.01283	98.7	48.39	47.78	0.61
0.0133	0.01336	100.4	49.54	49.72	0.18
0.0130	0.0132	101.5	48.39	49.31	0.92

The above results are very satisfactory compared with the previous determinations. Accordingly in all subsequent experiments where a rapid reaction was likely the acid was added at the inlet tube of the apparatus instead of at the joint.

Adsorption of Chlorate Ion.—Barium sulphate was precipitated in the regular way in the presence of excess barium chlorate and the adsorbed chlorate ion determined. The results are tabulated in Table XV.

TABLE XV

Adsorption of Chlorate Ion

N/100 $Na_2S_2O_3$ cc	Chloride ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
138.41	0.01925	481.32	5.767	5.837
135.45	0.01884	471.02	5.644	
146.39	0.02036	509.07	6.099	

Adsorption of Permanganate Ion

Advantage was taken of the same general procedure for determining permanganate ion as was found successful for determining chlorate ion.

Determinations on Known Weights of $KMnO_4$.—A weighed amount of potassium permanganate was mixed with 0.2 gram of barium chloride in the reaction vessel and 50 cc of sulphuric acid to which was added 3 drops of concentrated hydrochloric acid was allowed to flow in at the inlet tube. The evolved chlorine was conducted into potassium iodide solution and the iodine titrated in the usual way. The following reaction was expected to take place:

$$2KMnO_4 + 10HCl + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Cl_2 + 8H_2O$$

The results of the preliminary experiments were quite satisfactory as shown in Table XVI.

TABLE XVI

Determinations on $KMnO_4$

Weight of $KMnO_4$		Percent found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0100	0.0098	98.0	31.64	31.01	0.63
0.0103	0.0103	99.7	32.59	32.50	0.09
0.0156	0.0157	100.5	49.37	49.60	0.23

Adsorption of Permanganate Ion.—Since the results on known weights of permanganate proved satisfactory, experiments were made on permanganate ion adsorbed by barium sulphate precipitated in the regular way in the presence of excess barium permanganate. The results are given in Table XVII.

Table XVII
Adsorption of Permanganate Ion

$N/100$ $Na_2S_2O_3$ cc	Adsorption of permanganate ion by $BaSO_4$			
	Gram	Grams per 100 mols	Grams Equivalents per 100 mols	
				Average
56.32	0.01339	334.91	2.816	
56.90	0.01253	313.36	2.845	
57.48	0.01367	341.81	2.874	
57.35	0.01364	341.01	2.868	
56.66	0.01348	336.93	2.833	2.847

Adsorption of Nitrate Ion

The attempt was made to determine nitrate ion by the same method found so convenient for the halogens. Fresenius[1] gives a method for the determination of nitrates which consists in distilling the nitric acid liberated from a nitrate by the action of dilute sulphuric acid. However, as it is necessary to use concentrated acid in order to dissolve the barium sulphate, the method of Fresenius could not be used directly. After repeated unsuccessful attempts to modify it to suit our needs, it was decided to use the Foerster[2] modification of the Kjeldahl method for nitrogen. This fitted in with the scheme of things admirably since the concentrated sulphuric acid used at the beginning of this procedure served to dissolve the barium sulphate precipitate; the phenol, used with the concentrated acid having no interfering action. The only modification in the preliminary treatment over that given in Olsen's Quantitative Chemical Analysis was that in order to dissolve all the barium sulphate precipitate it was necessary to increase the amount of phenol-sulphuric acid used. The ammonia evolved was received in $N/100$ sulphuric acid and the excess titrated back with $N/100$ sodium hydroxide solution using cochineal as an indicator.

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[1] Rose: Zeit. anal. Chem., 1, 309 (1862); Gladstone: Jour. prakt. Chem., 64, 442 (1855).

[2] Chem. Zeit., 12, 1555 (1889); 13, 229 (1889).

At the outset great difficulty was experienced in getting a satisfactory end-point with the dilute solutions used; and determinations could not be checked to anything like the required accuracy. This difficulty was overcome by the use of a colorimeter constructed for the purpose. We had on hand a colorimeter which contained a set of glass prisms, by the use of which the color of the solutions in two receptacles might be compared with but a very fine dividing line between the two fields. The prisms were fitted in one side of a small box painted black; and a ground glass in the side opposite. Two specially constructed rectangular glass cells of approximately 300 cc capacity were used for holding the solutions whose color was to be compared. Figure II shows the arrangement of the parts of the apparatus.

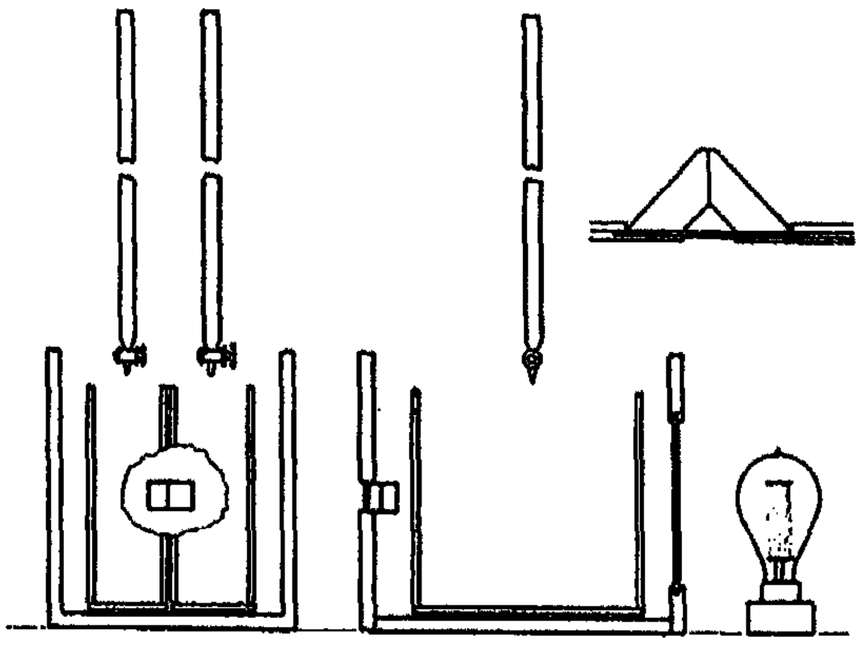

Fig. II

A standard colored solution was prepared by taking suitable equivalent volumes of the standard titrating solutions, adding three drops of cochineal solution[1] and diluting to a volume approximately equal to that obtained in the titrations of the unknown solutions. The solution was prepared new each day upon which titrations were made. Its preparation constituted a restandardization of the solutions each time.

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[1] Made by digesting 1 part of crushed cochineal with 10 parts of 25 percent alcohol.

The solution which served as a standard was placed in one of the glass cells and the solution to be titrated in the other. The titration was made directly in the cell and the colors were compared as the titration proceeded. By means of this colorimeter it was readily possible to duplicate results to within less than 0.1 cc of $N/100$ solution. The apparatus was used in all determinations of nitrogen by the Kjeldahl method.

Determination of "Blank."—As the reagents used contained small quantities of nitrates it was necessary to run a series of "blank" determinations for the purpose of making the necessary corrections. The same amounts of solutions were taken as used in the subsequent experiments and the directions in Olsen, previously referred to, were followed closely. The result of a series of determinations is given in Table XVIII. The correction that must be applied is expressed in cubic centimeters of $N/100$ solution.

TABLE XVIII

Determination of "Blank"

Determination	1	2	3	Average
Cc of N/100 solution	14.65	14.76	15.07	14.83

Determination on Known Weights of Nitrates.—Weighed samples of nitrates were taken and treated by the Foerster modification of the Kjeldahl process. The results are given in Table XIX.

TABLE XIX

Determinations on Nitrates

Salt	Weight		Percent found	Cc of $N/100$ solution		
	Taken	Found		Theoretical	Taken	Difference
KNO_3	0.0317	0.0321	101.2	31.33	31.64	0.31
$Ba(NO_3)_2$	0.0505	0.512	101.3	38.63	39.22	0.59

Adsorption of Nitrate Ion.—Barium sulphate was precipitated in the usual way with barium nitrate solution in excess.

The adsorbed nitrate ion was determined by the Kjeldahl method. The results are shown in Table XX.

TABLE XX

Adsorption of Nitrate Ion

Cc $N/100$ solution			Adsorption of nitrate ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
49.55	14.83	34.72	0.02152	538.16	8.680	
48.09	14.83	33.26	0.02062	515.53	8.325	
48.25	14.83	33.42	0.02072	518.02	8.358	
48.75	14.83	33.92	0.02102	525.51	8.480	
48.25	14.83	33.42	0.02072	518.01	8.358	
49.89	14.83	35.06	0.02173	543.43	8.765	
48.45	14.83	33.62	0.02084	521.11	8.405	8.482

The results given in the above table show that nitrate ion is adsorbed strongly. This is in line with the warning usually given in text books of analytical chemistry that nitrates must be absent from solutions in which sulphate is to be determined as barium sulphate. It also confirms the conclusions reached by Mendelejeff a long time ago that barium sulphate carries down nitrates more readily than chlorides. By referring to our results on chlorides it will be seen that under similar conditions 5 times as many equivalents of nitrate ion are adsorbed as of chloride ion.

Adsorption of Nitrite Ion

Since the Kjeldahl method for nitrogen proved so satisfactory for determination of the amount of adsorbed nitrate ion, it seemed likely that it would serve also for the determination of nitrite ion.

Determination of "Blank."—Since it was found in the previous experiments that the amount of nitrates present in the solutions used for the determinations was relatively large when compared with the amount of adsorption, it was necessary to make frequent "blank" determinations under conditions identical with those used in the regular experiments. The plan followed was to make up quantities of solutions sufficient to carry out the experiments on a given ion; and to make the determinations of the blank along side the others. Table XXI gives the blank determinations for the experiments on nitrites.

TABLE XXI

Determination No.	1	2	3	4	Average
Cc N/100 solution	16.57	16.31	16.70	16.31	16.47

Determinations on Known Weights of Nitrites.—As has been observed frequently in these investigations the rate at which the salt was attacked determined the accuracy of the analysis. In the first experiment with a known weight of barium nitrite in the form of a powder the action was very rapid and when the salt was treated with the phenol sulphuric acid, some nitrogen dioxide was unquestionably lost. The amount found under these conditions was less than 95 percent of the theoretical. In a second experiment a single crystal of barium nitrite was taken with the idea that the slower action on a single crystal would favor the retention of all the oxides of nitrogen by the phenol acid mixture. In this case the results showed an accuracy of approximately 98 percent of the theoretical. The method was therefore regarded as quite satisfactory for the determination of adsorbed nitrite ion since the action would be very slow indeed on account of the slow solubility of barium sulphate. The results of the two experiments above described are given in Table XXII.

TABLE XXII
Determinations on Barium Nitrite

Sample	Weight		Percent found	Cc *N*/100 solution		
	Taken	Found		Theoretical	Taken	Difference
Powdered	0.0417	0.0394	94.5	33.71	31.90	1.81
Single crystal	0.0424	0.0414	97.7	34.28	33.48	0.80

Adsorption of Nitrite Ion.—A series of six determinations were made of nitrite ion adsorbed in barium sulphate precipitated in the regular manner in the presence of excess barium nitrite. The results are given in Table XXIII.

TABLE XXIII

Adsorption of Nitrite Ion

N/100 solution			Adsorption of nitrite ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
45.85	16.47	29.38	0.01251	337.87	7.345	
45.98	16.47	29.51	0.01357	339.36	7.378	
46.87	16.47	30.40	0.01398	349.60	7.600	
46.74	16.47	30.27	0.01392	322.99	7.568	
46.61	16.47	30.14	0.01386	346.61	7.535	
45.97	16.47	29.50	0.01357	339.25	7.375	7.467

By comparing the results tabulated above with those obtained for nitrates it will be seen that there was little difference between the amount of adsorption in the two cases; as will be pointed out in the later discussions this result is what one might expect on account of the close similarity between the two ions.

In considering methods for the accurate determination of cyanide, sulphocyanate, ferrocyanide and ferricyanide ions, conflicting statements were found regarding the action of the different cyanides with concentrated sulphuric acid. Dyer[1] and Olsen[2] claim that certain cyanides with concentrated sulphuric acid do not give a quantitative yield of ammonia but that some oxides of nitrogen are formed. Olsen states that the Foerster modification of the Kjeldahl method for nitrogen is necessary in evaluating certain cyanides. Williams,[3] however, claims that in every case the cyanides give a quantitative yield of ammonium sulphate when treated with concentrated sulphuric acid. Nevertheless it was decided to use the Foer-

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[1] Chem. Centr., (3) 17, 433 (1886).

[2] "Quantitative Chemical Analysis," 189 (1910).

[3] "The Chemistry of Cyanogen Compounds," 90 (1915).

ster modification of the Kjeldahl method as we desired to keep the methods as uniform as possible and wished to guard against the loss of any oxides of nitrogen which might be formed.

Adsorption of Cyanide Ion

Determination of "Blank."—The blanks run in connection with these experiments are given in Table XXIV.

TABLE XXIV

Determination	1	2	3	4	Average
Cc N/100 solution	16.70	16.11	16.25	16.54	16.40

Determinations on Known Weight of Mercuric Cyanide.—The Kjeldahl method gives very reliable results for cyanide as shown by the experiments given in Table XXV.

TABLE XXV
Determinations on $Hg(CN)_2$

Weight		Percent found	Cc *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0502	0.0504	100.4	39.75	39.90	0.15
0.0498	0.0495	99.5	39.43	39.15	0.28

Adsorption of Cyanide Ion.—Four millimols of barium sulphate were precipitated in the regular manner with barium cyanide in excess and the adsorbed ion determined by the Kjeldahl method. The results are given in Table XXVI.

TABLE XXVI
Adsorption of Cyanide Ion

N/100 solution			Adsorption of cyanide ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
17.68	16.40	1.28	0.00033	8.32	0.320	
17.52	16.40	1.12	0.00029	7.18	0.280	
17.52	16.40	1.12	0.00029	7.18	0.280	
18.01	16.40	1.61	0.00042	10.46	0.403	
17.49	16.40	1.09	0.00028	7.08	0.273	0.310

Adsorption of Sulphocyanate Ion

Determination of "Blank."—The determinations of blanks made in connection with this set of experiments are given in Table XXVII.

TABLE XXVII

Determination No.	1	2	3	Average
Cc N/100 solution	14.85	14.79	15.04	14.89

Determination on a Known Weight of $Ba(SCN)_2.2H_2O$.—That the Kjeldahl method is quite as accurate for the determination of small amounts of thiocyanates as for cyanide is shown by the analysis tabulated in Table XXVII.

TABLE XXVII
Determination of $Ba(SCN)_2.2H_2O$

Weight		Percent found	Cc *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0324	0.0327	100.9	22.35	22.57	0.22

Adsorption of Sulphocyanate Ion.—The usual weight of barium sulphate was precipitated with barium sulphocyanate in excess and the adsorbed sulphocyanate determined. The results of a series of determinations are given in Table XXIX.

TABLE XXIX
Adsorption of Sulphocyanate Ion

Cc *N*/100 solution			Adsorption of sulphocyanate ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
15.86	14.89	0.97	0.00056	1.41	0.243	
15.53	14.89	0.64	0.00037	0.93	0.160	
16.02	14.89	1.13	0.00065	1.64	0.283	
15.90	14.89	1.01	0.00058	1.46	0.253	
15.53	14.89	0.64	0.00037	0.93	0.160	
15.53	14.89	0.64	0.00037	0.93	0.160	
16.02	14.89	1.13	0.00065	1.64	0.283	0.220

On account of the very small quantity of cyanide and sulphocyanate ions adsorbed by barium sulphate the results show considerable variation among themselves although the actual differences in terms of cc of *N*/100 solution are very slight. However, the average of a series of determinations such as those made gives a fairly satisfactory index of the amount adsorbed.

Adsorption of Ferrocyanide Ion

Preparation of Barium Ferrocyanide.—This salt was prepared in the following way:[1] A strong barium chloride solution was added to a moderately strong solution of sodium ferrocyanide. Barium ferrocyanide, $Ba_2Fe(CN)_6.6H_2O$, separated out as a light yellow crystalline powder. The precipitate was washed with water, filtered and recrystallized several times from water. 100 cc of water dissolved 0.34 gm of the salt at 15.5° and 1.01 g at 100°.

Determination of Blank.—Sufficient quantity of solutions were prepared for making the determinations on both ferrocyanides and ferricyanides. Consequently the same "blank" correction was applied to both. The determinations are given in Table XXX.

TABLE XXX

Determination	1	2	3	4	Average
Cc N/100 solution	16.44	16.50	16.30	16.64	16.47

Determination on a Known Weight of Potassium Ferrocyanide.—In order to test the Kjeldahl method for the determination of complex cyanides a sample of $K_4Fe(CN)_6.3H_2O$ was treated in the usual way. The results are given in Table XXXI.

TABLE XXXI

Determinations on $K_4Fe(CN)_6$

Weight		Percent found	Cc of *N*/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0091	0.0089	97.8	12.92	12.36	0.56
0.0120	0.0119	99.2	17.19	16.90	0.29

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[1] Williams: Loc cit., p. 95.

Since the results are quite satisfactory for the purpose, a series of experiments were carried out for the determiuation of both ferrocyanide ion and ferricynanide ion adsorbed in barium sulphate.

Adsorption of Ferrocyanide Ion.—The usual amount of barium sulphate was precipitated in the regular way in the presence of excess barium ferrocyanide. The results of the determination of adsorbed ferrocyanide ion in the precipitates so obtained are given in Table XXXII.

TABLE XXXII
Adsorption of Ferrocyanide Ion

Cc $N/100$ solution			Adsorption of ferrocyanide ion in $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
95.93	16.47	79.46	0.02809	702.14	13.242	
94.77	16.47	78.30	0.02767	691.78	13.050	
97.97	16.47	81.50	0.02881	720.17	13.583	
96.30	16.47	79.83	0.02822	705.41	13.305	
93.42	16.47	76.95	0.02720	680.00	12.825	13.201

Adsorption of Ferricyanide Ion

Preparation of Barium Ferricyanide.[1]—This salt was prepared by agitating barium ferrocyanide with an excess of manganous ferricyanide suspended in water. The solution was filtered and evaporated under reduced pressure. The salt, $Ba_3[Fe(CN)_6]_2.20H_2O$, appeared as fine red crystals which are quite stable and very soluble in water.

Adsorption of Ferricyanide Ion.—The usual quantity of barium sulphate was precipitated in the regular way with barium ferricyanide in excess and adsorbed ferricyanide ion was determined. Five determinations were carried out with the results as given in Table XXXIII.

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[1] Williams: Loc. cit., p. 138.

TABLE XXXIII

Adsorption of Ferricyanide Ion

N/100 solution			Adsorption of ferricyanide ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
39.19	16.47	22.72	0.00803	200.77	2.840	
38.05	16.47	21.58	0.00763	190.69	2.698	
37.54	16.47	21.07	0.00744	186.19	2.635	
37.41	16.47	20.94	0.00740	185.04	2.618	
37.93	16.47	21.46	0.00759	189.63	2.683	2.695

The results of the series of determinations on anions adsorbed by barium sulphate are summarized in Table XXXIV. The ions are arranged in the order of adsorption beginning with the least adsorbed.

TABLE XXXIV

Adsorption of Anions by Barium Sulphate

(*a*) Ion.

(*b*) Number of gram equivalent ions adsorbed by 100 mols of $BaSO_4$.

(*c*) Number of gram ions adsorbed per 100 mols of $BaSO_4$.

(*d*) Grams contamination per 100 grams of $BaSO_4$ in terms of the barium salt of the ion.

(*e*) Percentage contamination by weight of ion.

(*f*) Percentage contamination by weight of barium salt.

(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
Iodide	0.056	0.056	0.0469	0.0304	0.0468
Sulphocyanate	0.220	0.220	0.1195	0.0547	0.1193
Cyanide	0.310	0.310	0.1258	0.0346	0.1256
Bromide	0.831	0.831	0.5291	0.2846	0.5263
Chloride	1.760	1.760	0.7852	0.2801	0.7791
Ferricyanide	2.695	0.898	1.6088	0.7391	1.5833
Permanganate	2.847	2.847	2.2902	1.4512	2.2390
Chlorate	5.837	5.837	3.8401	2.0864	3.6981
Nitrite	7.467	7.467	3.7194	1.4725	3.5869
Nitrate	8.482	8.482	4.7500	2.2540	4.5346
Ferrocyanide	13.201	3.300	6.8830	2.9986	6.4398

It is needless to say that the absolute amounts of the various ions adsorbed by barium sulphate as given in the above table would be obtained only under the specific experimental procedure that was followed in the precipitation and subsequent treatment of the salt. By varying the conditions one would expect to find a variation in the absolute amounts adsorbed but the order of ions should remain approximately the same. In order to test this out, experiments were carried out on the adsorption of chlorate ion and permanganate ion in the presence of excess sodium sulphate. The conditions of precipitation and subsequent treatment of the salt are identical with those previously described under the determinations of the respective ions with the exception that 50 cc of *M*/10 sodium sulphate was added to 40 cc of *M*/10 barium salt. The results are given in Tables XXXV and XXXVI.

Table XXXV

Adsorption of Chlorate Ion

(Na_2SO_4 in Excess)

N/100 $Na_2S_2O_3$ cc	Chlorate ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
				Average
53.4	0.00742	185.37	2.225	
55.2	0.00768	192.05	2.300	
54.6	0.00760	189.96	2.275	2.266

Table XXXVI

Adsorption of Permanganate Ion

(Na_2SO_4 in excess)

N/100 $Na_2S_2O_3$ cc	Permanganate ion adsorbed by $BaSO_4$			
	Gram	Grams per 100 mols	Gram equivalent per 100 mols	
				Average
27.5	0.00655	163.63	1.375	
26.5	0.00631	157.68	1.325	
28.0	0.00667	166.60	1.400	1.366

From the above experiments it is evident that the absolute amount of the adsorption is less when the precipitation is carried out in the presence of excess sodium sulphate. However, the chlorate ion is adsorbed more than permanganate ion which is in accord with the previous results. The experiments on chloride ion adsorbed in the presence of excess sodium sulphate as described at the beginning of this paper show that chloride ion is adsorbed much less than either permanganate or chlorate ion. This is in the right direction but the results are not strictly comparable since the precipitation and subsequent treatment of the barium sulphate were different in the case of the chloride ion.

Discussion of Results

From the results of this investigation the order of adsorption of the ions by precipitated barium sulphate is: ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulphocyanate > iodide, the ferrocyanide being adsorbed the most and the iodide the least. From a consideration of this order and of the absolute amount of the adsorption in each case we find very little reason to place much credence in Schulze's law. Although we find a quadrivalent ion the most strongly adsorbed, we find four univalent ions more strongly adsorbed than the trivalent ferricyanide. Furthermore, contrary to what is implied in Schulze's law, we find a very wide variation in the amount of univalent ions adsorbed. This amount varies from 8.482 gram anions per 100 mols for nitrate ion to 0.056 gram ions per 100 mols for iodide ion. If the absorption values are expressed in gram anions instead of gram equivalent anions the order becomes: nitrate > nitrite > chlorate > ferrocyanide > permanganate > chloride > ferricyanide > bromide > cyanide > sulphocyanate > iodide,— the nitrate ion being adsorbed the most and the iodide the least. Here there is nothing even to suggest Schulze's law.

Although chemically dissimilar ions of the same valence may show a wide variation in the degree of adsorption, indicating that adsorption is a specific property of ions, it was observed that nitrate and nitrite ions which are more nearly related chemically were adsorbed to about the same extent. Notwithstanding that there are many exceptions to Schulze's law, there is a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence. This makes it seem probable that there are two factors that determine the adsorption of ions by a given disperse phase: the specific nature of adsorption and the valence of the ion. In the case of dissimilar ions of the same valence like nitrate ion and iodide ion there may well be a wide variation in the degree of adsorption just as was found; on the other hand with ions more nearly related and of the same valence like nitrate ion and nitrite ion one might expect to find a similar amount adsorbed, just as the experiments indicate. Now it was thought that if a series of ions of much the same general character were selected, thus eliminating the specific factor as far as it was possible, one might be able to get a clearer insight into the effect of valence. Among the ions considered in this investigation the cyanides seemed the most promising for such a comparison. This is particularly true of ferrocyanide and ferricyanide ions which are identical in chemical composition but differ in valence. The results of this comparison are summarized in Table XXXVII. The adsorption values are expressed in gram equivalent anions per 100 mols of barium sulphate.

TABLE XXXVII

Anion	Valence	Adsorption
Ferrocyanide	4	13.201
Ferricyanide	3	2.695
Sulphocyanate	1	0.220
Cyanide	1	0.310

In view of the quite generally known large adsorption of iron by barium sulphate, the objection may be raised that the increase in the adsorption value of the ferrocyanide over that of cyanide and sulphocyanate is due to the presence of iron in the ion. Even if this were admitted, it can clearly not account for the great increase in the adsorption value of ferrocyanide over that of ferricyanide, these two values being respectively 13.201 and 2.695. In the first place, the iron was not present as the ferric and ferrous ion but exists in complex ions; in the second place, the values are based on the determinations of the amount of nitrogen present in the precipitates; in the third place, if the iron had any great effect, it is rather hard to reconcile the conflicting facts that the trivalent ferric iron is present in the ion of lower valency, which is adsorbed less. These results then seem to point to the conclusion that there is both a specific and a valence factor influencing the adsorption of ions. If the specific factor could be maintained absolutely constant, the amount of adsorption of an ion would be directly proportional to the valence.

It is of interest to compare the order of ions obtained by direct analysis of barium sulphate with the order deduced from coagulation experiments. From Hofmeister's[1] experiments on the coagulation of albumin in neutral or slightly alkaline solution the order is sulphocyanate > iodide > chlorate > nitrate > chloride > acetate > citrate > phosphate > sulphate > tartrate, the sulphocyanate being adsorbed the most and the tartrate the least. In a slightly acid solution Pauli[2] found the order of ions to be: sulphocyanate > iodide > bromide > nitrate > chloride > acetate. Combining these two orders we get: sulphocyanate > iodide > bromide > chlorate > nitrate > chloride > acetate > citrate > phosphate > sulphate > tartrate. The result of combining the two series is to fix bromide ion in relation to the others as the order agrees for all the other ions. By comparing this order of ions with that obtained with barium sulphate we see that the two are almost exactly opposite. Selecting the ions common to the two series Hofmeister's and our own, we find that the former is: sulphocyanate > iodide > bromide > chlorate > nitrate > chloride; while the latter is iodide < sulphocyanate < bromide < chloride < chlorate < nitrate. The orders are al-

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[1] Pfluger's Archiv., 24, 247 (1887); Cf. Bancroft: Jour. Phys. Chem., 19, 350 (1915).

[2] Hofmeister's Beiträge zur. chem. Physiol., 5, 27 (1904).

most exactly reversed, the position of chlorides being irregular. Osaka[1] found the order of adsorption of anions by charcoal to be: iodide < nitrate < bromide < chloride < sulphate, the iodide ion being adsorbed the least. This order agrees with our own except in the case of nitrate ion. From experiments on hydrous ferric oxide[2] the order of adsorption of precipitating anions is: iodide < bromide < nitrate < chloride < hydroxyl < sulphate < dichromate, the iodide being adsorbed the least. This order is likewise more nearly in accord with the results we obtained and is again the reverse of Hofmeister's series.

On account of the specific nature of adsorption one might expect to get a variation in the order with each adsorbing media just as the results with barium sulphate, charcoal and ferric oxide seem to indicate. However, the similarity in the order with these three substances is rather striking considering that the actual conditions and method of determination were different in each case. We are at a loss to account for the almost complete reversal of the order of ions with albumin from what it is with barium sulphate and the other substances cited. It is usually considered that albumin constitutes a special case and that it is fundamentally different from other colloidal solutions.[3] This is certainly open to question; but there is no doubt but that further experimental work must be done before it will be possible to state with any degree of assurance, the cause of this apparent discrepancy. To this end it is planned to carry out further determinations on the absolute amount of adsorption by different substances.

In addition to the anions that should be avoided in the solution from which barium sulphate is precipitated for analytical purposes, the data indicate what barium salts should be used in making colloidal barium sulphate by double decomposition. Since barium sulphate is a positive colloid it is most stable in the presence of slightly adsorbed anions like

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[1] Mem. Col., Sci. Kyoto Imp. Univ., 1, 267 (1915).

[2] Freundlich: "Kapillarchemie," 352–358 (1909).

[3] *Ibid.*, 434 (1909).

sulphocyanate or iodide. This explains why von Weimarn[1] obtained such a stable colloidal solution of barium sulphate by mixing alcoholic solutions of barium sulphocyanate and cobalt sulphate. In view of the stability of von Weimarn's colloid, we should expect to find cobalt ion strongly adsorbed by barium sulphate since this would likewise have a stabilizing effect. Kato[2] used barium acetate in the preparation of his colloidal barium sulphate. Although we have not as yet determined the adsorption of acetate ion by barium sulphate, it is probably slight.

Summary

The results of this investigation may be summarized as follows:

1. The adsorption of the following anions by pre-cipitated barium sulphate has been determined: chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, sulphocyanate, ferrocyanide, and ferricyanide. Barium sulphate was precipitated by mixing a solution of sodium sulphate with a solution of barium salts and the absolute amount of anion adsorbed was determined by direct analysis of the precipitate by a suitable method. The conditions of precipitation and the subsequent treatment of the salt were maintained as nearly constant as possible, throughout.

2. The order of adsorption of anions is: ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulphocyanate > iodide, the ferrocyanide ion being adsorbed the most and the iodide ion the least. Changing the conditions affects the absolute amount of adsorption but not the order of the ions.

3. The order of adsorption is not in accord with Schulze's law: Although the tetravalent ferrocyanide ion is adsorbed the most, there are four univalent ions more strongly adsorbed than the trivalent ferricyanide ion. Furthermore, there is a wide variation in the amount of univalent ions adsorbed.

4. Determination of the order of ions by direct analysis

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[1] Zeit. Kolloidchemie, 3, 282 (1908).

[2] Loc. cit.

of the adsorbing phase when this is possible, is preferable to deducing the order from coagulation data, on account of the greater accuracy of the former. It is probably inaccurate in any case to assume that the ion with the same charge as the colloidal particles has no effect in determining the critical coagulation concentration of the colloid by electrolytes. It is more probable that the relatively small effect of the ion with the same charge as the colloid may be lost sight of altogether because of the errors inherent in the experimental method.

5. The order of adsorption of anions by barium sulphate is the reverse of that deduced from Hofmeister's data on the coagulation of albumin by electrolytes. The order of adsorption by charcoal and by hydrous ferric oxide is apparently more nearly what it is with barium sulphate. Further experimental work is necessary in order to find out the cause of the apparent discrepancy in the case of albumin.

6. Two factors determine the adsorption of ions by a given adsorbing agent: the nature of the ion and the valence of the ion.

7. With ions of the same general character the specificity of adsorption should not be so pronounced and the valency factor should predominate. Thus, we find nitrate and nitrite ion adsorbed by barium sulphate to about the same extent; and the order of adsorption of the cyanides by barium sulphate is ferrocyanide > ferricyanide > cyanide, sulphocyanate, which is in accord with Schulze's law.

8. With ions which are not similar and yet have the same valence, the specificity of adsorption may be very pronounced. Thus, we find that barium sulphate adsorbs nitrate ion much more than iodide ion.

9. Mendelejeff's observation that nitrates are carried down by barium sulphate more readily than chlorides has been confirmed, as has been the statement, frequently met with in text-books of analytical chemistry, to the effect that chlorates and nitrates should be absent from solutions in which sulphate is to be determined as barium sulphate.

10. Colloidal solutions of barium sulphate are usually

positive due to strong preferential adsorption of barium ion. The stability of the colloid should be greatest in the presence of a weakly adsorbed anion. This partly accounts for the stability of von Weimarn's colloidal barium sulphate, precipitated from barium sulphocyanate solution.

11. Since barium ion is adsorbed more strongly by barium sulphate than is sulphate ion, one should expect, other conditions remaining the same, to have greater peptization and greater anion adsorption in the presence of excess barium salt than in the presence of excess sulphate. In like manner, since hydrogen ion is more readily adsorbed than any other univalent cation one should expect, under otherwise constant conditions, to find greater anion adsorption when barium sulphate is precipitated from sulphuric acid solution than from sodium sulphate solution. These conclusions have been confirmed.

12. Methods have been applied and evolved for the estimation of minute amounts of material adsorbed by barium sulphate.

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THE COLORS OF COLLOIDS. IV

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Interference and Diffraction

Tyndall[1] calls attention to the fact that "when a film of variable thickness is illuminated by white light, it displays a variety of colors. These colors are called the colors of thin plates. The colors of the soap-bubbles; or oil or tar upon water; of tempered steel; the brilliant colors of lead skimmings; Nobili's metallochrome; the flashing of colors of certain insects' wings, are all colors of thin plates. The colors are produced by transparent films of all kinds. In the bodies of crystals we often see iridescent colors due to vacuous films produced by internal fracture. In cutting the dark ice under the moraines of glaciers, fracture often occurs and the colors of thin plates flash forth from the body of the ice with extraordinary brilliancy."

The colors of thin films were investigated first by Boyle.[2] "In 1665, Hooke devised the method of producing the colors by means of an air film between two lenses of large radius of curvature. He found that the colors were distributed in concentric rings, showing that they depended on the thickness of the film and that equal thickness always gave the same color. The subject was investigated more carefully by Newton, who made careful measurements of the colored rings (since known by his name) produced by the air film between a lens and a plate of glass. It remained for Young, however, to give the true explanation that the rings were due to the interference between the wave trains reflected from the upper and lower surfaces of the film." Where the two beams differ by half a wave-length, they destroy each other giving a dark line. If the source of light emits two wave-lengths as with the lithium and thallium flame, we get red and green rings where dissonance occurs and yellow (subjective) at the points

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[1] "Electricity and Light," 97 (1895).

[2] Wood: "Physical Optics," 152 (1911).

where the red and green are superposed. With white light we get colored rings because we have an infinite number of ring systems. If the air film is infinitely thin at the center and the incident monochromatic light is nearly normal, one would naturally expect the rays reflected from the center to reenforce one another; but as a matter of fact they destroy each other and the center is black.[1] "The explanation is that the two reflections take place under different conditions. At the lower surface the reflection is from a dense medium to a rare; at the upper surface from a rare to a dense. The waves reflected at the rarer medium are reflected without a change of phase, those reflected at the denser medium suffer a phase change of 180°. This is, of course, equivalent to a path difference of half a wave-length. This explanation was given by Young who devised a very beautiful experiment in support of it. By using a lens of crown glass and a plate of flint glass with a film of cassia oil between them, he secured a system in which reflection from the upper and lower surfaces of the film took place under the same condition, the oil having a refractive index intermediate between those of the crown and the flint glasses. The ring system formed under these conditions had a white center exactly in accordance with his theory....

"With films of such thickness that no light is reflected, the energy is not lost, but is transmitted; therefore, such films have an increased transmitting power for monochromatic light, none being lost by reflection from the first surface."

Some special cases of the behavior of thin plates are discussed by Wood.[2] With thin transparent laminae, such as a soap-film, the amplitudes of the disturbances reflected from the two surfaces are equal and consequently destroy each other completely when the phase-difference is 180°. Since only a small percentage of the light is reflected from each surface, the colors are not intense though they are saturated. If a plate of mica be pressed against a pool of molten

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[1] Wood: "Physical Optics," 155 (1911).

[2] "Physical Optics," 170 (1911).

selenium on a glass plate and if the whole be allowed to cool under pressure, removal of the mica plate will leave on the surface of the selenium films of mica of variable thickness and these will show Newton's colors in great beauty. If the mica is cemented to the glass plate with sealing wax or with any of the common resinous cements, very little trace of the colors is to be seen because the refractive indices of the two media are so nearly the same that practically no energy is reflected from the boundary. The use of selenium can be avoided by silvering the surface of the mica very lightly and then cementing it to the glass with any good refractory cement, the metallic layer taking the place of the medium of high refractive index. Still more brilliant films can be prepared by silvering the mica thickly, cementing the silvered side to the glass plate and then stripping the mica off. The colors are scarcely visible owing to the disproportionality between the amplitudes of the two interfering streams of light; but appear as soon as the upper surface of the mica is half-silvered which can be done by immersing the plate in a silvering solution until the colors reach their maximum brilliancy. Another method is to substitute a thin film of collodion for the mica, half-silvering the film as before.

"In the case of transparent films, the wave-lengths absent in the reflected light appear in excess in the transmitted light there being no destruction of energy. If the second surface is a perfect reflector, the energy thrown upon it by interference at the first surface will all be returned. If we consider the upper metallic surface as non-absorbing, and work out the case by the method of multiple reflections, we find that no color will be produced, light of all wave-lengths being reflected with equal facility. The fact that brilliant colors appear means that light is absorbed at one or both of the silvered surfaces, since this is the only way in which the energy of the absent wave-lengths can disappear.

"We will now consider a remarkable case of interference which appears to differ essentially from any previously discussed. As Lord Rayleigh points out in his article on 'Wave

Theory of Light,' the theory of thin films shows that a transparent film on a perfectly reflecting surface shows no interference colors. On the other hand, a thin film of collodion deposited on a bright surface of silver shows brilliant colors in reflected light. It, moreover, *scatters* light of a color complementary to the color of the directly reflected light. This is apparently due to the fact that the collodion film 'frills,' the mesh, however, being so small that it can be detected only by the highest power of the microscope. Commercial ether and collodion should be used. If chemically pure ether obtained by distillation is used, the film does not frill and no trace of color is exhibited. Still more remarkable is the fact that if sunlight is thrown down upon the plate at normal incidence, brilliant colors are seen at grazing emergence, if a Nicol prism is held before the eye." The waves absent in the reflected light are scattered by the granular surface. If a spot on the film which appears purple by reflected light is illuminated with sunlight, it will be found that green light is scattered, not in all directions but through a range corresponding to the size of the granulations as in the case of mixed plates.

At first sight it may seem as if the colors could be classed[1] with the phenomena of mixed plates, "their brilliancy and saturation reminding one of the appearances produced by laminary retardation. The films, however, show no color by transmitted light when deposited on glass, and the effective doubling of the retardation, by the reflection back through the film by the metal surface, can hardly account for the observed effects. Moreover, the energy stream reflected from the surface of the collodion appears to be essential, for if we employ light polarized perpendicular to the plane of incidence, and set the plate at the polarization angle of collodion, so that no reflection occurs except at the metal surface, all trace of color disappears. If the angle of incidence is larger than the polarizing angle, the color of the reflected light changes to its complementary tint when the plane of polarization is made parallel to the plane of incidence.....

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[1] Wood: "Physical Optics," 172 (1911).

"A collodion surface reflects only about five percent of the incident energy, and it is found impossible to account for the strong colors seen in the reflected light by compounding the feeble stream of light from the collodion with the powerful stream coming from the metal. It appeared, however, that the observed effects could be accounted for if the somewhat arbitrary assumption were made that the granulated surface reflected more strongly than a smooth surface. As has been said, the granulations are too small to interfere with the regular reflection of light, the scattering being selective, so to speak, *i. e.*, confined to the waves which, owing to interference, are compelled to traverse the film a number of times."

Lommel[1] has discussed the production of stationary waves by interference and their application in color photography. "When a parallel beam of light rays (or a plane light wave) impinges perpendicularly upon a plane mirror, the interference of the incident with the reflected wave produces a stationary wave of such character that, at a given distance from the mirror, *i. e.*, everywhere in a plane parallel to it, the same phase of vibration exists. The nodes and antinodes form two systems of planes parallel to the mirror, whose distances, for planes of the same system, equal half a wave-length, and are bisected by the planes of the other system. Suppose, now, that this system of stationary waves is cut by a plane inclined to the mirror. The two systems of planes must then intersect this plane in two systems of parallel, equidistant, straight lines, which correspond alternately to antinodes and nodes of vibration. If the cutting-plane is perpendicular to the mirror, the distances of these straight lines will be only half a wave-length, and, hence, so small that the unaided eye cannot perceive them separately. The distances of the lines become greater, however, the smaller the inclination of the cutting-plane to the mirror, and this inclination may be chosen so that the lines are separated by from 0.5 to 2 mm. To render these lines visible, Wiener (1890) used a plate of glass, upon which a thin, transparent,

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[1] "Experimental Physics," 599 (1911).

sensitized film of collodion was spread, and placed it with the film toward the mirror at such an inclination that, between the film and the mirror, only a thin wedge-shaped column of air remained within which the stationary wave was formed. The strongest photographic effect occurred along the line of antinodes, and the weakest along that of the nodes, so that, after developing the plates, there appeared upon the film a system of alternate dark and bright bands, the former corresponding to the nodes and the latter to the antinodes.

"With the help of stationary light-waves, Lippmann (1891) succeeded in photographing the spectrum and other colored objects in their natural colors. As a sensitive plate, he used a thin film of albumin, spread upon a glass plate, within which silver iodide and bromide were mixed uniformly, and in an extremely finely divided state. This plate formed, with its film inward, the front wall of a glass trough filled with mercury. The photograph of the spectrum taken upon it, when developed and fixed in the usual way, showed before the dark background, when seen in reflected light, the spectral colors, each in its characteristic place, and when seen in transmitted light, the complementary spectral colors. During the photographing process stationary waves were formed within the sensitized film and by the combined effect of the incident rays and of those reflected at the surface of the mercury, having the planes of their nodes and antinodes parallel to the surface of the film. Only those of the greatest intensity react upon the silver salt, and even they, after being fixed, leave transparent layers more or less strongly reflecting. The film is thus divided into a series of very thin plates, whose thickness for each color equals the distance of two antinodes, or equals half a wave-length of the respective color. If now white light falls upon such a plate, the light reflected at the first surface will interfere with that reflected from the back surface, by reason of the difference in distance traversed, which difference equals double the thickness of the plate. While the interference of the two beams of light intensifies this color, it weakens all the others. At this part of the image, therefore, the plate has exactly the necessary thickness to reproduce by interference in reflected light the color photographed at this particular place. The colors shown by the image are nearly the colors of thin plates. They appear, however, much clearer and more thoroughly saturated than the latter. The reason for this is that in the sensitized plate, by reason of the extreme smallness of the light waves, a very large number of such thin plates lie superposed (about 200 if the plate is $^1/_{20}$ mm thick). The more reflecting surfaces are present, the purer the reflected color will be; for the surfaces, succeeding each other at equal distances, form a grating which intensifies the beam of the corresponding color, whose difference of distance equals an integral number of wavelengths, while it destroys the rays producing other colors."

Some very remarkable phenomena connected with the colors of thin films are seen sometimes in crystals of potassium chlorate.[1] "That the seat of the coloration is in a thin twin stratum, admits I think of no doubt whatsoever. A single twin plane does not show anything of the kind. For the production of the color the stratum must be neither too thick nor too thin. Twin strata a good deal thicker than those that show color are common enough; and among the crystals sent to me I have found some twin strata which were a good deal thinner, in which case the crystal showed no color. The more complicated spectra which are frequently observed seem referable to the existence of more than two twin planes in close proximity. There is no reason to think that the explanation of these spectra would involve any new principle not already contained in the explanation of the appearance presented when there are only two twin planes, though the necessary formulae would doubtless be more complicated.....

"It seems evident that the thickness of the stratum affects the result through the difference of phase which it entails in the two refracted waves on arriving at the second twin plane. But whereas in the ordinary case of the production of color by the interposition of a crystalline plate between

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[1] Stokes: "Mathematical & Physical Papers," 5, 175 (1905).

a polarizer and an analyzer, we are concerned only with the difference of retardation of the differently polarized pencils which are transmitted across the plate, and not with the absolute retardation, it is possible that in this case we must take into account not only the difference of retardation for the differently polarized pencils which traverse the stratum, but also the absolute retardation; that is, the retardation of the light reflected from the second relatively to that reflected from the first twin plane.

"I have not up to the present seen my way to going further. It is certainly very extraordinary and paradoxical that light should suffer total or all but total reflection at a transparent stratum of the very same substance, merely differing in orientation, in which the light had been travelling, and that, independently of its polarization. It can have nothing to do with ordinary total internal reflection, since it is observed at quite moderate incidences, and *only within very narrow limits* of the angle of incidence."

The subject has also been discussed by Wood.[1] "The colors are extremely brilliant and pure, much more so than any exhibited by soap films.[2] One of the most remarkable facts connected with the phenomenon is that the spectrum of the reflected light is frequently found to consist almost entirely of a comparatively narrow band. The same phenomenon is also exhibited by the fiery opal. One in possession of the author at a certain angle of incidence reflects yellow light, which when examined in the spectroscope, is found to consist of a narrow band not much wider than the distance between the yellow mercury lines. In the case of a *single* thin film, of such thickness that but a single region of the spectrum is reflected, this region is always of considerable breadth. To account for the reflection of light of such a high degree of purity Lord Rayleigh assumes that the reflection takes place at a number of thin laminae sensibly equidistant, the distance between any two being of the order of magnitude of the

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[1] "Physical Optics," 160 (1911).

[2] Lord Rayleigh: Phil. Mag., 26, 256 (1888).

light wave. Quoting from his paper, 'In order to explain the vigor and purity of the color reflected in certain crystals it is necessary to suppose that there are a considerable number of thin surfaces disposed at approximate equal intervals. At each angle of incidence there would be a particular wave-length for which the phases of the several reflections are in agreement. The selection of light of a particular wave-length would thus take place upon the same principle as in diffraction spectra, and might reach a high degree of perfection.' Lord Rayleigh[1] describes an interesting acoustical analogue, the sound of a bird call, giving a pure tone of high pitch, being most copiously reflected from a number of equidistant screens made of thin muslin, stretched upon brass rings at a certain distance apart.....

"Stokes observed that many crystals reflected two or even three narrow bands in the visible spectrum, and inferred that, in these cases, there must be several sets of multiple twin planes. It seems curious that he was led to adopt this hypothesis, as the more obvious explanation would be to refer the colors to different orders.

"A thin film, or a number of parallel thin films of equal thickness D, reflects at normal incidence light of wave-lengths given by the equation $2D = 0$, $2D = \lambda$, $2D = 3\lambda$, $2D = 4\lambda$, etc., if we consider no phase-change to occur. If $2D = 0.0006$ mm the film will reflect red light, and ultraviolet light of wave-lengths 0.00030 and 0.000020. If, however, 2D is equal to some wave-length in the infra-red region, say at 0.0012 mm (1.2 μ), it is clear that we shall have more than one reflected color in the visible region, the maxima occurring at wave-lengths 0.0006, 0.0004, 0.0003, 0.00024, etc. Such a film should appear purple, since it reflects red and violet light. If the first-order color is at 2 μ the higher order will fall at 1 μ, 0.66 μ, 0.50 μ, 0.40 μ, etc., and the film will reflect narrow regions in the red, green, and violet."

Looking with the eyes partially closed, toward the flame of a remote candle, a series of images may be seen at both

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[1] Nature, 40, 227 (1889).

sides of the flame.[1] "Similar phenomena may be seen at night by looking through the meshes of the cloth of an umbrella towards street lamps, or by observing the bright image of the sun upon the face of a sundial through the vane of a sparrow's feather. In the latter case a luminous point is seen at the intersection of an oblique cross, whose arms are composed of a series of images tinted with the hues of the rainbow. To produce these phenomena at one side of the source, a portion of the light must have been deflected laterally from its rectilinear path to the eye during its passage through the narrow interstices between the eyelashes, or between the threads of cloth, or finally between the barbules of the feather. Technically it must have been *diffracted*. The simplest, and, therefore, the most satisfactory, diffraction phenomena are obtained by allowing the rays of the sun, deflected by means of a mirror through a small vertical aperture into a dark room, to pass through a narrow slit and be caught upon a screen situated at some distance behind the slit. Covering the opening with a piece of red glass, so that homogeneous red light alone may be admitted, one sees upon the screen, at both sides of the bright luminous streak, which appears in the direction of the incident rays, a series of alternately dark and bright streaks (or rectangles), the latter of which diminish rapidly in intensity towards the sides. The appearance of perfectly dark streaks at places which are illuminated just as strongly as the bright intervening spaces, again furnishes proof that light is a mode of vibration. For only on this assumption is it conceivable that light rays acting in conjunction with light rays (*interfering*) can produce darkness. The undulatory theory gives a thoroughly satisfactory explanation of the phenomenon. If green glass be used instead of red, green rectangles will be obtained in place of the red; but they will be narrower and more closely packed than the red, and with a blue glass the streaks crowd still more closely together. It is clear that, the shorter the wave-length, the smaller the inclination of the diffracted radiation need be to produce the

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[1] Lommel: "Experimental Physics," 589 (1900).

difference of distance required for the respective bands. The dark stripes lying nearer the center of the field of diffraction show again that to the simple colors of the spectrum there correspond wave-lengths diminishing in continuous succession from red to violet.....

"The most beautiful of all diffraction phenomena are produced by gratings. This term is applied to a number of narrow parallel slits produced either by stretching fine wires in a light frame at equal distances apart (wire gratings), or by ruling upon a blackened glass plate a number of fine parallel lines with a graduating engine. Very excellent gratings are also produced by scratching a large number of exceedingly fine lines with a diamond point upon a glass plate (glass grating), or upon a reflecting metallic surface (Rowland's reflecting grating). In reflected light also, gratings and other finely-ruled surfaces exhibit the phenomena arising from the interference of diffracted rays. Mother-of-pearl, for instance, is composed of extraordinarily thin layers of calcium carbonate deposited by the animal itself. These layers being inclined to the surface give rise to a number of extremely fine lines. By engraving fine lines upon metallic surfaces (Burton's iris buttons) a play of colors, resembling that of mother-of-pearl can be produced.

"The colored wreath or garland of light, frequently observed around the disk of the sun and moon when the sky is covered with a filmy veil of clouds is called a corona. Looking at the flame of a candle through a glass plate strewn with lycopodium powder, the flame is seen surrounded by a bright reddish luminosity which is encircled by several rings, tinted with rainbow colors and having their violet edges turned inwards. This phenomenon is due to the diffracting effect produced by the grains of the powder upon the rays of light passing their surfaces. According to Babinet's principle, each of these grains acts as a circular dark screen, and produces the same phenomena of diffraction, viz., colored rings, as would be produced by a circular aperture of the same diameter. If a still finer powder is used, for instance the fine powder of a puff-ball, the rings appear larger, their diameters always being in the inverse ratio to the diameters of the grains of powder. The conditions necessary to the formation of the color rings is that all powder grains shall be of equal size. When small particles of unequal size are mixed together, the variously colored rings overlap and blend into a whitish shimmer. In this same way the halos about the sun and moon are produced by the diffraction of light due to the particles of vapor composing the clouds. The diameters of the particles producing the haze may be determined from the diameters of the rings, the first of which appears under an angle of 1°–4°. It is found that these particles are larger on the average in the winter than in the summer. With approaching rain the little particles swell rapidly and the lunar corona contracts. Lunar coronas are more frequently observed than solar, because the light of the sun is so blinding as to render the feebly illuminated rings beside it invisible. Solar coronas may, however, be seen at once by observing the less brilliant image of the sun upon the surface of water or upon a plate of glass."

Tyndall[1] says that "one of the most interesting cases of diffraction by small particles that ever came before me was that of an artist whose vision was disturbed by vividly colored circles. He was in great dread of losing his sight; assigning as a cause of his increased fear that the circles were becoming larger and the colors more vivid. I ascribed the colors to minute particles in the humors of the eye, and ventured to encourage him by the assurance that the increase of size and vividness on the part of the circles indicated that the diffracting particles were becoming *smaller*, and that they might finally be altogether absorbed. The prediction was verified. It is needless to say one word on the necessity of optical knowledge on the part of the practical oculist."

Interference colors due to mixed plates were discovered by Young, and described in the *Philosophical Transactions* for 1802, and were subsequently studied by Sir David Brewster.

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[1] "Light and Electricity," 91 (1893).

Verdet and other writers on optics have classified them with Newton's thin-film colors, and have given treatments which are not very rigorous, and fail to show where the energy goes to.[1]

"The colors are obtained very easily by pressing a little white of egg between two pieces of plate glass, separating the plates and squeezing them together a number of times so as to form a froth. The plates are to be pressed firmly together with a rotary sliding motion just before the froth becomes sticky, enclosing a film made up of air and albumen in the form of a mosaic. The colors are best seen by holding the plate towards a distant window or other bright source of light on a dark field. Certain wave-lengths will be found to be absent in the directly transmitted light. Young's explanation was that the path-difference between a ray passing through an air-space and one passing through the albumin was an odd number of half wave-lengths for such colors as failed to appear in the transmitted light. Neither Young nor subsequent writers, so far as I have been able to find, show what becomes of these absent colors, though both Young and Brewster observed the colored fringes which appeared against the dark background to one side of the source of light. Brewster published a paper in the *Philosophical Transactions* for 1837 in which he referred the colors to diffraction, though his treatment was not very complete, and concerned chiefly the case of diffraction by a transparent lamina bounded by a straight edge. Verdet objected to this explanation on the ground that the colors are independent of the size and arrangement of the air-bubbles, depending only on the thickness of the albumen-film and the angle of incidence. The interference phenomena of mixed plates are easily explained by the elementary theory of diffraction, and they should be classed with laminary diffraction effects, and not with thin film interferences, as is usually the case.....Mixed plates throw the light absent in the direct image into a halo or ring, which is seen to surround the source of light......

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[1] Wood: "Physical Optics," 252 (1911).

"Laminary diffraction phenomena, which we have just discussed, and mixed plates belong to the same class, the case being best defined as laminary diffraction by a great number of irregularly distributed transparent disks. If the patches of the mosaic were of uniform size, the halo would be sharply defined and separated from the direct image by a dark space, which would become wider as the size of the elements of the mosaic decreased. Though it is easy to obtain very perfect halos in some cases, separated by a dark area of considerable size, the variation in the size of the elements usually causes the halo to take the form of a disk, the center of which is occupied by the direct image.

"If the plates are held close to the eye and a distant lamp-flame viewed through them the flame will, for example, appear purple and the surrounding halo green. If a small sodium flame is employed, parts of the mosaic will show it much blurred, and surrounded by a halo, while other parts, where the retardation is a whole number of half-waves, show it perfectly sharp and distinct. The distribution of the light in the halo depends on the form of the elements of the mosaic. By pressing the plates firmly together and sliding one over the other, the circular air-bubbles can be deformed into ellipses. The light in the ring will be more or less concentrated on opposite sides of the halo. If the ellipses were drawn out indefinitely, we should pass over to the grating, and the points of concentration would become first order spectra, the rest of the halo disappearing.

"A very curious and interesting example of this concentration of light in a halo was observed by the author when copying some diffraction gratings on bichromatized albumin. The original grating was ruled on glass, 14,400 lines to the inch, a spacing so fine that copies were only obtained with considerable difficulty. Some of the films were found to have frilled in the process of washing, the buckling of the film following the grooves of the grating to a certain extent. The albumin surface was seen by the microscope to have frilled into oval patches of varying length, but of fairly constant width, the width being equal to three lines of the original grating. When held before the eye this plate showed a ring of wide aperture surrounding a brilliant source of light with four distinct concentrations, two very bright and two quite faint."

The question of resonance is discussed in some detail by Wood.[1]

"Some remarkable effects were observed by Gouy,[2] and more carefully studied by Wien,[3] of the colored light diffracted into the region of the shadow by thin sheets of copper, gold, silver, etc. Wien focussed sunlight upon the highly polished edges of thin plates of various metals, and observed that light was diffracted far into the region of the shadow, the edge of the plate appearing luminous. The color of the light varied in a remarkable manner with the nature of the metal, appearing red with copper and gold screens, orange with silver, yellow and yellow-green with platinum and tin-foil. The color only appeared when the edge was clean and quite free from dust; it was complementary to the color most strongly absorbed by the metal, and polarized with the vibration perpendicular to the diffracting edge. If the incident light was polarized to start with, the color was only seen when the vibration was perpendicular to the edge. The phenomenon is evidently related in some way to resonance, vibrations being set up in the metal along the edge, which emit energy into the region behind the screen. In addition to the colored light, Wien found that white light was also present, and that it could also be cut off by a Nicol prism, though its plane of polarization appeared to depend upon the azimuth in which the incident light was polarized, and also upon the angle of diffraction.....

"The first experiments on optical resonance were made by Wood.[4] It was observed that films of the alkaline metals, deposited on the inner walls of exhausted glass bulbs, exhibited

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[1] "Physical Optics," 634 (1911).

[2] Comptes rendus, 97, 1573 (1884).

[3] Inaug. diss., Berlin, 1886.

[4] Phil. Mag., April, 1902, October, 1902, August, 1903.

brilliant colors which could not be explained by any of the known laws of interference or diffraction. Examination with the highest powers of the microscope revealed the fact that the deposits were granular, the size of the metal grains being of the order of magnitude of the light-waves. It seemed highly probable that the phenomenon was the optical analogue of the experiment performed by Garbasso with the tin-foil strips, the metal granules having free periods of electrical vibration of the order of the periods occurring in the case of visible radiation.....

"If the metal is heated at one end of a rather long tapering bulb, the color is most intense near the metal and gradually fades away to nothing at the other end of the bulb. If the bulb is placed in strong sunlight with a black background, it is seen that in some places where the deposit is too slight to show much color by transmission, the light is scattered or diffused, and this diffused light is colored. The claret-colored or purple film, where the deposit is slight, scatters a green light, the surface appearing as if fluorescent. Now the spectrum of the transmitted light in these purple films has a heavy absorption-band in the yellow-green, consequently the scattered light is the complementary color of the transmitted. If the film is greenish blue, the scattered light is reddish. The microscope shows that in these deposits, which have the power of scattering light, the individual particles are rather widely separated; that is, the distance between them is large in comparison to their diameters. The appearance of a bulb in strong light is very much as if certain portions of its interior surface had been painted over with a solution of fluorescein. No trace of regular reflection is shown by these films, except of course, the reflection due to the glass. The particles are so far apart that they apparently act as independent sources, the interference necessary for rectilinear propagation not being, present. If the incident light is polarized, the fluorescent light (as we may call it for convenience) is also polarized, which is not the case for ordinary diffuse reflection. On the resonance theory, we may regard this fluorescent light as the energy radiated from the resonators, as a result of their forced vibrations. Passing now to a part of the film where the color of the transmitted light is deeper, we find that there is no longer any trace of this fluorescent light. The color absent in the transmitted light is now regularly reflected, the particles being so close together that interference, as imagined by Huygens, takes place.

"It appears as if the case was very similar to the hypothetical one considered by Planck in his paper on absorption, which has been already alluded to. It will be remembered that Planck considers the energy stopped by his resonators as re-emitted by them either as diffused light or regularly reflected light, the diffusion and reflection being, of course, selective. This seems to be precisely what occurs in the present instance, the particles diffusing or reflecting regularly according to their proximity. On portions of the bulb close to the heated spot, the metal is deposited in granules too large to show resonance colors, a silky lustre being exhibited by reflected light. This is obviously the ordinary diffusion or diffraction produced by small particles.

"It has been shown by Aschkinass and Schaefer that the length of electro-magnetic waves to which a system of resonators respond is increased by immersing the resonator system in a medium of high dielectric constant. The same phenomenon occurs in the case of the sodium and potassium films. The bulbs usually contain traces of hydrocarbon vapor, which can be condensed upon the inner wall by touching a spot on the outside with a piece of ice. It is a good plan to moisten the bit of metal with a little ligroin before its introduction into the bulb. The color changes are most remarkable. Pink and purple films become blue, while pale apple-green films change to a deep blue-violet, as deep as dense cobalt glass. Blue films often became perfectly transparent, the absorption-band originally in the red, moving out of the visible spectrum entirely. Spectroscopic examination showed that the immersion of the resonators in the liquid dielectric caused the absorption-band to move towards the region of longer wave-lengths, as it should do according to theory.....

"To ascertain whether the color effects were common to all metals in a state of fine subdivision, experiments were made with gold obtained by electrical discharges in high vacua from a gold cathode. The color of the gold deposit varies with the conditions under which the deposition takes place. Gold cathodes of two forms were employed, a flat plate about 3 cm square, and a thick wire, screening off the radiation from all but the tip with a mica screen. The most interesting deposits were obtained from the small source. In one instance the film showed a brilliant green surface color resembling fuchsine, the transmitted light having a purple tint. Owing to the transparency of the film a good deal of white light is mixed with the selectively reflected light; this can be cut off with a Nicol, if the reflection takes place at the polarizing angle for glass, and the colored light from the film, which is unpolarized, then appears in great purity. One plate showed patches of brilliant carmine red, deep blue, and green, of a surprising intensity and saturation. The color of the selectively reflected light depended somewhat on the angle of incidence, a phenomenon observed also in the case of the sodium and potassium films. Increasing the angle of incidence changed the color from green to blue; the period of vibration of the resonator system appears, therefore, to be less when the angle of incidence is large.

"If the glass plate is placed near the tip of the gold wire, the green deposit, similar to gold leaf in its optical properties, is deposited at the center. The color of the green film is probably due to the same causes which operate in the case of gold leaf, *i. e.*, to molecular resonance. These films are not granular, the metal vapor not condensing into drops before reaching the glass. Surrounding this is a film appearing light yellow by transmitted light, and bluish by reflected light. This seems to be what we should expect, for the smallest particles, which will resonate for blue light, will be deposited when the distance from the cathode is a little greater than that at which the molecular deposit occurs. Increasing the distance, we get larger particles, and the point of maximum resonance moves up into the green, giving us a purple film with green surface color. At a still greater distance we get particles large enough to resonate for red, and the film appears deep blue by transmitted light. All of these variously colored films can be changed into the green structureless film by heating. We may regard the change as due to the fusing together of the resonators.....

"Allusion has been made to the deep violet light scattered by a condensing cloud of sodium vapor. The author has frequently observed that the color of the light transmitted through the sodium tubes, in the experiments upon the optical properties of the vapor, was colored a deep yellow instead of blue, as is usually the case. It was difficult to understand this at first, since the vapor is perfectly transparent to blue light, and somewhat less so to yellow-green light. The cause was finally found to be a scattering of the violet and blue rays by the fog of condensing vapor, which was so powerful that none of these rays was transmitted. The phenomenon was investigated further with the large tube used in the experiments on fluorescence, some potassium being introduced into the retort. The light from the arc was focussed about 20 cm in front of the retort and the tube powerfully and rapidly heated by a blast lamp. Under this condition the vapor is puffed out in clouds from the aperture of the retort, and the condensing clouds are most wonderfully colored, red and orange predominating. It was found that if the heating was carefully regulated, a steady state could be maintained in which the fog scattered red light at the outer boundary, where the cone of rays entered it, yellow a little farther in, and green at the point where it was first forming and where the cone of rays passed out into the vapor in which it was, of course, invisible. The cone of rays seen from the side, which can be accomplished by looking in at the edge of the glass widow, resemble a spectrum, the blue end of which was wanting. A potassium fog thus scatters longer waves than a sodium fog, and the scattering power is confined to a comparatively narrow region of the spectrum, which apparently varies with the size of the particles in the fog. It is probable that we are dealing with something analogous to the phenomenon exhibited by the granular deposits of these metals already described. Further investigations along these lines should be made, especially with polarized light. A large brass tube without a retort, or even a glass tube, could be used.

"An exhaustive study has been made by Kirchner[1] of the colors exhibited in transmitted light by Lippmann plates. These plates, after development, appear reddish brown, green, or blue, according to the developer used. The color phenomena have nothing to do with the presence of silver laminae, which are chiefly responsible for the colors seen in reflected light in Lippmann's color photographs, for they are equally pronounced in the case of plates immersed in benzene during their exposure to light. Standing waves and the formation of the laminae are, of course, out of the qestion in such a case.

"Kirchner came to the conclusion that the color was due to the resonance of the minute silver aggregates reduced in the film by the action of the developer. In ordinary photographic plates these are too large to serve as resonators for visible radiations, and the plates appear black in consequence, the light being stopped by the opaque masses. The position of the absorption-band was found by Kirchner to shift when the dry films were moistened, the band moving towards the blue. This is in accordance with theory, for the refractive index of wet gelatine is much less than that of dry. The dispersion of the colored films was also investigated and found to be anomalous. The refractive indices for the various wavelengths are given in the table.

DISPERSION OF REDDISH BROWN SILVER FILM

λ	500	525	550	560	570	575	589	600
n	1.542	1.557	1.567	1.585	1.595	1.601	1.555	1.535

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[1] Drude's Ann., 13, 239 (1904).

"The absorption-band begins in the red and extends to the blue, increasing in intensity. There is a decrease in the values of n, as the observations are pushed into the band, which is in accordance with theory, and the maximum value of n is found on the red side of the band, though, perhaps, farther within the band than is usually the case with absorbing media. These results are interesting, as confirming those obtained by Wood with granular deposits of the alkali metals and allotropic silver. Kirchner's work was practically completed when the paper above referred to was published, his results having been obtained independently.

"The subject of optical resonance has also been studied extensively by Kossonogoff, whose paper appeared in the *Physikalische Zeitschrift* for 1903. Resonating films were prepared by blowing a spray from an atomizer charged with a solution of the metal salt upon a strongly heated glass plate. He also obtained evidences of resonance in granular deposits of non-metallic substances, and made a careful study of the colors of the wings of butterflies, which he regards as due to similar causes. Bock, in the same journal, has published results which are claimed to show that minute waterdrops also exhibit the phenomenon."

If the medium in which light moves is completely homogeneous, it is possible, by taking sufficiently thin films, to see other objects through it with completely unchanged sharpness though with lessened brightness.[1] "We speak of a turbid medium when particles having different optical properties are scattered through the homogeneous mass. Milk, blood, porcelain, and misty air come under this head. The particles give rise to an internal diffuse reflection. When looking through these turbid media, one gets vague images of objects on the other side. Such are called translucent."

Von Bezold[2] says: "It is a well-known fact that mixtures of two colorless substances which are not miscible in all proportions and which are, therefore, turbid, appear yellowish

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[1] Winkelmann: "Handbuch der Physik," 2, I, 18 (1894).

[2] "Die Farbenlehre," 88 (1874).

red by transmitted light and blue by reflected light. One can see this well if one dilutes milk with water or, better still, if one pours an alcoholic solution of rosin into water. Similar phenomena can be observed with solids, for instance with the so-called opalescent glass through which a gas flame appears deep red, or with the fiery opal which has given the name to the whole group of phenomena which we call opalescence. The painter encounters the colors of turbid media occasionally, though not often—notably when he glazes opaque colors with white. A thin film of white over a dark ground often shows a trace of blue."

Wood[1] has discussed the general question of the behavior of a dispersed phase consisting of very fine particles. "If a beam of light is passed through a transparent medium containing in suspension small particles, the refractive index of which differs from that of the surrounding medium, light will be given off by the particles in all directions. If the particles are very small, the color of the scattered light is blue, and it is more or less completely plane-polarized, the direction of vibration being perpendicular to the direction of the incident beam. If the incident beam is plane-polarized to start with, no light is scattered by the cloud of particles in directions parallel to that of the incident vibration. In the case of particles of the order of magnitude of the light-waves, the amount of light scattered increases as the wave-length is decreased, which explains the preponderance of blue always observed in these cases. The subject was investigated experimentally by Tyndall with clouds precipitated by the chemical action of light upon the vapor of iodide of allyl. Whenever the particles obtained were sufficiently small, the laterally emitted light was blue in color and polarized in a direction perpendicular to the incident beam. Tyndall was unable to explain the polarization, and imagined that it contradicted Brewster's law, there being no angle of maximum polarization, as in the case of reflection from flat surfaces of isotropic media. That there is no contradiction here is at once apparent

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[1] "Physical Optics," 624 (1911).

when we consider that the nature of the phenomenon is radically different in the two cases. In ordinary reflections we are dealing with surfaces large in comparison with the wave-length, and the amount of reflected light is independent, or nearly so, of the wave-length. While, in the case which we are considering, regular reflection in the ordinary sense does not occur, and the intensity of the light is a function of the wave-length. By making the particles sufficiently small we may obtain a violet of great intensity and purity. The fog formed by the condensation of sodium vapor has been observed by the author to give a deeper color than any other media heretofore employed. The experiment, however, is rather difficult to perform, and a description of it would be out of place here. The blue color is easily seen in tobacco smoke rising from the end of a lighted cigar. On standing, the smoke particles appear to collect into larger aggregates and blue color disappears. This is usually the case with smoke exhaled from the mouth. The blue color of the sky has its origin in a similar action exerted either by small dust particles or even by the molecules of air themselves. The absence of long waves in the light coming from the blue sky on a clear day is well shown in a photograph made by the author with a screen or ray filter made by combining a sheet of very dense cobalt glass with a deep orange aniline dye. This screen absorbed all rays below wave-length 6900. The spectrum of the sun or arc photographed through this screen on a Cramer or Wratten and Wainwright spectrum plate is reduced to a band extending from $\lambda = 6900$ to $\lambda = 7400$. The rays within this region are visible to the eye, if all other rays are excluded, but they play little or no part in ordinary vision, on account of their very feeble action upon the retina of the eye. Landscapes photographed through the screen present a remarkable appearance. The grass and trees in full sunlight appear as if snow-white, while the sky is as black as midnight. This is due to the fact that the chlorophyll of the vegetation reflects the infra-red light very powerfully, while the light of the blue sky is nearly or wholly wanting in it. The shadows in all of the infra-red photographs are very black, since practically no light comes from the sky, and it is the sky light which is chiefly responsible for the illumination of the shadows. The scattering of light has been exhaustively studied by Lord Rayleigh, who explains the phenomenon in the following way: Conceive a beam of plane-polarized light to move among a number of particles all small compared with any of the wavelengths. The foreign matter may be supposed to load the ether so as to increase its inertia without altering its resistance to distortion, If the particles were away, the waves would pass on unbroken, and no light would be emitted laterally. Even with the particles retarding the motion of the ether the same will be true if, to counterbalance the increased inertia, suitable forces are caused to act on the ether at all points where inertia is altered. These forces have the same period and directions as the undisturbed luminous vibrations themselves. The light actually emitted laterally is thus the same as would be caused by forces exactly the opposite of those acting on the medium otherwise free from disturbance, and it remains only to see what the effect of such forces would be. In the first place there is necessarily a complete symmetry around the direction of the force; the disturbance consisting of transverse vibrations is propagated outwards in all directions from the centre; and in consequence of the symmetry the direction of vibration in any ray lies in the plane containing the ray and the axis of symmetry; that is to say, the direction of vibration in the scattered or refracted ray makes with the direction in the incident or primary ray the least possible angle. The symmetry also requires that the intensity of the scattered light should vanish for the ray which would be propagated along the axis. For there is nothing to distinguish one direction transverse to the ray from another. Suppose for distinctness of statement that the primary ray is vertical, and that the plane of vibration is that of the meridian. The intensity of the light scattered by a small particle is constant, and a maximum for rays which lie in the vertical plane running east and west, while there is no scattered ray along the north and south line. If the primary ray is unpolarized, the light scattered north and south is entirely due to that component which vibrates east and west, and, is therefore, perfectly polarized, and the vibration is performed in the horizontal plane. In other directions the polarization becomes less and less complete as we approach the vertical."

"What actually occurs as a physical process, that is the exact manner in which the particles load the ether, is not definitely stated. We shall have no difficulty in remembering that the direction of vibration of the light scattered when the incident beam is plane-polarized, if we imagine the obstacle actually set in vibration. Transverse waves would then not be given off in the direction in which the vibration takes place, *i. e.*, in the direction parallel to the vibration of the incident light. But it is inconceivable that particles as small as the molecules are actually thrown into vibrations as rapid as those of light. We may imagine if we like that the contained electrons are set into vibration as a whole, *i. e.*, that the centre of gravity of the system is periodically displaced by the electric forces in the light-waves. This would be equivalent to "loading the ether" and though it may not be a correct conception, serves, perhaps, as something tangible to fix the mind on. This conception neglects everything analogous to dispersion, the free periods of the electrons not being considered and forces of restitution being neglected. We are merely concerned with the inertia of the system as a whole which we conceive as having no free period of vibration.

"The intensity of the scattered light as a function of the wave-length, for obstacles of fixed size, small in comparison to λ, was calculated by Lord Rayleigh.[1] Let i be the ratio of the amplitude of the incident to that of the scattered light, and T the volume of the disturbing particle. If r is the distance from the particle of a given point, the value of i at this point is shown to be proportional to $T/\lambda^2 r$, that is the amplitude varies inversely as the square, and the intensity inversely as the fourth power of the wave-length.

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[1] Phil. Mag., 47, 107, 274 (1871).

"Observations were made of the distribution of energy in the spectrum of the light of the blue sky by comparing its spectrum with the spectrum of direct sunlight, diffused by white paper. These values were compared with values calculated on the assumption that the intensity of the scattered light (*i. e.*, blue-sky light) varied as $1/\lambda^4$. The two sets of values are given in the following table for four of the Fraunhofer lines:

	C	D	b_4	F	
	25	40	63	80	calculated
	25	41	71	91	observed

Lord Rayleigh's formula for the intensity of the scattered light in a direction making an angle β with the incident rays is, if the incident light is unpolarized,

$$\frac{A^2(D' - D)^2}{D^2}(1 + \cos^2\beta)\frac{m \pi T^2}{\lambda^4 r^2},$$

in which A^2 is the intensity of the incident light, D′ and D the densities of the particles and the medium in which they are immersed, *m* the number of particles, and λ the wave-length. The formula shows that the intensity is twice as great in the direction from which the light comes as in the direction perpendicular to it.

"Tyndall found that as the particles in his precipitated clouds increased in size, the blue color disappeared, the scattered light appearing white. If, however, it was received through a Nicol prism held in the position in which it would ordinarily extinguish the scattered light, the blue color appeared again in increased splendor. This blue color he named the 'residual blue.' Lord Rayleigh[1] considers this phenomenon in a subsequent paper, and shows that if the incident light is polarized with its vibration parallel to the *z* axis, the intensity of the light scattered along the *z* axis varies as the 8th power of the wave-length, so that the residual blue is purer than the

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[1] Phil. Mag., (5) 12, 81 (1881); Proc. Roy. Inst., 16, 119 (1899).

blue seen under ordinary conditions. With smaller particles no light at all would be seen in this direction under the conditions specified. It remains to be seen whether in this case there is any direction in which the scattered light vanishes. Lord Rayleigh derived an equation which showed that zero illumination was to be expected in a direction inclined backwards, *i. e.*, towards the source of light, and this was found to be the case. The experiments were made with a precipitate of sulphur, obtained by adding a small quantity of dilute sulphuric acid to a weak solution of hyposulphite of soda. The more dilute the solution, the slower is the process of precipitation, and the slower the change in the size of the particles. Solutions of such strength that no precipitate appears for four or five minutes will be found to give the best results, and the process can be arrested at any stage by the addition of a few drops of ammonia. The experiment should be performed in a dark room, a beam of sunlight rendered convergent by means of a long-focus lens being passed through a glass tank containing the solution. The scattered light should be examined by a Nicol prism. Quoting from the paper above referred to: In the early stages of the precipitation, polarization is complete in a perpendicular direction and incomplete in other directions. After an interval the polarization begins to be incomplete in a perpendicular direction, the light which reaches the eye when the Nicol is in the position of minimum transmission being of a beautiful blue, much richer than anything that can be seen in the earlier stages. This is the moment to examine whether there is a more complete polarization in a direction somewhat more oblique, and it is found that with θ positive (*i. e.*, towards the source) there is in fact an oblique direction of more complete polarization, while with θ negative the polarization is less perfect than in the perpendicular direction itself.....

"In one of his more recent papers Lord Rayleigh has shown that the blue light of the sky can be regarded as caused by the scattering power of the air molecules themselves, in the absence of any suspended particles."

The refraction and diffraction of light by drops of water in the atmosphere give rise to a variety of optical phenomena, of which perhaps the most familiar example is the rainbow.[1] "Snell's law of refraction is one of the corner-stones of optical science, and its applications today are million-fold. Immediately after its discovery Descartes applied it to the explanation of the rainbow. A beam of solar light falling obliquely upon a rain-drop is refracted on entering the drop. It is part reflected at the back of the drop, and on emerging it is again refracted. By these two refractions, at its entrance and emergence, the beam of light is decomposed, quitting the drop resolved into colored constituents. The light thus reaches the eye of an observer facing the drop, and with his back to the sun. Conceive a line drawn from the sun to the observer's eye and prolonged beyond the observer. Conceive another line drawn through the eye, enclosing an angle of 42.5° with the line drawn from the sun, and prolonged to the falling shower. Along this second line a rain-drop at its remote end, when struck by a sunbeam, will send a ray of red light. Every other drop similarly situated, that is, every drop at an angular distance of 42.5° from the line aforesaid will do the same. A circular band of red light is thus formed, which may be regarded as the boundary of the base of a cone, having the rays which form the band for its surface, and its apex at the observer's eye. Because of the magnitude of the sun, the angular width of this red band will be half a degree. From the eye of the observer conceive another line to be drawn, enclosing an angle, not of 42.5° but of 40.5°, with the prolongation of the line drawn to the sun. Along this line a solar beam striking a rain-drop will send violet light to the eye. All drops at the same angular distance will do the same, and we shall, therefore, obtain a band of violet light of the same width as the red band. These two bands constitute the limiting colors of the rainbow, and between them lie the bands corresponding to the other colors.

"Thus the line drawn from the eye to the *middle* of the

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[1] Tyndall: "Six Lectures on Light," 24 (1883).

bow, and the line drawn through the eye to the sun, always enclose an angle of about 41°; to account for this was the great difficulty, which remained unsolved up to the time of Descartes. Taking a pen in hand, and calculating by means of Snell's law the track of every ray through a rain-drop, Descartes found that, at one particular angle, the rays, reflected at its back, emerged from the drop, *almost parallel to each other.* They were thus enabled to preserve their intensity through long atmospheric distances. At all other angles the rays quitted the drop divergent, and through this divergence became so enfeebled as to be practically lost to the eye. The angle of parallelism here referred to was that of forty-one degrees, which observation had proved to be invariably associated with the rainbow.

"From what has been said, it is clear that two observers standing beside each other, or one above the other, nay, that even the two eyes of the same observer, do not see exactly the same bow. The position of the base of the cone changes with that of its apex. And here we have no difficulty in answering a question often asked—namely, whether a rainbow is ever seen reflected in water. Seeing two bows, the one in the heavens, the other in the water, you might be disposed to infer that the one bears the same relation to the other that a tree upon the water's edge bears to its reflected image. The rays, however, which reach an observer's eye after reflection, and which form a bow, would, were their course uninterrupted, converge to a point vertically under the observer and as far below the level of the water as his eye is above it. But under no circumstances could an eye above the water-level, and one below it see the same bow—in other words, the self-same drops of rain cannot form the reflected bow and the bow seen directly in the heavens. The reflected bow, therefore, is not in the usual optical sense of the term, the *image* of the bow seen in the sky."

The sunset colors are due to suspended particles and so are the coronas and halos; but I have discussed these in a previous paper.[1] The metallic colors seen on films of oil are the colors of thin films. They are especially striking in Washington because the black asphalt pavements do not reflect back any appreciable amount of light and consequently do not interfere with the reflections from the two liquid surfaces. The heat colors on steel are due to thin films and may be used as approximate temperature measurements, though the thickness and, consequently, the color of the film vary both with the temperature and the time of heating. One can also produce thin films by precipitating lead peroxide electrolytically on a polished anode and the colors thus obtained are called Nobili's rings. While the colors of mother-of-pearl might be discussed now, I prefer to consider these under lustre. The colors of water have been discussed in a separate article.[2]

Cornell University

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[1] Bancroft: Jour. Phys. Chem., **22**, 385 (1918).

[2] Bancroft: Jour. Franklin Inst., **187**, 249 (1919).

BLUE COPPER OXIDE

BY H. E. SCHENCK

Tommasi[1] showed many years ago that traces of a manganese salt stabilized the blue, hydrous copper oxide to such an extent that the latter could be boiled with water without turning black. Blucher and Farnau[2] showed that the same stabilization could be obtained with salts of nickel, cobalt, chromium, aluminum, mercury, magnesium, zinc, and manganese. Scheetz[3] showed that by increasing the ratio of alumina to ferric hydroxide, it was possible to get a precipitate which would stay yellow at temperatures at which it seemed impossible that any hydrous ferric oxide could exist, thus confirming the conclusion drawn by Keane[4] that sufficiently finely divided ferric oxide may be yellow. It was suggested by Professor Bancroft that some experiments be made with copper and aluminum sulphates, and this work was done as part of my senior research in the winter of 1916–1917.

A mixture of copper and aluminum sulphates was made up such that $CuO : CuO + Al_2O_3 = 5 : 100$ approximately. This mixture was dissolved in water and the hydrous oxides precipitated by a slight excess of NaOH. The precipitate was washed thoroughly on a filter and dried in an air-bath at 110°. The color of the dried precipitate was a baby blue. The precipitate was ground to a fine powder and heated in a porcelain crucible, first with a Bunsen burner and then with a blast lamp. The color changed to a light grayish blue. The blue tint was quite distinct and there were no signs of blackening.

Another mixture was made up containing about 10% CuO instead of 5% and was treated as before. This mixture remained blue when heated in the Bunsen burner; but showed

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[1] Bull. Soc. chim. Paris, (2) **37**, 197 (1882); Comptes rendus, **99**, 37 (1884).

[2] Jour. Phys. Chem., **18**, 629 (1914).

[3] Ibid., **21**, 570 (1917).

[4] Ibid., **20**, 734 (1916).

signs of turning black when heated in the blast lamp. It is, therefore, clear that a mixture of copper and aluminum oxides blacken at lower temperatures, the higher the percentage of copper oxide in the precipitate. Since the blue color persists in some precipitates when heated in the blast lamp, it cannot be due to hydrous copper oxide, and this was confirmed by analyses which will be taken up later.

The blue color cannot be due to a copper aluminate coexisting with alumina as a second phase because the color should then appear at the same temperature in all cases. It cannot be due to a copper aluminate dissolved in alumina because the blue color would then return if the precipitate were heated until it blackened and were then held at a somewhat lower temperature until the dissociated copper oxide and alumina recombined. It is only fair to say that this possibility was not thought of at the time and that the experiments do not exclude the possibility of a black precipitate turning blue again if heated sufficiently long at a suitable temperature. This should be tested carefully. One reason why this was not tried is that a blue precipitate is obtained in aqueous solutions where no alumina is present and it seemed probable that the change from blue to black was due to the same cause in all cases, the alumina merely retarding the change. If this is so and it seems to be, copper oxide itself must be blue when sufficiently finely divided. The change from blue, hydrous copper oxide to black oxide is then merely an agglomeration, the water acting as a rather inefficient stabilizer of the fine material. The alumina is more efficient and may keep the copper oxide finely divided at relatively high temperatures. This is the more probable because, at low temperatures, so many gelatinous oxides stabilize the blue precipitate more or less.

Since one is dealing with stabilization, it was possible to assume that the alumina stabilized the CuO_2H_2, in case such a compound existed, and that the water had not all been driven off even after continued heating in the blast lamp. To disprove this assumption the grayish blue precipitate was analyzed after having been heated in the blast lamp to constant weight. The weighings were made in air-tight weighing bottles to prevent adsorption of moisture. After the fine, dry precipitate had been weighed, it was transferred to a beaker and dissolved in boiling nitric acid. The ignited alumina is very hard to dissolve and complete solution was obtained only after continued boiling down with aqua regia and with nitric acid. The copper was determined electrolytically. The dissolved alumina was precipitated with ammonium hydroxide, filtered, ignited, and weighed. The results of the analysis show the copper was present as oxide and not as hydroxide.

Wt. of sample taken	0.7296 g
Wt. of copper found	0.0288 g.
Wt. of Al_2O_3 found	0.6900 g
CuO	4.94%
Al_2O_3	94.56%
Total oxides	99.50%

In making this analysis care must be taken to prevent adsorption of moisture during weighing. Heating to constant weight takes time, for the water is given off very slowly and it is necessary to heat for several hours.

Some preliminary runs were also made with other oxides and the following colors were obtained:

Mixture	Color before heating	Color after heating
5% CuO	Blue	Grayish blue
5% MnO	Pink	Brown
5% Fe_2O_3	Light yellow	Darker and brown
5% Cr_2O_3	Bluish green	Green
5% CoO	White, blue tinge	Deep blue
5% NiO	Green	Yellow

The general conclusion to be drawn from this investigation is that sufficiently finely divided copper oxide is blue and that the change of hydrous copper oxide from blue to black is due to an agglomeration of the particles. It is very desirable that some independent confirmation of this should be obtained.

Cornell University

NEW BOOKS

Methods of Measuring Temperature. *By Ezer Griffiths. 22 × 17 cm; pp. xi + 174. Philadelphia: J. B. Lippincott Company, 1918. Price: $2.75.*—In the preface the author says: "The present volume is written for those concerned with the measurement of temperature, whether in scientific investigations or in the control of industrial operations. Attention has been devoted chiefly to the experimental basis of the methods in general use, the calibration of the instruments, and the precautions which must be observed in practice. While the volume is complete in itself, it is assumed that the reader is conversant with the fundamental principles of physics, and the aim has been to extend the general treatment given in standard text-books, such as those of Poynting and Thompson. It was not deemed desirable to devote much space to descriptions of the constructional details of pyrometers, since the information is readily accessible in the catalogues of the manufacturers. A connected account is given of the classical researches with the gas thermometer, which have established in a concrete form, the absolute scale of temperature over the range —200° C to 1550° C. It is well to remember that although the electrical and radiation methods enable 'relative' measurements to be made with a high degree of precision, they are dependent on the gas thermometer work for their evaluation in terms of the fundamental scale of temperature."

In an introduction, Principal Griffiths says: "A perusal of Dr. Griffiths' book has made me realize how rapid our progress has been in recent times in this essential and hitherto somewhat neglected branch of physical measurement. Accurate measurement of temperature is the basis of nearly all accurate measurements in physics and it is sad to reflect on the amount of valuable work which has had to be scrapped owing to lack of attention to this important matter. That unreliable instrument, the mercury thermometer has been used in the past with little knowledge of its imperfections. We can judge best of the advances that have been made by recalling the conditions under which an observer had to work some thirty years ago. About 1888 I had the privilege of being called into consultation by Messrs. Heycock and Neville, who were engaged in an enquiry into the freezing-point of various metals as a basis for their investigations into the nature of certain alloys. We made a careful study of what we then regarded as the standard determinations of temperatures above the boiling point of water. The discrepancies between the various observers were most startling. For example, the freezing-point of zinc ranged from 342° to 450°; that of antimony varied by 100°; and at higher temperatures the data were unreliable. We ultimately decided for the purposes of standardization to accept the following as authentic:

Boiling Points at 760 mm

Aniline	184.41° by Ramsay
Naphthalene	218.06° by Crafts
Benzophenone	306.08° by Crafts
Mercury	358.2° by Ramsay
Sulphur	448.38° by Regnault

We were fortunate in our selection, for, with the exception of sulphur, later determinations have led to but small modifications of the above numbers." The true boiling point of sulphur is now taken as 444.53°.

The subject is treated under the headings: the fundamental scale of temperature; the mercurial thermometer; the resistance thermometer; the thermo-couple; the "fourth-power" law of radiation and total radiation pyrometers; total radiation from oxide and metallic surfaces; the distribution of energy in the spectrum of a "full" radiator and the principles of optical pyrometry; distribution of energy in the heat emission spectrum of the metals; high temperature melting-points and boiling-points; appendix.

On p. 14 the author says: "Since the thermodynamic scale of temperature is the ultimate standard of reference, it is desirable to choose as gas to be employed in the thermometer that one which approaches nearest the 'ideal gas.' In practice it has not always been possible to do this. Hydrogen, which has a very small correction to bring its scale up to the thermodynamic scale, has been found to be entirely satisfactory up to temperatures of about 400° C. At higher temperatures the ready diffusivity of hydrogen through platinum and its alloys has necessitated recourse being made to nitrogen, which has been employed up to 1600° C. The discovery of the monatomic gases, helium, argon, and neon, with no chemical affinity, has placed at the disposal of gas thermometer workers elements which approach the 'ideal gas' nearer than hydrogen or nitrogen. Helium also possesses the very valuable characteristic of an extremely low liquefaction point, and is now coming into general use for work at low temperatures. At higher temperatures it diffuses readily through quartz and glass; consequently argon will probably be employed for this part of the range in future."

The Siemens pyrometer was the early form of resistance thermometer, p. 30. It consisted of a platinum wire wound on a pipe-clay cylinder and enclosed in a tube of wrought iron. The readings varied because the reducing atmosphere produced by the highly heated iron casing caused the platinum to combine with a trace of the reduced silicon taken from the pipe-clay cylinder. Siemens showed that a sheath of platinum eliminated this trouble. If a resistance thermometer is standardized at 0°, 100° and 444.5° C, the parabolic formula will give temperatures up to 1080° C, identical within the limits of experimental error to which the gas thermometer scale is known.

The thermoelectric method of measuring temperature has attained a degree of precision second only to the resistance thermometer, and for temperatures exceeding 1100° C it is the only convenient and sensitive electrical method available. It must be emphasized, however, that the thermoelement is only a subsidiary element whose scale will not stand extrapolation over extended temperature ranges, which practice has led to much confusion in high temperature work in the past. For most scientific work at high temperatures and a great many industrial installations, platinum and its alloys with rhodium and iridium are used. Such couples are non-oxidizable and withstand temperatures up to 1600° C. Care must be taken, however, to shield them from reducing gases, carbonaceous matter, and metallic vapors. Carbon alone does not appear to contaminate platinum-alloy thermoelements: its presence must be avoided when with other materials which yield contaminating products on reduction. The platinum-iridium alloy is satisfactory up to about 1000° C; but iridium volatilizes at higher temperatures and prolonged exposure to such temperatures causes contamination of the pure platinum half of the couple. The alloy containing 10% rhodium is more permanent at higher temperatures because rhodium is much less volatile than iridium under the same conditions.

For very high temperatures some form of radiation pyrometer must be used. Since the ideal radiation pyrometer would give galvanometer deflections proportional to the intensity of the radiation emitted by the hot object, and hence the difference in the fourth powers of the absolute temperatures, a calibration at one temperature would be sufficient to supply all the data necessary for the computation of the temperature scale. When T is large compared with T_0, the deflections should be proportional to T^4($T_0{}^4$ being negligible). It is generally found, however, that the exponent is not 4, but varies between 3.8 and 4.2 for various instruments. The total radiation pyrometer is of very limited use with molten metal surfaces. Such surfaces can never be freed from haze or fog, and the radiation from the walls of the furnace or crucible reflected at the molten surface is apt to produce serious errors. Burgess found that the apparent freezing point of copper (clear surface) was 600° C instead of 1083° C. At 1075° C the emissivity of cuprous oxide was over 0.54 while the emissivity of molten copper was 0.16.

While theoretically the total radiation type of pyrometer has the advantage of being based on principles whose validity has received ample confirmation, the optical type of pyrometer possesses considerable practical advantages in so much that it does not demand an object of large dimensions to sight upon. Also the influence of imperfect "black body" conditions are not so serious as in the case of the total radiation types. The two common forms of optical pyrometers are the "disappearing filament" type of which the original form was invented by Morse, and the "polarizing" type, first developed by Wanner. The filament type is essentially a telescope and consequently it is easy to select out the object whose temperature is desired. The polarizing type does not permit of a sharply defined image; in fact, the field should be a uniformaly illuminated semi-circular patch. A blurred image of the hot object is, however, distinguishable by moving the eye about a little. With the polarizing type, it is necessary, when taking the temperature of a metallic surface to sight normally, since the light given out at oblique incidence is largely polarized. The polarizing type has the advantage that extrapolation of the scale on the basis of Wien's or any other radiation law is effected easily as the instrument is essentially a photometer; also that the temperature scale is independent of the permanency of the electric lamp which is set from time to time against an amyl acetate lamp. Since a one percent variation in the current through the lamp causes a nine percent variation in the emitted light, the current requires accurate adjustment. *Wilder D. Bancroft*

THE COLORS OF COLLOIDS. V

BY WILDER D. BANCROFT

Metallic and Vitreous Lustre

It has been stated already that whenever light in one medium falls upon the surface separating it from another medium some of the light is reflected within the first, while the remainder passes out into the second medium, except when the first is of lower refractivity than the second and the light falls at an angle greater than that of total reflection. Similarly, when light impinges upon a cut stone, some of it is reflected and the remainder passes into the stone. What is the relative amount of reflected light depends upon the nature of the stone—its refractivity and hardness—and determines its lustre; the greater the amount the more lustrous will the stone appear.[1] "There are different kinds of lustre, and the intensity of each depends on the polish of the surface. From a dull, *i. e.*, an uneven surface the reflected light is scattered, and there are no brilliant reflections. All gem-stones take a good polish, and therefore have considerable brilliancy, so long as the surface retains its polish; turquoise, on account of its softness, is always comparatively dull.

"The different kinds of luster are:

"(1) Adamantine, characteristic of diamond.

"(2) Vitreous, as seen on the surface of fractured glass.

"(3) Resinous, as shown by resins.

"Zircon and demantoid, the green garnet called by jewelers 'olivine,' alone among gem-stones have a lustre approaching that of diamond. The remainder all have a vitreous lustre, though varying in degree, the harder and the more refractive species being on the whole the more lustrous.

"Some stones—for instance, a cinnamon garnet—appear to have a certain greasiness in the lustre, which is caused by stray reflections from inclusions or other breaks in the homogeneity of the interior. A pearly lustre, which arises from

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[1] G. E. H. Smith: "Gem Stones," 37, 38, 20, 54, 295, 291 (1913).

cleavage cracks and is typically displayed by the cleavage face of the topaz, would be seen in a cut stone only when flawed. Certain corundums when viewed in the direction of the crystallographic axis display six narrow lines of light radiating at angles of 60° from a center in a manner suggestive of the conventional representations of stars. Such stones are consequently known as asterias, or more usually star-stones—star-rubies or star-sapphires, as the case may be, and the phenomenon is called asterism. These stones have not a homogeneous structure, but contain tube-like cavities regularly arranged at angles to the crystallographical axis."

"Chatoyancy is a somewhat similar phenomenon, but in this case the fibers or cavities are parallel to a single direction, and a single broadish band is displayed at right angles to it. Cat's eyes as these stones are termed are cut *en cabochon* parallel to the fibers. The true cat's eye is a variety of chrysoberyl, but the term is also often applied to quartz showing a similar appearance. The latter is really a fibrous mineral, such as asbestos, which has become converted into silica. The beautiful tiger's eye from South Africa is a silicified crocidolite, the original blue color of which has been altered by oxidation to golden brown. Recently tourmalines have been discovered which are sufficiently fibrous in structure to display an effective chatoyancy.

"The milky sheen of moonstone owes its effect to reflections from twin lamellae. The wonderful iridescence which is the glory of the opal, and is therefore termed opalescence, arises from a structure which is peculiar to that species. Opal is a solidified jelly; on cooling, it has become riddled with extremely thin cracks, which were subsequently filled with similar material of slightly different refractivity, and thus it consists of a series of films. At the surface of each film, interference of light takes place just as at the surface of a soap-bubble, and the more evenly the films are spaced apart the more uniform is the color displayed, the actual tint depending upon the thickness of the films traversed by the light giving rise to the phenomenon."

"Upon the fact that the refractive index of a substance varies for light of different colors depends such familiar phenomena as the splendor of the rainbow and the 'fire' of the diamond. When white light is refracted into a stone it no longer remains white, but is split up into a spectrum. Except in certain anomalous substances the refractive index increases progressively as the wave-length of the light decreases, and consequently a normal spectrum is violet at one end and passes through green and yellow to red at the other end. The width of the spectrum which may be measured by the difference between the refractive indices for the extreme red and violet rays also varies, though on the whole it increases with the refractive index. It is the dispersion, as this difference is termed, that determines the 'fire'—a character of the utmost importance in colorless transparent stones, which, but for it, would be lacking in interest. Diamond excels all colorless stones in this respect, although it is followed closely by zircon, the color of which has been driven off by heating; it is, however, surpassed by two colored species: sphene which is seldom seen in jewelery, and demantoid, the green garnet from the Urals, which often passes under the misnomer olivine."

"Alexandrite, a variety of chrysoberyl, is a curious and instructive case. The balance in the spectrum of light transmitted through it is such that, whereas in daylight such stones appear green, in artificial light, especially in gas-light they are a pronounced raspberry red. The phenomenon is intensified by the strong dichroism characteristic of this species."

"Any mollusc, whether of the bi-valve or the uni-valve type, which possesses a nacreous shell, has the power of producing pearls; but only two, the pearl oyster, *Meleagrina margaretifera*, and the pearl mussel, *Unio margarifer*, repay the cost of systematic fishing. The outside of the shell is formed of the horny matter called conchiolin; while the inside is composed of two coats of which the outer consists of alternate layers of conchiolin and calcium carbonate in its crystallized form, calcite, and the inner of the same organic matter, but with calcium carbonate in its other crystallized form, aragonite. The latter coat forms the nacreous lining known as mother-of-pearl, which is identical in consistency with pearl, but somewhat more transparent. The iridescence of mother-of-pearl is due not only to the fact that it is composed of a succession of thin transparent layers; but also to the fact that these layers overlap like slates on a house, and form a series of fine parallel lines on the surface; diffraction therefore as well as interference of light takes place, and a similar diffraction phenomenon is displayed even by a cast of the inside of the shell. The animal has the property of secreting calcium carbonate which it absorbs from the sea-water, in both its crystallized conditions as well as conchiolin. At the outer rim it secretes conchiolin, further in calcite, and at the very inside aragonite. The shape and appearance of a pearl depend therefore on the position in which the intruding substance is situated within the shell."

"Built up in a haphazard manner and not confined by the inexorable laws of intermolecular action, a pearl may assume any and every variety of shape from the regular to the fantastic. It may be truly spherical, egg- or pear-shaped—pear-drops or pear-eyes, as they are termed—or it may be quite irregular—the so-called baroque or barrok pearls. The first is the most prized, but a well-shaped drop pearl is in great demand for pendants or ear-rings. The color is ordinarily white, or faintly tinged yellowish or bluish, and somewhat rarely, salmon-pink, reddish, or blackish gray. Perfect black pearls are valuable, but not as costly as the finest of the white. Though not transparent, pearl is to a varying extent translucent, and its characteristic lustre—'orient' in the language of jewelery—is due to the same kind of interaction of light reflected from different layers that has been remarked upon in the case of opal and certain other stones. The translucency varies in degree, and some jewelers speak of the 'water' of pearls just as in the case of diamonds. If a pearl be sliced across the middle and the section be examined under the microscope, it will be seen that the structure consists of concentric shells and resembles that of an onion. Because of their composite character, pearls have a specific gravity ranging from 2.65 to 2.69—2.84-2.89 in the case of pink pearls—which is appreciably less than that of aragonite: the hardness is about the same, namely 3.5 to 4 on Mohs' scale. That the arrangement of the mineral layers is approximately parallel is evinced by the distinctness of the shadow-edges shown on examination with the refractometer. Pearls require very careful handling because they are soft and therefore apt to be scratched, and because they are chemically affected by acids, and even by the perspiration from the skin. Acids attack only the calcium carbonate, not the organic matter; the well-known story therefore of Cleopatra dissolving a valuable pearl in vinegar, which is moreover too weak an acid to effect the solution, must not be accepted too literally. Pearls are not cut like stones, and therefore as soon as the precious bloom has once gone, nothing can be done to revive it. Attempts are sometimes made in the case of valuable pearls to remove the dull skin and lay bare another iridescent layer underneath, but the operation is exceedingly delicate. Even with the best of care pearls must in process of time perish owing to the decay of the organic constituent. Pearls that have been discovered in ancient tombs crumbled to dust at a touch, and those formerly in ancient rings have vanished or remain only as a brown powder, while the garnets or other stones set with them are little the worse for the centuries that have passed by."

Farrington[1] differentiates more lustre by name, though he does not give any adequate definitions. "The lustre of gems is one of their most important and distinctive characters. Not only does it form one of the easiest means of distinguishing gems, but it is also one of the most reliable characters sought by those experts who depend for their determination of gems on ocular examination alone. One familiar with the lustre of quartz, as compared with that of diamond, for example, is in little danger of confusing the two, for the lustre of one can be recognized as adamantine, that of the other as

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[1] Gems and Gem Minerals, **16**, 219 (1903).

vitreous. The lustre of a gem is produced by the light which it reflects back to the eye, and this may vary in quantity and quality with the nature of the surface. Since the latter is largely the result of the molecular structure of the mineral, it follows that different species will have distinctive lustre. The terms used to describe the different kinds of lustre are derived from that afforded by some well-known object. Thus adamantine lustre means the lustre of the diamond; vitreous lustre, the lustre of broken glass; oily lustre, the lustre of oil; waxy lustre, the lustre of wax; resinous lustre, the lustre of resins; pearly lustre, the lustre of pearl; silky lustre, the lustre of silk; and metallic lustre, the lustre of shining metals.

"Of the above kinds of lustre, the vitreous is the most common among gems, being displayed by quartz, topaz, beryl, tourmaline, sapphire, and many others. The adamantine lustre belongs almost exclusively to the diamond, although it is displayed to some extent by sphene and colorless zircon, and is suggested by some sapphires. It is characteristic of minerals of a high degree of refraction. Metallic lustre is strictly possessed only by opaque minerals, and hence among gems is confined to pyrite and hematite. The lustre of turquoise is of the waxy order. Essonite displays a somewhat resinous lustre, and chrysolite an oily one. Pearly lustre is best seen in the pearl, but is also illustrated by the moonstone and opal. Tiger eye and cat's eye afford examples of silky lustre."

"There are numerous ways of producing imitation pearls, one of which, invented many years ago by a French beadmaker named Jacquin, gives remarkably accurate reproductions. The Jacquin pearls are made from an easily fusible, bluish glass, which is first drawn into tubes, and, from these, hollow globules of the desired size are blown. These are covered on the inside with a solution of isinglass, and a substance called essence of pearl, which is blown in warm, and spread over the interior by rapid motion. When dry the globules are filled with wax. The essence of pearl, which constitutes the important feature of Jacquin's process, consists of a silvery substance found beneath the scales of the fish known as the bleak (*Cyprinus alburnus*). It is in the form of thin, irregular rhombic plates, and is obtained by washing the scales, one pound of essence being derived from seven pounds of scales. From eighteen thousand to twenty thousand fish are required to produce the latter amount of scales. The substance is, therefore, costly; and owing to this fact, and the amount of labor and skill required to make the pearls, they bring a considerable price. They can be distinguished from genuine pearls by their greater hardness, and a colder feeling in the hand."

The colors of mother-of-pearl have been studied by Pfund.[1] "A perpendicular section of the shell of a fresh-water mussel, *Abovaria ellipsis* (Lea), taken near its growing edge shows that, speaking roughly, the shell may be said to consist of three layers:

"1. An outer horny layer (*a*) (*periostracum*) which is composed of organic matter (*conchiolin*).

"2. An intermediate layer (*b*) of minute prisms of $CaCO_3$ separated by thin layers of conchiolin. This layer is termed the 'prismatic layer.'

"3. An inner layer (*c*) composed of alternate laminae of $CaCO_3$ and conchiolin. This is the true mother-of-pearl or 'nacre.'

"That minute layers of conchiolin exist between those of $CaCO_3$ is shown by placing a shell in hydrochloric acid. The calcium carbonate disappears, leaving a flabby, honeycombed mass of conchiolin in, practically, the form of the original shell.

"Whereas the minute layers of nacreous matter are continuous on the inside of the shell, they terminate abruptly on the outside. Each layer projects slightly beyond the edge of its predecessor, hence the outside of the nacreous portion will show innumerable steps or ridges running parallel to the growing edge of the shell. Such a surface structure is identical with that of a diffraction grating, hence, in case the spacing

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[1] Jour. Franklin Inst., 183, 453 (1917).

is sufficiently regular, diffraction colors might be looked for on the outside of a shell.

"In order to study these colors it is first necessary to grind off the horny and prismatic layers and polish the nacreous layers by means of a buffing wheel. By permitting the light from an incandescent lamp to be reflected from this surface, pure diffraction colors are observed. As a rule these colors are rather inconspicuous since they are masked by the flood of light coming from the underlying portions. These phenomena may be studied most readily by means of celluloid copies or replicas which are made by flowing celluloid dissolved in amyl acetate over the surface of the shell. After the amyl acetate has evaporated, the shell is immersed in water for about 20 minutes. The celluloid is then removed and dried on a plate of clear glass.

"A microphotograph obtained from such a replica was compared with a similar photograph of a replica taken from a Rowland diffraction grating having 7230 lines per inch. Since the scale of enlargement is the same in both cases it appears that the steps or ridges on the outside of the shell are spaced at the rate of about 9000 per inch. This particular shell belonged to a mussel taken from the Mississippi River. As might be expected replicas taken from the inside of the shell revealed no grating structure.

"It is obvious that the microscope may be dispensed with entirely in a study of the spacing of these lines for, by measuring the angle of diffraction of light of known wavelength, the grating space may be obtained at once. If a piece of cardboard with a pin-hole 0.5 mm in diameter be placed in contact with the replica and if a Nernst lamp be viewed through this opening, the two first order diffraction spectra may be seen. If the pin-hole be moved perpendicular to the direction of the lines a study may be made of the striking periodicities in the spacing of the lines. At intervals the lines will be spaced at the rate of 6–8000 lines per inch while the regions in between will show a spacing of 15–20,000 lines per inch. This is not the place to discuss the question as to how these layers are deposited by the living mussel or what the cause of the periodicity giving rise to layers of such remarkable uniformity is. Yet a study of these questions might be much facilitated by the use of replicas which, when viewed in the white light from a small, intense source, show extremely brilliant colors and color changes over the surface, thus enabling one to tell at a glance where the spacing is coarse or fine.

"Upon grinding the surface of mother-of-pearl with fine emery all traces of diffraction colors disappear and the brilliant iridescence alone remains. These colors can, obviously, be due only to interference in the parallel laminae. A rough test of this inference consists in reflecting light almost normally from a patch on the shell appearing red. By increasing the angle of incidence and moving the eye so as to receive always the reflected beam, the color changes in succession to orange, green, and finally blue. The same phenomenon is observed with Lippmann color-photographs and crystals of $KClO_3$ whose structure is known to be laminar. In order to prove even more conclusively the correctness of this explanation, white light of great intensity was reflected from the mother-of-pearl into a spectrometer and, by means of suitable apparatus, the intensity of the radiation in the near infra-red and visible spectrum was studied with the view of finding indications of interference maxima.....

"The maxima lie, respectively, at 1.4 μ, 0.71 μ and 1.86 μ, 0.93 μ, and 0.63 μ. As before, the wave-lengths of successive maxima bear the ratios $1 : {}^1/_2 : {}^1/_3$ to a very fair degree of approximation—hence the conclusion may be drawn that the iridescent colors of mother-of-pearl owe their existence to interference of light reflected from the parallel and equidistant laminae.....

"Having investigated highly colored shells it seemed of interest to take up the study of nacreous matter which showed no color but a brilliant 'pearly' lustre. A suitable region on the inner surface of a Mississippi River mussel shell was found and from this a reflection curve shown was obtained.

The lack of sharpness of the maxima indicates that the thickness of the laminae is far from being constant. It is possible to simulate the appearance of such a specimen by heating a piece of mica in a Bunsen flame. In consequence of the heating, the mica is split up into numerous laminae of widely varying thickness.

"An unsuccessful attempt was made to study, in a similar manner, that area on the outside of the shell which exhibits neither color nor pearly lustre. The character of the chalky material in the shell was such as to scatter the light diffusely—thus preventing regular reflection from successive laminae. That laminae exist in this region also is certain, for the diffraction colors seen indicate a spacing of the laminae which is practically the same as that shown by neighboring iridescent portions."

The final conclusion is that mother-of-pearl owes its colors to the diffraction of light due to a grating-like structure of the terminal edges of successive laminae, and the interference of light due to reflection from numerous parallel laminae of sensibly equal thickness.

Pfund urges biologists to attack anew the problem of ascertaining the manner in which the layers of nacreous material are deposited. "The truly remarkable constancy of thickness of the laminae demands explanation. That periodic variations in external conditions such as light and darkness, tides, temperature, etc., should be responsible for the deposition of discrete layers seems improbable since the total number of laminae possessed by a shell of known age is entirely too great to be accounted for on any such hypothesis. Possibly the animal, as such, has nothing to do with the periodicity which gives rise to the laminae—for, just as the crystals in the minute laminae exhibited by $KClO_3$ grow only in definite thickness, so may the minute crystals of $CaCO_3$, surrounded by conchiolin, grow only until a certain thickness is reached."

Crookes[1] says: "When a good fiery opal is examined in

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[1] Proc. Roy. Soc., 17, 448 (1869).

daylight, sunlight, or artificial light, it appears to emit vivid flashes of crimson, green, or blue light, according to the angle at which the incident light falls, and the relative position of the opal and the observer; for the direction of the path of the emitted beam bears no uniform proportion to the angle of the incident light. Examined more closely, the flashes of light are seen to proceed from planes or surfaces of irregular dimensions inside the stone, at different depths from the surface and at all angles to each other. Occasionally a plane emitting light of one color overlaps a plane emitting light of another color, the two colors becoming visible alternately upon slight variations of the angle of the stone; and sometimes a plane will be observed which emits crimson light at one end, changing to orange, yellow, green, etc., until the other end of the plane shines with a blue light, the whole forming a wonderfully beautiful solar spectrum in miniature. I need scarcely say that the colors are not due to the presence of any pigment, but are interference colors caused by minute striae or fissures lying in different planes. By turning the opal around and observing it from different directions, it is generally possible to get a position in which it shows no color whatever. Viewed by transmitted light, opals appear more or less deficient in transparency and have a slight greenish yellow or reddish tinge. In order to adapt them better to the purposes of the jeweler, opals are almost always polished with rounded surfaces, back and front; but the flashes of colored light are better seen and examined when the top and bottom of the gems are ground and polished flat and parallel. A good opal is not injured by moderate heating in water, soaking in turpentine, or heating strongly in Canada balsam and mounting as a microscopic slide.....

"If an opal which emits a fine broad crimson light is held in front of the slit of a spectroscope or spectrum-microscope, at the proper angle, the light is generally seen to be purely homogeneous, and all the spectrum that is visible is a brilliant luminous line or band, varying somewhat in width and more or less irregular in outline, but very sharp, and shining brightly on a perfectly black ground. If now the source of light is moved so as to shine into the spectrum-apparatus *through* the opal, the above appearance is reversed, and we have a luminous spectrum with a jet-black band in the red, identical in position, form of outline, and sharpness with the luminous band previously observed. If instead of moving the first source of light (the one which gave the reflected luminous line in the red), another source of light be used for obtaining the spectrum, the two appearances, of a colored line on a black ground and a black line on a colored ground, may be obtained simultaneously, and they will be seen to fit accurately. Those parts of the opal which emit red light are therefore seen to be opaque to light of the same refrangibility as that which they emit; and upon examining in the same manner other opals which shine with green, yellow or blue light, the same appearances are observed, showing that this rule holds good in these cases also. It is doubtless a general law, following of necessity the mode of production of the flashes of color."

When the transmission spectra are examined, they are found to consist of a black band, often spiral in shape, against a bright field, the band moving along the spectrum almost from one end to the other as the opal is moved sideways. "All these black bands can be reversed and changed into luminous bands by illuminating the opal with reflected light. They are, however, more difficult to see; for the colored light is only emitted at a particular angle, while the special opacity to the ray of the same refrangibility as the emitted ray holds good for all angles. It is scarcely necessary to say that the color of the moving luminous line varies with the part of the spectrum to which it belongs. The appearance of a luminous line, moving slowly across the black field of the instrument and assuming in turn all the colors of the spectrum, is very beautiful.

"The explanation of this phenomenon is probably as follows: In the case of the moving line, the light-emitting plane in the opal is somewhat broad, and has the property of giving out at one end, along its whole height and for a width equal to the breadth of the band, say, red light; this merges gradually into a space emitting orange, and so on throughout the entire length of the spectrum, or through that portion of it which is traversed by the moving line in the instrument, the successive pencils (or rather ribbons) of emitted light passing through all degrees of refrangibility. It is evident that if this opal is passed slowly across the slit of the spectrum-microscope, the slit will be illuminated successively with light of gradually increasing refrangibility, and the appearance of a moving luminous line will be produced; and if transmitted light is used for illumination, the reversal of the phenomenon will cause the production of a black line moving along a colored field. A diagonal line will be produced if an opal of this sort is examined in a sloping position. The phenomenon of a spiral line in relief rolling along as the opal is moved, is doubtless caused by modifying planes at different depths and connected by cross planes. I can form a mental picture of a structure which would produce this effect, but not clearly enough to enable me to describe it in words.

"It is probable that similar phenomena may be seen in many, if not all, bodies which reflect colored light after the manner of opals. A magnificent specimen of Lumacelli, or Fiery Limestone, from Italy, kindly presented to me by my friend David Forbes, shows two sharp, narrow and parallel bands in the red. I have also observed similar appearances in mother-of-pearl. The effects can be imitated to a certain extent by examining Newton's rings, formed between two plates of glass, in the spectrum instrument."

Madan[1] considers that both the iridescent colors of potassium chlorate crystals and the colors of opals are due to the presence of prismatic cavities. "I may mention that plates of opal—at any rate those portions which give a uniform color—afford spectra extremely similar in character to those of the iridescent crystals; definite bright bands in the reflected light, and dark complementary bands in the transmitted light,

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[1] Nature, 32, 102 (1885).

changing their position in the spectrum with change of incidence. Now the iridescence of opal is pretty well known to be due to the reflection of light from the surfaces of rows of filaments embedded in the same.[1] I cannot say that I have yet succeeded in actually bringing out such rows of tubes under the microscope. It is easy to see with a $^1/_6$ inch power, when the illuminating beam is properly adjusted, a sort of wavy structure at the twin-film (like that seen in opal under the same conditions); but I have not yet made out such definite rows of cavities as would seem to be required to produce the singularly uniform sheet of color. They may be beyond the power of a microscope altogether."

Stokes[2] disagrees entirely with Madan's view. "The appearance of Mr. Madan's paper induces me to offer some additional remarks on this subject. In the discussion that followed the reading of my paper [on chlorate crystals] Mr. Crookes referred to the closely analogous spectra exhibited by opals, as described in his paper. This paper, though it came before me at the time when it was read, was not in my mind when I wrote my own. I called shortly afterwards at Mr. Crookes' house, and saw the spectra of his opals. Supposing that there were sufficient grounds for the commonly received idea that the colors of the opal are due to fine tubes in the mineral, we did not at the time conceive that the phenomena could be the same; were it not for this, I should certainly have added to my paper a reference to that of Mr. Crookes.

"Mr. Crookes was so good as to lend me his opals for more leisurely study. The further examination has so impressed me with the similarity of character of the spectra, that I am strongly disposed to think that the colors of the opal and those of the chlorate crystals may be due to the same cause. This does not, however, lead me to attribute tubes or striae to the chlorate crystals, the structure of which can

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[1] Brewster: Brit. Assoc. Reports, 1844, II, 9.

[2] Nature, 32, 224 (1885).

comparatively easily be made out, but to doubt very greatly the theory which attributes the colors of opal to fine tubes.

"Mr. Madan does not profess to have actually seen in the chlorate crystals such tubes as he supposes to exist, nor could I see anything of the kind on examining some of the crystals I have got after the appearance of his paper. On the other hand, I notice that Brewster did not state that he had actually seen the supposed tubes, but merely inferred their existence from a comparison of the appearance under the microscope of the precious opal with that of hydrophane. And Mr. Crookes tells me that an opal is not spoiled or affected by being immersed in water or even oil. The fact is that it is extremely difficult to make out what the actual structure is with which we have to deal in the case of the opal, whereas in the case of the chlorate crystals it is unmistakable. Moreover, in the case of the chlorate crystals there is a wonderful uniformity in the phenomena presented by the same crystal, extending, it may be, over nearly the whole of even a large crystal, whereas in the opal the color extends over comparatively small patches; and even a single patch is seen under the microscope to present differences of structure in different parts. Hence if the colors in opal and those in the chlorate crystals are really due to a similar cause, it seems much more likely that a study of the phenomena of the chlorate crystals will throw light on those of the opal, than that the phenomena of the opal should furnish the key to the explanation of the colors of the chlorate crystals.

"In truth, I do not see how the presence of tubes, if such there be in the opal, would account for the phenomena, and especially for the very peculiar spectrum exhibited. The supposition of the existence of rows of tubes leads one to look in the direction of diffraction. But I do not see how monochromatic light, or, at least, light almost monochromatic, can be obtained by diffraction. And even independently of this consideration there is one feature of the production of color in the chlorate crystals which shows, at once and decisively, that at least in their case the color cannot be due to diffraction. If an iridescent crystal be chosen with an even surface, and the flame of a candle in a dark room be viewed by reflection in it, it is found that the color is seen in the direction of the regularly reflected light. In fact, the colored light forms a well-defined image of the flame of the candle, coinciding with, or overlapping, the colorless image due to reflection from the first surface. This differs altogether from what we get in the case of a grating, or in that of mother-of-pearl or Labrador spar. It agrees so far with the colors of thin plates, or the colors shown by reflection by certain quasi-metallic substances, such as several of the aniline dyes, though the production of color in these three cases is due to three totally different causes.

"It has been conclusively proved that the seat of the color in the chlorate of potash crystals is in a very thin twin stratum; and I entertain myself little or no doubt that the color depends in some way on the different orientation of the planes of polarization in the two components of a twin, and on the difference of retardation of the two polarized pencils which traverse the thin stratum. But anything beyond this is at present only a matter of speculation.....

"In conclusion, I would mention an interesting paper on 'The Spectrum of the Noble Opal,' by Prof. H. Behrens, a copy of which I have just received by the kindness of the author. In this paper, which is printed in the Neues Jahrbuch fur Mineralogie, etc., 1873, the author, who was evidently unacquainted with Mr. Crookes' paper when he wrote his own, has described and figured the peculiar spectra of several opals."

A glass surface from which light is totally reflected shines with a bright metallic lustre[1] and "forms the clearest and most perfect mirror known to science. In the construction of optical instruments totally reflecting prisms are therefore used frequently to turn the rays of light in any desired direction."

This shows that the sensation of metallic lustre does not necessarily involve the presence of a metal or of metallic

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[1] Lommel: "Experimental Physics," 519 (1900).

electrons, a fact which is also brought out very clearly by experiments of Dove[1] and others on binocular lustre as it is sometimes called. Dove combined black and white figures stereoscopically and also colored figures obtaining the effect of metallic lustre in both cases although the single figures showed no lustre. "In one of two pictures for a stereoscope the section of a foreshortened pyramid was painted a saturated blue while the other was painted yellow. When green was seen as a result of stereoscopic combination it seemed as though the colors had become transparent and were seen one through the other. That many people do not see these colors combined but only alternately is due to the fact that [the accommodation for the two colors changes continually and that] these people are conscious only of the end-states and not of the intermediate ones. When a green color was seen, it seemed to me and to others that the color was covered with a varnish. This lustrous effect of the mixture was also noticed by Oertling when he combined in a stereoscope different colored sectors of a hemisphere painted like a balloon. These phenomena are not very striking and many people do not see them. On the other hand if one combines stereoscopically the yellow and blue sections of a pyramid while holding a violet glass before one eye, the image resembles a polished metallic surface, whereas the surface is matt when seen with either eye alone. Probably the violet glass brings the two colors to the same intensity.

"In all cases where a surface appears lustrous, there is always a specular, transparent or translucent layer of extreme thinness, through which one sees the other substance. The effect of lustre is therefore produced when light specularly reflected from the surface is combined with internally reflected or scattered light. The lustrousness increases with the number of alternations from one to another. Thus mica films have metallic lustre and a pile of glass plates the lustre of mother-of-pearl. The two sets of reflections act on the eye from different distances. If the eye adjusts itself so as

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[1] Pogg. Ann., 83, 169 (1851).

to see the substance behind the transparent film, the light that is reflected from the surface cannot be seen distinctly and the consciousness of a vaguely seen reflection gives the appearance of lustre. Lustre is therefore really a false or secondary phenomenon which dazzles and prevents us from seeing clearly the underlying surface. It disappears therefore if one eliminates the surface reflection by looking through a nicol prism at the varnish of a picture below the polarization angle. The interference phenomena due to the difference in phase of the light reflected from the two surfaces are therefore not the cause of the phenomenon of lustre but rather consequences of the conditions under which lustre occur."

Burckhardt[1] points out that "instead of combining white and black in the stereoscope the eye can also do it by irradiation, short-sighted people far off and far-sighted people close up. When the black predominates in woolen goods striped black and white, these goods seem to me and to others perfectly lustrous exactly like the lustre of silk. Silk makers must have known this for a long time for they are very prone to increase the lustre of silk in this way."

Brewster[2] does not accept Dove's explanation of the phenomenon. "Some years ago it was observed by Professor Dove that when the right and left eye figures of a pyramid or other mathematical solid, the one drawn on a white and the other on a dark ground, were inserted in the spectroscope, the solid in relief appeared with a particular lustre. Prof. Dove described the lustre as metallic, and in another place, where he describes the two diagrams as drawn, the one with white lines on a black ground, and the other with black lines on a white ground, he stated that the pyramid in relief appears lustrous, as if made of graphite. Other observers described the lustres differently, some as resembling ground glass, and others as like paper darkened with a black lead pencil, while Professor Rood regarded it as recalling the idea of highly polished glass. In order to explain this phenomenon, Professor Dove re-

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[1] Fortschritte der Physik, 10, 310 (1854).

[2] Brit. Assoc. Reports, 1861, II, 29.

marked that 'in every case where a surface appeared lustrous, there was always a transparent, or transparent-reflecting stratum of much intensity, through which we see another body. It is therefore externally reflected and dispersed light, whose combined action produced the idea of lustre. This effect, he elsewhere added, we see produced when many watch-glasses are laid in a heap, or when a plate of transparent mica or talc, when heated red-hot, is separated into multitudes of thin layers, each of which, of inconceivable thinness, is found to be highly transparent, while the entire plate assumes the lustre of a plate of silver.' To these examples of lustre, produced by thin plates not in optical contact, or if in actual contact, having different reflective powers, were to be added the following: pearls, mother-of-pearl, pearl-spar, and composite crystals of calcareous spar, and decomposed glass of all colors. The cause of these various kinds of lustre, and of that of metals had already been well known, and when binocular lustre attracted the attention of philosophers, it was natural to ascribe it to the same cause. Professor Dove did this, and considered the dark surface in the one picture as the dispersed light, and the white surface as the regularly reflected light, the dark surface being seen through the white surface. This theory of binocular lustre, he had reason to believe, was not satisfactory.... In order to test this explanation by other means, he combined surfaces that had no geometrical figures upon them, and he found that binocular lustre was not produced. This experiment seemed decisive of the question. He was led to infer from it that the lustre observed in the combination of right and left eye figures of solids was not due to the rays from a dark surface passing through a lighter one to the eye, but to the effect of the eyes in combining the two stereoscopic figures, and to the dazzle occasioned by the alternating intensities of the two combined tints, the impression of one of the tints sometimes disappearing and reappearing....

"Binocular lustre was a species of lustre *sui generis*. It was a *physiological*, not a *physical* phenomenon, and had no relation whatever to those varieties of lustre which arose from the combination of lights reflected from the outer and inner surfaces of laminated, transparent, or translucent bodies. He assigned various causes for the physiological character of the phenomenon and then added, 'If binocular lustre arises from a physiological and not from a physical cause, we must look for this cause in the operations which take place in the eyes of the observer when binocular lustre is distinctly seen. These operations are of two kinds. First, in combining geometrical or other figures to represent solids whose parts are at different distances from the eye, the optic axes are in constant play, not only in varying the distance of their focus of convergence to unite similar points at different distances in the two diagrams, but in maintaining the unity of the picture by rapidly viewing every point of its surface. Secondly, when the two surfaces have different shades or colors, the retina of one eye is constantly losing and recovering the vision of one of them. Each optic nerve is conveying to the brain the sensation of a different tint or color. The brain is therefore agitated sometimes with one of these sensations and sometimes with both of them combined, and it is therefore not an unreasonable conclusion that, in the dazzle produced by this struggle of flickering sensations, something like lustre may be produced. In studying this subject of lustre there are some facts deserving of attention. In a daguerreotype for example, of two figures in black bronze with a high metallic lustre, it is impossible by looking at either of the pictures to tell the materials of which they are made. No lustre is visible; but when the two equally shaded pictures are combined in the stereoscope, the lustre and true character of the material is seen instantly. Another instructive example is seen in the stereoscopic representations of a boy blowing a soap-bubble. The lustre of the watery sphere is not visible in either of the two pictures; but when they are combined, it is seen distinctly. In both these cases and in others of the same kind, tints of similar intensity are combined, and there is not ground for assuming that the two surfaces combined appear at different distances, and the one is seen through the other as in Professor Dove's theory."

Rood[1] has made some very interesting experiments in connection with Dove's theory of lustre, in which Dove considers that externally reflected light in combination with internally reflected or dispersed light produces the sensation of lustre. This view of the nature of lustre opens the possibility of producing the individual lustre and appearance of gold, copper, brass, etc., by the stereoscopic combination of suitably colored surfaces. By combining tin-foil stereoscopically with yellow, orange, and ultramarine paper, Rood was able to produce the effect of gold, copper, and graphite, respectively.

Upon substituting dark gray paper for the tin-foil, the same effects in degree were not produced, owing apparently to the fact that the well-known texture and appearance of the paper forced itself so strongly on the attention as to preclude the sensation of a metallic surface. To get round this, a crumpled sheet of tin-foil was photographed and the positives from this gave almost as good a sensation of gold when combined with yellow paper as did the original tin-foil.

"Prof. Helmholtz,[2] in his admirable work in physiological optics mentions that by a peculiar arrangement he was able to cause the homogeneous golden yellow light of the spectrum to appear brown, proving thus that the brown tint is only weak yellow light. These stereoscopic experiments give us on the other hand the means of apparently converting brown into metallic golden yellow, for many specimens even of brown wrapping paper, when combined in the stereoscope with very black prepared paper, acquire the lustre and appearance of yellow plates, in the shade and reflecting images of dark paper. In the same manner and corresponding to the investigations of Helmholtz, I found that the stereoscopic union of black glazed paper with red imitated with surprising perfection the appearance of a glazed plate of chocolate....

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[1] Am. Jour. Sci., (2) 31, I, 339 (1861).

[2] "Physiologische Optik," 281 (1860).

"I made some experiments to ascertain how far the stereoscopic mixtures of two masses of different colored light correspond to their true mixture by the method of rapid rotation, use being made of the imitations above described. It is, however, so difficult to compare a varying with a fixed tint that I will not record the results obtained; in many cases a certain moderate amount of agreement in the resultant tints was observed. Brücke found that, when a deeply colored yellow glass was held before one eye and a blue cobalt glass before the other, a landscape viewed through this combination was simply darkened in appearance. I repeated this experiment with similar glasses and obtained a like result; objects appeared darkened, but in their natural colors, though sometimes the blue or yellow tint predominated a little. But when I presented to a single eye these two masses of light a very different result was obtained; the plates of glass were attached to a blackened disc opposite suitable perforations, and it was set in rapid rotation; a landscape viewed through it appeared a deep purple, though not a trace of this color was to be perceived in the binocular use of these glasses. When these two glasses were held before the same eye, a landscape viewed through them was very much darkened but scarcely colored.

"Sir David Brewster opposes Dove's theory of lustre, as he has found that when black and white surfaces without drawings are combined in the stereoscope, no lustre is produced. The lustre, then, according to this philosopher is due not to one mass of light passing through another, but to the effort of the eyes to combine the stereoscopic pictures. Admitting the correctness of Sir David's experiments, Dove has shown that the objection founded on it is without weight.[1]

"In repeating Brewster's experiment I always obtain the opposite result; in combining uniform black and white surfaces, without drawings, I always obtain a distinct impression of lustre, like that of the blackened mirror of a polariscope, and, in strict accordance with Dove's theory, when the black

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[1] "Optical Studies," 3.

field is so darkened that no light is sent from it to the eye, this lustre vanishes and the white paper alone is perceived. This disagreement is not a cause of astonishment when we reflect that de Haldat's original experiment waited nearly half a century for confirmation. To Brewster's own theory, the simple objection, which has already been made by others, that we daily perceive lustre plainly with one eye, would seem sufficient.

"I proceed now to describe some experiments where the idea of lustre is produced by the action upon a single eye of two masses of light of unequal intensity.

"1. If a disc of colored card-board, out of which a number of sectors has been removed, be made to rotate rapidly, and an object be viewed through it by a single eye, two masses of light will reach the eye, which apparently proceed from the object; one is reflected from the surface of the disc, the other emanates from the object behind the disc, and passes through the first mass of light. Dark objects viewed in this way assume to me to a small extent an appearance like that of blackened glass. The effect is not at all striking, and would be overlooked by many persons; I therefore prepared paper in a peculiar way so as to imitate distinctly the appearance of foliated graphite or crumpled mica.

"White smooth drawing paper was rubbed over irregularly with a brush slightly moistened with a weak wash of India ink or lampblack; when dry, another wash of a deeper hue applied as before, care being taken to leave many small spots untouched. The final wash was laid on with pure black. If the brush be kept nearly dry and passed only lightly over the paper, it is easy to obtain a surface bearing some very distant resemblance to the minerals above mentioned; it is of course without lustre. Similar papers were prepared with red and blue water colors.

"When these papers were held behind discs of ultramarine or orange-tinted paper, from which equal alternate sectors had been removed, and which were revolving at such rates that their surfaces seemed uniform, or at lower rates, they often appeared to a single eye highly lustrous. This was true of the prepared paper in a state of rest; when moved slightly by the hand it glittered strongly. Dark photographs of tin-foil held behind a revolving disc of ultramarine paper and viewed by a single eye, assume often to a striking degree the lustre and appearance of foliated graphite.

"2. If a piece of this peculiarly blackened paper $^1/_2$ of an inch square be placed in a blue field (rather light ultramarine paper), and be steadily regarded for some minutes by one eye it assumes a red-orange hue and appears suspended over the blue paper and nearer to the eye than the latter; at the same instant it appears lustrous like crumpled mica. The illusion with me often lasts half a minute in great perfection; this is particularly the case when the eye is not quite accurately focussed on the paper.

"3. If a sheet of this prepared paper be brightly illuminated by light from a window, and be held so near one eye as to produce indistinct vision, it often apparently becomes highly lustrous. In this case enlarged images of the white and gray points are formed on the retina which overlap, so that again we have two masses of light, one passing through the other.

"4. If a *roll* of black paper like the above, but coarser in its markings, be brightly illuminated on one side and viewed through deeply colored plates of glass (red, green, blue), in a few seconds it appears lustrous resembling a roll of polished zinc which has been irregularly and deeply corroded by an acid. Upon removing the glass the surface of the paper appears lustrous for an instant.

"5. A sheet of the finer variety of this prepared paper viewed through a large rhomb of calc spar gives often in spots the appearance of lustre, particularly when the head of the observer, or the rhomb, is slightly moved. Some persons compared this to the appearance of water.

"It would seem probable that, in all cases where two masses of light reach a single eye, one passing through the other, particularly when there is any perception of their individuality, the appearance of more or less lustre is produced, though from habit we often overlook it. Thus Helmholtz[1] remarks upon the combination of two colored surfaces in monocular vision by means of a simple instrument he figures: 'It is particularly favorable when the drawings, or spots on the two surfaces are made to shift their position. Then we often believe that we see both colors simultaneously in the same place, the one through the other. We have an impression in such cases of seeing objects through a colored veil or reflected from a colored surface.'"

"I found in fact that, by placing stereographs consisting of colored paper for one eye and a photographic drawing of tin-foil for the other in this instrument, lustre could be perceived, particularly with the imitations of copper....

"Analogous to this is the observation of Brewster[2] speaking of uniting similar pictures (patterns on hanging paper) in binocular vision, he remarks: 'The surface of it (the wall) seems slightly curved. It has a silvery transparent aspect.' Here the images, though of the same intensity, etc., moving with each slight movement of the head induce in the mind the idea of one object seen through another.

"In closing I will remark that while many of the experiments above mentioned are easily repeated, others require considerable practice in this kind of observation."

Brücke[3] has made an elaborate study of metallic lustre which must be included.

"Six gall-stones from the bladder of an ox had a surprisingly brilliant metallic lustre, so marked that one might easily have mistaken the concretions for an imitation gold alloy. I wrapped one of the stones in paper and struck it a light blow with a hammer. It broke into fragments of thin concentric layers. The inner and the outer surfaces were absolutely smooth and showed distinct metallic lustre. The thinnest of these pieces were transparent and the thicker ones opaque. I boiled one portion of the fragments in turpentine

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[1] "Physiologische Optik," 273 (1860).

[2] "The Stereoscope," 91 (1856).

[3] Sitzungsber. Akad. Wiss. Wien, 43, II, 177 (1861).

to replace the air films by a strongly refracting medium. They became more transparent and lost their metallic lustre. I embedded them in dammar varnish and examined them under the polarization microscope. They showed very distinct double refraction and with crossed Nicols showed partly the first order gray and partly colors of the higher orders. Here and there were to be seen small and very beautiful systems of rings with black crosses interspersed. Another portion of the fragments was dissolved in dilute acetic acid. Much carbon dioxide was given off and the filtrate contained calcium acetate and a little magnesium acetate in addition to free acetic acid. The part that was not dissolved by the acetic acid proved under the microscope to be organic matter which was brown in color and still kept the form of the fragments. It was very soft and without any signs of double refraction, was laminated, but showed no structure in the histological sense of the word. The concretion consisted therefore of this organic foundation, crystallized calcium carbonate and a little magnesium carbonate.

"In my collection I have gall-stones from another ox which are similar in form but only slightly lustrous. They are brown in color and have a scarcely perceptible metallic iridescence. Except for the lesser lustre they look like these cast zinc objects which are covered with a brown varnish to make them look like oxidized bronze. When broken they formed irregular fragments and not concentric layers. They were laminated however and this structure showed up clearly in the dark-colored organic material after treatment with acetic acid. They differed in chemical composition from the other samples by containing small amounts of phosphates.

"In Steiermark chamois are sometimes shot with teeth having a coating near the gums which glitters like gold. The hunters believe that in the inaccessible crevices among the rocks there are gold-bearing springs at which these animals quench their thirst. I have once had in my hands a lower jaw-bone with similar golden concretions on the teeth. The animal was shown by our late colleague, V. Kollar. I made no chemical experiments at the time but the laminated structure could be seen with the eye and most distinctly with a magnifying glass. I have no doubt but the material was the same kind of thing as the gall-stones.

"While studying these latter I wondered to what this very surprising metallic appearance could be due, and have therefore tried to find out what are the characteristics of metallic lustre and to what it is due. So long as one assumed that metals had very high indices of refraction, it was possible to ascribe the lustre to this, although it was not evident why one should get any sensation from the high optical density in view of the extreme opacity of the metals. Nowadays this assumption is untenable because the high indices of refraction were deduced from the angle of the polarization maximum and Cauchy has shown that entirely different results are obtained if one calculates the index of refraction from his well-established formulas. He finds the index of refraction of mercury to be 1.7 which is smaller than that of spinel and only one-third of the value previously assumed.

"It is also impossible to deduce the metallic lustre from the elliptic polarization which is produced by the reflection from a metal of a plane-polarized ray whose plane of polarization is neither parallel with nor perpendicular to the plane of the incident light. Apart from the fact that in plane-polarized light we see the rays discovered by Haidinger, the unaided eye gives no clue as to the polarization of light which reaches it. It is easy to show that the metallic effect is quite independent of the elliptic polarization by looking at a metal through a Nicol prism. In that case only plane-polarized light reaches the eye; but the metal still looks metallic. If one rotates the prism, the intensity of the lustre varies and to some extent the color itself but the general appearance remains metallic.

"We must therefore find other criteria which will establish a real connection with our optical sensations. With non-metallic, lustrous substances the color of the light reflected at the surface is [practically] independent of the absorption color of the substance. The reflected light has [practically] the same color as the incident light. This fact has been known for a long time for single cases. Oersted discussed it with many illustrations and it was generally accepted. Later Arago found that the light corresponding to the absorption color was incompletely polarized perpendicularly to the incident plane. He concluded that this light came from the interior of the substance while the light giving the lustre was reflected from the surface and was polarized in the incident plane.

"If one looks at a colored lustrous surface in ordinary daylight—a colored gloss paper or a polished table top for instance—at a suitable angle through a Haidinger dichroscopic glass and turns it so that the main axis of the Iceland spar is parallel to the incident plane or makes an angle of 90° with it, one has two images, one of which is nearly white and is due to the reflected light and one of which shows the absorption color. The experiment was first done in this form by Botzenhart[1] and is well suited to make clear that in these cases the color of the lustre has nothing to do with the lustre. Metals behave differently, for the absorption color is determined by the color of the reflected light or, more properly speaking, the color we ascribe to a metal is that reflected by it when the incident light is white. Thus a red metal has a red lustre and a yellow metal a yellow one. If one repeats Botzenhart's experiment with a brilliantly colored metal, gold for instance, the two images are surprisingly different. The light polarized in the incident plane is much lighter and has a touch of red, while the other has a saturated golden yellow color. The difference in the color of the two images is still more striking in the case of copper. One might expect therefore to get the same effect as with non-metallic lustrous substances but less conspicuously because ordinary light is only polarized incompletely by metals even when it is below the angle of the polarization maximum. As a matter of fact the

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[1] Pogg. Ann., 68, 291 (1846).

result of Botzenhart's experiments with metals is to be interpreted quite differently.

"The reflection of light from metallic surfaces has been studied so successfully by Sir David Brewster, MacCullagh, Cauchy, de Sénarmont and Jamin, that it is now one of the best-developed branches of optics and Jamin was able to put forward a theory of the colors of metals which rests just as directly on the general principles of the undulatory theory (as the explanation of refraction and diffraction colors) of Newton's rings, etc. From Cauchy's formula combined with Jamin's experimentally determined constants, it followed that colored metals change the color of reflected white light one way when the light is polarized in the incident plane and differently when the light is polarized perpendicularly to this plane, the color being more saturated in the first case and paler in the second case.[1] Since we must consider ordinary light as a succession of oscillations with continuously varying azimuths, each one of which when reflected behaves like a train of waves polarized below the azimuth of the same amplitude and oscillation frequency, it is clear that we cannot get two images of the same color, when we break up the light reflected from the metal into light polarized in the incident plane and light polarized perpendicularly to it. But the light of the two images which we see in the dichroscopic glass is reflected light. This determines the color which we ascribe to the metal and the color of the metal is the color of the lustre. This close connection between color and lustre is recognized by the eye and causes us to give the term metallic lustre to non-metallic substances which show similar phenomena.

"If we are to make an exhaustive study of the characteristics of metallic lustre, there are one or two other points to be considered. The opacity of the metals is a point which is of the greatest importance in its bearing on the real cause of the phenomenon. We never see anything back of the

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[1] Jamin: Ann. Chim. Phys., (3) 22, 311 (1848).

surface of a metal, but merely what is reflected at or by the surface. We therefore cannot ascribe metallic lustre to any metallic substance which is not sufficiently opaque that we do not notice any transparency under ordinary conditions. In other words we get metallic lustre only when any light coming from the interior of the substance is masked completely by that reflected from the surface. Another point which characterizes metals is the intensity of the reflected light, even when the surface is not well polished. This is due in part to the high reflecting power and in part to the viscosity of the metals. A scratch on a brittle polished substance like glass or a gem, appears matt to the eye and so does a group of scratches. A scratch on a reguline metal is a lustrous groove.

"In order to get the full extent of metallic lustre one must see the surface as such. If a metallic surface is ground and polished very highly, and if one is some distance away, the surface disappears completely and one sees only one's own image. It is doubtful whether a man who had never seen such a mirror would recognize it as a metal plate without further test, even though he were otherwise familiar with metallic objects. If one sees the surface owing to scratches from grinding or to defective polishing, the character of the defective spots shows one at once that one is looking at a metallic surface. It can be shown that we get the impression of a metallic surface even with substances which have in themselves no metallic lustre, provided we have simultaneously a roughened surface and a high reflection of light. The most familiar instance of this is the silvery streak which marks the reflection of the moon from a water surface rippled by the evening breeze. The wavelets make the surface of the water seem rough and the accompanying high reflection of light makes the water look metallic, more metallic than the disc of the moon itself.

"I am now interested in showing that when we have metallic lustre with substances which are not metals, they satisfy the criteria which we have found to be necessary for metallic lustre. These criteria are the relation between lustre and color, relative opacity, and relatively high reflecting power even when the surface is not highly polished... One well-known case of metallic lustre is that of total reflection. How does this happen? The intensity of the reflection or the amount of the reflected light resembles metallic reflection; but the illusion is complete only when no dioptically seen light comes from the reflecting surface to our eyes. The two other essential conditions are then fulfilled, that the reflecting surface appears to be that of an opaque body and that no light comes from the reflecting surface which can be distinguished by its color from that of the lustre and which might therefore seem to be the absorption color of the lustrous substance. Pour some water on a table near a window and place a beaker filled with water on the spilled water in such a way that there are air bubbles on the under side of the beaker. If one turns one's face toward the window and looks down at an angle through the water in the glass, the air bubbles look exactly like drops of mercury pressed out flat by the weight of the glass. This is much more striking than the better-known method of getting metallic lustre by dipping an empty test-tube into a cylindrical stand-glass containing water. The reflection at a surface does not have to be absolute. The same effect can be produced by a closely packed layer of superposed films. Thus exfoliated mica sheets will have a metallic lustre at an angle at which no single sheet would reflect totally, provided the sum total of the successively reflected light drowns out all the transmitted light.

"The pile of mica sheets suggests another group of illustrations, the metallic lustre of iridescent feathers. Why is the lustre of the peacock feathers, of the neck feathers of the pigeon, etc., so distinctly metallic? I have examined the feathers from the neck of a gray pigeon. The sheen is entirely on the outer surface and only on the edge of the feathers which are relatively firm and rigid, not where they are downy. When passing from perpendicular to grazing incidence the color changes from red to green or from green to red. If the feather is wetted, the colors disappear, reappearing when the feather dries again. It is best to use alcohol for this experiment because it is taken up more readily than water by the feather and evaporated more rapidly.

"Under the microscope with reflected light one can see the cells where the color appears. The dividing lines appear dark where two cells come together and one can also distinguish the nuclei. Since the dark pigment interferes with the microscopical examination by transmitted light, I took a white pigeon. The play of colors is of course much fainter on account of the large amount of white light; but the colors can be seen with the naked eye and are quite distinct under the microscope, where they are really quite beautiful, probably because with colors mixed with a great deal of white, the effect increases up to a certain point with decreasing intensity of light. When the dry feather is examined under the microscope, the colors of transmitted light are seen also though of course weaker than those of reflected light, just as happens with Newton's rings. The nuclei appeared as water-clear spots in their darker and colored surroundings, and the lines separating the adjacent cells also appeared bright; so that the parts which by reflected light were dark and colorless are now light and colorless. If the feather is moistened with alcohol, the darker parts become lighter and if the feather is soaked in turpentine and dammar varnish, everything becomes so clear and transparent that the boundaries of the cells are scarcely visible, instead of being light, colorless lines on a dark colored ground. In some places which had not been penetrated completely by the varnish, there were dark, mostly long-drawn out, microscopically small bubbles.

"This shows clearly that the colors on a pigeon's neck are the colors of thin films and are due to two reflections, one when the light passes from the light into the solid and the other when the light comes out from the solid into the air. The outer skin of the chameleon also shows iridescent colors and I have shown conclusively elsewhere,[1] that they are

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[1] Denkschriften Akad. Wiss. Wien, 4, 179 (1852).

formed exactly as Newton's rings are. There the distance between the reflecting surfaces is very variable, so that the microscope always shows several colors simultaneously in the same cell. This is much less the case with the neck feathers of the pigeon, so that there is always one main color, with others appearing here and there. When examined under the microscope the important rays are those which are nearly perpendicular, in which case the predominant color is red by transmitted light and green by reflected light.

"Somewhat less definite results were obtained from a study of the tail feathers of the peacock, which are so beautiful in their iridescent colors and vividness of the metallic lustre. The dark brown pigment interfered with the microscopic examination and the tail feather of a white peacock showed no trace of iridescent colors. Depending on the way the light struck it, the position of the matt and the lustrous surfaces changed just as is the case with damask. In another point the peacock feathers differ markedly from those of the pigeon. They do not lose their colors when wetted, not even when boiled in turpentine, though the lustre and the tint are changed somewhat. For this reason it seems to me impossible that the iridescence of the peacock feathers can be due to a grating effect as with the iridescent buttons. I have found no trace of anything like that even with the highest magnification available. The theory of the iridescent buttons does not apply, but the theory of thin films does. If one places the so-called eye on the outer end of a peacock's feather between oneself and a source of light, horizontally on a support which turns on a vertical axis, it will be found that the colors remain the same during the rotation; but they change if the feather is raised or lowered. They are therefore independent of the direction of the light and vary with the angle of incidence. When passing from perpendicular to grazing incidence the green changes through blue to purple and copper-red changes to green.

"After these preliminary remarks on iridescent colors of feathers, we can discuss the properties to which they owe their metallic lustre. We find again the connection between lustre and color, which is of course a necessary consequence of the interference colors. There is also the opacity, the effect of which is quite noticeable, for the neck feathers of the white pigeon, though iridescent, show no trace of metallic lustre but only a sort of mother-of-pearl lustre. The third condition is also realized of high intensity of lustre and the degree of it in various parts of the feather determines the more or less metallic appearance. Quite apart from this, the copper-red and golden yellow portions of the feathers seem more metallic than the other portions because we are familiar with red and yellow metals.

"Now let us take a couple of illustrations which seem not to confirm what I have said about the relation between color and lustre in a substance showing metallic lustre. This lack of agreement is apparent and not real. The natural red iron oxide, haematite, is red but its lustre is white or gray like that of iron and is metallic. We are apparently dealing with a metallic lustre, the color of which has nothing to do with the absorption color. The relation between the two is quite different from that in substances which do not show metallic lustre. If one looks at a lustrous portion of the surface of haematite with a dichroscopic glass, one does not see one white or gray image and a second which is red, as one does with red paper or red sealing wax. Both images are gray, one being lighter than the other. The difference is therefore that sealing wax and red paper are red when they are lustrous, whereas haematite is red only when the surface is matt and is not red but gray where it is lustrous. The opacity of the substance makes its lustre seem metallic and like the lustre of iron or of graphite.

"Indigo is another case of the same sort. Indigo is blue but its lustre is copper-red and metallic. When it shows a metallic lustre there is no sign of blue and when one looks through the dichroscopic glass at a reflecting surface polished with steel or agate, one sees two reddish images of slightly different tint as in the case of copper, but no blue image.

The blue which we notice on the matt surface of indigo is an absorption color and is the same color which very small particles of indigo show under the microscope by transmitted light. Indigo is blue only where single particles are so detached that light from one side may pass through the particle and be reflected at the other side. If the particles are pressed down by a steel polishing tool, the reflections disappear and consequently the blue. The surface is now lustrous and since no light comes from the interior owing to the great opacity of indigo, the surface appears copper-red.

"I will cite another case in which a lustre which is distinctly not metallic becomes metallic suddenly if one removes the light which was coming through the lustrous surface. I have a large colorless gall-stone of cholesterin which I sawed in two and polished the section in order to show the beautiful crystalline structure. If one looks at this through a Nicol prism below the polarizing angle, so that the main axis of the calc-spar is parallel with the plane of incidence, one sees the structure of the gall-stone very clearly because one is no longer disturbed by the light reflected from the surface. If one turns the prism 90°, the light coming from the interior disappears and with it the structure, while the lustrous surface with its slight irregularities and its scratches looks exactly like a ground and polished surface of iron.

"The dichroscopic glass of course registers both impressions simultaneously and adjacent in the two images. I have found the same phenomenon of an apparent metallic lustre in the image given by the light polarized in the incident plane at the ground surfaces of a diamond lying on a black ground and at the natural surfaces of a piece of cerussite in the royal mineral cabinet. This suggests an explanation of the so-called metallic-like lustre of demantoid (the green garnet usually sold as olivine). If a mineral has a very high power of reflection, this is a property in which it resembles both the metals and the diamond. If it transmits light, this is a property in which it differs from the metals. If the amount of transmitted light is not too large, it may be relatively small in comparison with that reflected from some of the surfaces, in which case these latter will appear actually metallic, while the absorption color may be noticeable at other surfaces. Consequently a mineral which seems to combine metallic with adamantine lustre will show more adamantine lustre, the more light it transmits, while it will look more metallic the less light it transmits. This is confirmed by three samples of red silver ore which Director Hörnes had the goodness to show me and in Mohs' mineralogy under red silver ore, I find the statement that demantoid lustre is common in the light forms (proustite) and semi-metallic lustre in the darker one (pyrargyrite).

"We can now take up a case in which the objective conditions for any lustre are not present and still less for metallic lustre; but where we think we see metallic lustre. My honored teacher, Professor Dove, showed some years ago that two projections of a body, for instance a pyramid, in which one surface was black and the other white, gave a solid image in the stereoscope with lustrous surfaces as though cut out of graphite. The question why we have any luster at all has been explained by Oppelt and Helmholtz as being due to the fact that one sees a light surface with one eye where one sees a dark surface with the other. One cannot put forward as an objection that it is possible to see the lustre of smooth objects with one eye or that Burckhardt[1] has produced a sensation of lustre for one eye by certain combinations of white and black. This is only a suitable answer to those who consider that all lustre is due to unequal simultaneous impressions of corresponding surfaces on the two retinas. It is not a question of this but rather why in our special case we consider the relief that we see in the stereoscope as lustrous. When we look at matt surfaces, they appear to both eyes as equally illuminated. We therefore cannot conclude that the stereoscopic relief is due to matt surfaces, because we see white with one eye and black with the other. Lustrous surfaces are often dark to one eye and light to the other.

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[1] "Fortschritte der Physik," 310 (1854).

In fact, if one looks at a lustrous surface from close up, the light and the dark are never distributed the same for the two eyes. It is therefore natural in our experiment to get the sensation of lustre when we see the same point dark with one eye and light with the other.

"It is easy to convince oneself how important is the contrast between the impressions upon the two eyes. If one takes the two projections of a four-sided, flattened pyramid and paints two of the opposite sides black leaving the other pair white in one image and reversing this in the other image, one sees a lustrous pyramid in the stereoscope; but it looks as though it were subject to a more or less changing and flickering lighting. This is the effect of the conflict between the corresponding portions of the retinas which are receiving opposing sensations. Depending on whether the sensation in one or the other retina gets the upper hand, in the brain, one or the other pair of surfaces appears the more strongly illuminated.

"This does not explain however why the lustre is metallic. Dove's comparison with graphite has been accepted by everybody. The lustre of graphite is called metallic by the mineralogists and we find the three criteria satisfied: high reflecting power, opacity, and lack of an absorption color distinct from the lustre. If we cut a piece of graphite with a knife, the surface has a metallic lustre but it is not smooth and does not reflect regularly. If we try to polish it, the natural graphite takes no real polish for small crystals break out under the buffing steel. If one examines such a surface under the microscope by reflected light, one notices that the reflecting facets send back white light of considerable intensity; but the others appear absolutely black. The distances between the two types of facets are so small however that to the naked eye the light from the bright facets appears to spread over the dark intervening spaces and consequently the graphite has a gray, lustrous appearance.

"If we go back to the stereoscopic phenomena, we see the surfaces lustrous because what we see dark with one eye we see light with the other; but we do not see them either as smooth or polished partly because there is no regular reflection and also because we see the more or less rough paper with one eye and the black, matt, surface of ink with the other. The black seen by one eye combines with the white seen by the other to give an alternately lighter or darker gray. We therefore see the surfaces gray and a gray which we cannot account for as gray pigment. Consequently we see the surface as somewhat rough and not polished, as lustrous and distinctly not matt, and since the sensations are nearest to those that we get with graphite and consequently we conclude that the surface looks like graphite.[1]

"In describing the experiment with the flattened four-sided pyramids, I mentioned that the conflicts between the two fields of vision produced the impression of a flickering illumination. The more marked this effect the less continuous the metallic appearance and, in cases where the black predominated, I could persuade myself that the whole surface was covered with a glossy black paper. If one is to get the impression of metallic lustre, the impressions on the two eyes must blend to a gray. The reason for this is clear so soon as we ask ourselves why lustrous black substances do not have metallic lustre, even though they are opaque and show no absorption color differing from the color of the lustre. The third condition for metallic lustre is lacking. They do not show metallic lustre because they are black and therefore reflect too little light. If they reflected enough light to have metallic lustre, a smooth surface would send back light as polished steel does, and therefore would not appear black. An uneven surface would also not appear black but lighter or darker gray according to circumstances, because the images on the retina of the single specular surfaces would reflect light enough to cover the dark intervening spaces by so-called irradiation, as happens with graphite.

"We have now analyzed metallic lustre in a number of cases in which it was observed in non-metallic substances,

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[1] [It would hardly produce this effect upon people who had never seen lustrous graphite.—W. D. B.]

including cases where the objective conditions for lustre were not present at all. We will now return to our starting point to the gall-stones with metallic lustre and will ask ourselves if they are similar to any of the cases studied. From what has been said as to their structure, it is clear that they are analogous to the exfoliated mica sheet. On account of the close series of reflections, they reflected back a great deal of light and were practically opaque because the light which was reflected twice from each layer could not penetrate deeply. The yellow color is due to the passage of the light through the colored organic ground. Since the colored light is specularly reflected, it is the color of the lustre even though in origin it did not differ from an ordinary absorption color.[1] The gold color arose here just as it does in certain imitation gold frames which are first covered with silver foil to give the metallic lustre and then coated with a thin film of deeply colored varnish to change the white of the silver into the yellow of the gold."

This would be more satisfactory if Brücke had actually prepared a golden gall-stone. As it stands, it does not seem to me that Brücke has really made matters clear.

Helmholtz[2] gives the following explanation of the phenomenon of metallic lustre when the two images in a stereoscopic picture are colored or illuminated slightly differently.

"When light falls on a matt surface, it is scattered uniformly in all directions and the surface appears equally bright from whatever angle it is viewed. Consequently, under normal conditions it appears equally bright to both eyes. Polished surfaces, on the other hand, give a more or less regular specular reflection. There may be a large number of larger or smaller, rounded protuberances. If these projections are polished so as to give surfaces predominating in one plane, incident light is reflected predominantly in the direction in which a perfect reflecting surface would send all

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[1] [This seems to be reasoning in a circle.—W. D. B.]

[2] "Handbuch der physiologischen Optik," 933 (1896).

the light. It will often happen that one eye will be in line with the reflected light and the other not, in which case the one eye will see the surface more brilliantly lighted than the other will. When we look through at a stereoscopic picture, of which one image is brighter than the other, we receive the impression to which we are accustomed with polished surfaces but which we never get from a matt surface, and the picture looks polished. In a similar way, if a polished surface is surrounded by a colored one, the reflected light that reaches one eye may be colored differently from that which reaches the other eye, whereas a matt surface, under normal conditions, will appear colored uniformly. In a stereoscopic image, if one field is colored slightly differently from the other, this causes a sensation similar to that which a polished substance would produce. As a rule the color of the polished substance itself mingles with the two reflected colors, so that the difference in the colors reflected to the two eyes is ordinarily not great and consequently it is easier to produce the impression of lustre by combining two colors which are not very different, than by combining very lustrous but very different colors. In the latter case there is more effect of contrast than of lustre.

"According to Wundt's observations lustre can be obtained most easily by the combination of two colored fields when the two differ about equally from the background. When the contrast is great, one field or the other is apt to predominate too strongly... Dove's observation is important that when one or the other color predominates very much, the lustre disappears but reappears at the moment of change from one to the other when the two fields are seen simultaneously.

"Metallic lustre is characterized by the fact that the regularly reflected light is itself colored and not white as in the case of transparent substances. Metallic lustre is therefore to be seen with substances which give the colors of thin films, such as the brilliant feathers of some birds, and with substances like indigo which are very strongly colored and have high indices of refraction."

It is not clear from this why we should not get the effect of metallic lustre by looking at suitable portions of the landscape through spectacles having two differently colored glasses. With a yellow and a blue glass in the spectacles one is combining two different images in much the same way as when one looks through a stereoscope at a blue and a yellow picture, and yet I am assured that no effect of metallic lustre can be obtained in this way.

Spring[1] has published some experiments which seem to him to reconcile the views of Dove and Brücke. "Metals have a peculiar, indefinable lustre which is so characteristic that to many people the word metal connotes it. I do not mean by this that everything which shows a metallic lustre is a metal and still less that a metal cannot occur in a form where one sees no lustre. The statement is too broad and the converse is not always true. Besides there is nothing absolute about the word metal itself. Since metallic lustre is not a fundamental property of matter, one may ask what physical conditions give rise to it.

"Unless I am mistaken Dove[2] made the first attempt to account for the phenomenon. He had looked through a stereoscope at two images of a pigment, one colored blue and the other yellow. He expected to get an image in relief which would be colored green. To his great surprise the mixture of colors gave a glistening surface like that of polished steel. When he repeated the experiment by superposing a black and a white image he obtained the gray metallic lustre of lead or tin. Dove concluded that metallic lustre, or rather the shine, is always due to the reflection of light from two surfaces placed one behind the other. The focus of the eye being different for each color, the stereoscope cannot give a complete superposition of two images which are colored differently. In the case of a metal there are also produced two reflections of light, one from the true surface and the other from below the surface.

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[1] Bull. soc. chim. Paris (2), 50, 218 (1888).

[2] Pogg. Ann., 83, 169 (1851).

"This hypothesis postulates a definite transparency of metals, in fact quite a marked transparency because the reflections of light must take place from surfaces whose distance apart is of the order of the differences in the focal lengths of the eye for different colors. In addition Dove's hypothesis does not account for lustre on really transparent substances. The hypothesis is nevertheless generally accepted and Brewster[1] develops it further saying that metallic lustre is a *subjective* phenomenon due to the effort made by our eyes in accommodating themselves to the different colors. One other explanation has been offered, that by Brücke.[2] According to him the color of the light reflected from the surface of a substance not having metallic lustre will be independent of the real color of the reflecting substance, while for the metals the color of the reflected light is that which we attribute to the metals, the incident light being white. Brücke mentions as another condition for metallic lustre the intensity of the reflected light, an intensity dependent on the opacity of the metals. He points out also that total reflection of light gives a complete imitation of metallic lustre.

"Brücke's theory is diametrically opposed to that of Dove, the first attributing to the opacity of metals what the second attributes to their transparency. I have made an observation which may perhaps help toward the solution of the question. It takes from the metallic lustre everything that is specific and thereby harmonizes the two theories.

"In the studies which I have made for ten years to see whether the properties characteristic of liquids and gases are to be found to some extent in solids, I have had occasion to submit a considerable number of substances to high pressures. The compression was carried out[3] in a steel cylinder with polished inner walls. The powders to be compressed were always very fine and, so far as possible, they were prepared by chemical precipitation. This was always so for the

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[1] "Fortschritte der Physik," 8, 311 (1852).

[2] Ibid., 17, 313 (1861).

[3] See Bull. Acad. roy. belg., (2) 11, 9 (1880).

sulphides, oxides and carbonates, and usually so for the salts and substances soluble in water.

"Some of the substances have formed cylinders with more or less marked metallic lustre, even when the powder was not that of a metal; others on the other hand formed cylinders having surfaces showing a glassy lustre which was more or less perfect, depending on the degree of agglomeration. For instance bismuth sulphide, copper sulphide and manganese dioxide showed a metallic lustre while zinc sulphide, mercuric oxide, copper carbonate, etc., appeared to be varnished on the surface. If the fine powders of substances belonging in these two categories are examined under the microscope by transmitted light, it is easy to see what is the controlling physical factor. Without exception the substances which show metallic lustre when compressed are opaque when powdered or at least appear so under the conditions of the experiment, while the other class of substances are more or less transparent in the form of fine powder.

"Metallic lustre therefore appears when a polished surface is formed from a sufficiently opaque substance. The more complete the opacity and the smoother the surface, the more pronounced is the metallic lustre. Since there is probably no substance absolutely opaque, there is probably also no substance absolutely transparent. It all depends on the thickness of the film. Between vitreous lustre and metallic lustre there may therefore occur all the intermediate stages which one can distinguish between transparency and opacity. According to this, metallic lustre does not depend in any way on the specific chemical nature of a substance but on its physical state. An allotropic form of a metal which was sufficiently transparent would have a vitreous lustre. This point of view harmonizes the theories of Dove and Brücke. Metallic lustre is produced when light is sent back from two reflecting surfaces (theory of Dove); but only when the two surfaces are so close together as to give almost total reflection (theory of Brücke)."

Michelson[1] has studied the special case of metallic lustre as observed in butterflies and beetles. "It has been abundantly proved that the usual 'flat,' 'dead,' 'uniform' coloring, brilliant as this sometimes can be, *e. g.*, in birds, butterflies, and flowers, finds its simple explanation in the existence of pigment cells; so that the same cause (doubtless with many modifications) is here effective as in the great majority of cases previously considered. But the lively, variable 'metallic' glitter of burnished copper or gold; the reflection from certain aniline dyes; the colors of certain pigeons, peacocks, humming birds, as well as a number of butterflies, beetles, and other insects, require another explanation.....

"The designation 'metallic' at once suggests that there may be some common property of all these colors which is typified by the metals themselves. But, as is well known, the principal characteristic which distinguishes the metals from all other substances in regard to their action on light is their extraordinary opacity. A very important consequence of such opacity is that light is practically prevented from entering the substance at all, but is thrown back, thus giving the brilliant metallic reflexion so characteristic of silver, gold, copper, etc. In fact, the distance to which light can penetrate in most metals is only a small fraction of a light wave; so that a wave-motion such as constitutes light, strictly speaking, cannot be propagated at all. Again, as this opacity may be different for different colors, some would be transmitted more freely than others, so that the resulting transmitted light would be colored; and the reflected light would be complementary to the transmitted color. For most metals the difference is not very great; so that the reflected light, except in the case of gold and copper and a few alloys, is nearly white. In the case of the aniline dyes, however, there is a marked difference, as is clearly shown by their absorption spectrum. In transmitted light, even a very small thickness of fuchsine shows no yellow, green, or blue, and gives as a resultant of the remaining colors a beautiful crimson. The

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[1] Phil. Mag., (6) 21, 554 (1911).

light which it reflects, however, is just this yellow and green which it refuses to transmit, and it accordingly shimmers with a metallic, golden green color, which changes when the surface is inclined, becoming full green or even bluish green when the illumination is sufficiently oblique.[1]

"The chief characteristics by which metallic reflexion may be distinguished may be summarized as follows:

"1. The brightness of the reflected light is always a large fraction of the incident light, varying from 50 percent to nearly 100 percent.

"2. The absorption is so intense that metal films are quite opaque even when their thickness is less than a thousandth of a millimeter.

"3. If the absorptio nvaries with color, that color which is most copiously transmitted will be the part of the incident white light which is least reflected—so that the transmitted light is complementary to the reflected.

"4. The change of color of the reflected light has already been mentioned. It follows the invariable rule that the color always approaches the violet end of the spectrum as the incidence increases. If the color of the normal reflexion is violet the light vanishes (changing to ultra-violet), and if the normal radiation be infra-red it passes through red, orange, and yellow as the incidence increases.

"While the criteria just considered are the simplest and most convenient for general observation, it is to the more rigorous results of more refined optical methods that we must look for the final test of the quality of reflection in any given case; to determine whether or not a color phenomenon may be due to metallic reflection or to one of the other general causes. Such optical tests are furnished by the effect of reflection upon polarized light. The elements of the resulting elliptic vibrations may be expressed in terms of the

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[1] The change in color is very much more marked when the light is polarized perpendicularly to the plane of incidence. As the angle of incidence approaches the angle corresponding to the "polarizing angle," the color is a deep blue or even purple.

amplitude ratio R of the components, and of the phase difference P corresponding to the angle of incidence I."

When P and R are plotted as ordinates against I as abscissas, we get the phase curve and the amplitude curve, and "it is evident that metals have a smoother phase curve than semi-metallic substances like graphite and selenium, and these show less abrupt changes than do transparent substances such as glass and quartz. In fact we may take the steepness of the curve where it is steepest (better where the phase difference is $^1/_4$) as a measure of the transparency of the substance; and theory shows that this *steepness* is in fact proportional to the *absorbing power* of the substance......

"In the aniline colors the absorption varies enormously with the color, and we have all the gradations from metallic reflection to almost perfect transparence combined in a single specimen. The measurement of the phase change and the amplitude ratio for fuchsine and diamond green show changes in the form of the curves almost identical with those found for silver, steel, graphite, selenium, flint glass, crown glass, and quartz... The phase curve is much more characteristic in its changes than the amplitude curve. These specimens [of fuchsine and diamond green] are prepared by dissolving the aniline color in hot alcohol, filtering hot, and covering a hot glass surface with the solution. The alcohol evaporates rapidly leaving a mirror surface of a thickness of the order of a thousandth of a millimeter.

"A quite remarkable alteration occurs in the phase curves when the solution is diluted. The film deposited is very much thinner than before (from one-tenth to one one-hundredth of the former thickness), and for some colors, the thickness is so small that considerable light is reflected from the surface of the glass. The resulting curve may then be *negative*, in this case for the colors red, orange, and yellow. Such a result has been predicted from theoretical considerations;[1] but, so far as I am aware, no attempt has been made to show that this depends on the color of the incident light.

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[1] Drude: "Theory of Optics," 294.

This, however, follows if we consider that the condition for such a negative phase curve is that the transition layer has an index of refraction greater than that of the second medium; and as the refractive index for magenta is low at the blue end of the spectrum and high at the red end, the inversion of sign is strictly in accord with the theory, of which indeed it furnishes a striking confirmation.

"On applying the simpler general tests of metallic reflection to the case of iridescent plumage of birds, scales of butterflies, and wing-cases of beetles, one is at once struck with the close resemblance these bear to the aniline colors in every particular:

"1. The intensity of the reflected light is much greater than for the 'non-metallic' plumage, etc.; in some cases approaching the value of the reflection factor of the metals themselves.

"2. The reflected light is always colored, showing either a rapid change of index of refraction, or of coefficient of absorption with the wave-length or color; and, indeed, it may perhaps be objected that these colors are far more vivid than any of the reflexion hues of the aniline dyes, or of any other case of 'surface color' hitherto observed.

"3. In the cases which could be investigated for this relation (unfortunately rather few) the transmitted light is approximately complementary to that which is reflected.

"4. The change of color with changing incidence strictly follows the law already mentioned—the color always changing toward the blue end of the spectrum as the incidence increases.

"This remarkable agreement has been pointed out by Dr. B. Walter in an admirable essay, 'Die Oberflächen- oder Schiller-Farben' and it is shown that none of the other causes of color phenomena (in particular interference and diffraction) can be effective; the laws which govern these last being totally different. It is therefore somewhat surprising to find that the contrary view is still held by many eminent naturalists, and it is hoped that the further evidence here presented may serve to emphasize the distinction between 'metallic' or 'surface' color and the remaining classes of color (due to pigments, interference, and diffraction).

"In attempting to apply the more rigorous optical test of the measurement of the phase-difference and the amplitude-ratios. one is met at the outset with the serious difficulty of the absence of true 'optical' surface. In fact, the materials we have to deal with (feathers, butterfly scales, beetle wing-cases) are so irregular that the quantity of 'regularly' reflected light which is brought to a focus by the observing telescope is insignificant, and is often masked by the light diffusely reflected. But by the simple device of replacing the objective of the collimator and of the observing telescope by low-power microscope objectives of small aperture, these difficulties are so far removed that it has been possible to obtain results which compare favorably with those obtained with the aniline films. In some of the measurements it has been found possible to deal with a single butterfly scale; and in these the irregularities of the surface were often quite insignificant, or of such nature that they could be taken into account......

"The correspondence between the results of a set of measurements on a beetle having a lustre resembling that of burnished copper and of a set of measurements on a *thin* film of magenta is so remarkable that it leaves no room to doubt that in this case the metallic coppery color of the wing-case is due to an extremely thin film of some substance closely analogous in its optical qualities to the corresponding aniline dye.[1] The thickness of the magenta film was not very accurately determined; but, from the fact it was deposited from a solution of 1/20 of the concentration of that which produced the corresponding *thick* film (whose thickness is about 0.005 mm), it is estimated that the thickness of the film is of the order of 0.00025 mm. It is, doubtless, unsafe to draw any more definite conclusion from this regarding

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[1] The character of the curves for the organic film is considerably more "metallic" than the corresponding curves for magenta.

the film of the wing-case than to say that it is probably of the same order.

"An attempt was made to check this estimate by the following simple device. A portion of the ellipsoidal wing-case of mean radius R was removed by passing it very lightly over a piece of the finest emery-paper fastened to a flat piece of wood. This left a clean elliptical hole of mean radius r showing the edges of the 'metallic' film whose width, h, could not be appreciated in a microscope with a half-inch objective. If this be estimated at less than 0.001 mm the relation $t/h = r/R = 0.5 \text{ mm}/5 \text{ mm}$ gives t, the thickness of the film, less than a ten-thousandth of a millimeter.

"A second specimen of the same general coppery lustre gave a set of curves which showed a double reversal; the phase-curve being positive for crimson and red, negative for orange and orange-yellow, and positive again for the yellow, green, and blue. A series of curves for a very thin film of magenta (estimated thickness 0.00005 mm) gave results surprisingly resembling those of the beetle, the second point of inversion being, however, in the green instead of the yellow, and the 'metallic' character of the film being much less marked than in the beetle wing-case. The resemblance in the lower curves, showing the variation of maximum with the color, is even more striking. It can scarcely be doubted, therefore, that here again the metallic color is produced in a film whose thickness is of the order of a ten-thousandth of a millimeter or less.....

"The beetle wing-cases furnish in many cases a fairly smooth surface, and the difficulties in obtaining the necessary measurements are far less than when working with feathers of birds or with butterfly scales. Nevertheless, the same general characteristics obtain in these, in both the phase-curves and the amplitude-ratios. The two curves do not always correspond; but it is probable that the difference may be explained by the difficulty in obtaining accurate results with surfaces so irregular. It is worthy of note that in all of these curves (except that furnished by a *red* humming-bird feather) the curves are negative; from which it is fair to conclude that the film which produces the surface color is very thin.

"The total number of specimens which have been examined is perhaps not so large as it should be to draw general conclusions, and it is clearly desirable that it be extended; but, so far, the evidence for *surface film*, as the effective source of the metallic colors in birds and insects, is entirely conclusive. It is clear that in all of these curves the descriptive color corresponds in general to that color for which the phase-curve is least steep and for which the amplitude curve is highest; and is complementary to the color for which the phase curve is steepest and the amplitude curve is lowest, as we should expect; since the former corresponds to high reflective power, while the latter is characteristic of transparent substances with but moderate reflecting power."

Some exceptions were found by Michelson.[1] "The measurements of the phase-difference in the light reflected from the blue-winged butterfly (*Morpho alga*), instead of being zero at incidence, had values which ranged from +0.15 to —0.15, and which were found to vary with the orientation of the specimen. There were also corresponding changes in the general character of the phase- and amplitude-curves, all of which showed clearly that the whole phenomenon is considerably complicated by a structure of the scales. An examination under the microscope revealed the presence of exceedingly fine hairs (which can only be seen in reflected light) arranged without much regularity with their length parallel with that of the scale.[2] It was at first natural to attribute the blue color to the light diffracted from these hairs; and it is not impossible that some of the silky sheen which these butterflies exhibit is at least in part due to these hairs, whose diameter is much less than a light-wave, and which are therefore in the same relation to the light-waves

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[1] Phil. Mag., (6) 21, 564 (1911).

[2] There are three varieties of scales, of different shapes. These are arranged in overlapping layers, the outer layer being quite transparent and the lower one opaque. The middle layer is the one showing blue by reflection and brownish yellow by transmitted light.

as the small particles which cause the blue color of the sky. But the changes in color with varying incidence, so characteristic of true 'surface colors,' were precisely the same in this specimen, and were practically independent of the orientation; whereas the changes with the angle of incidence, which should result on the hypothesis that the color is due to diffraction, should follow an entirely different law.

"Another species of butterfly (*Papilio Ulysses*) was also examined and found to yield normal 'surface-color' curves. There is in this case no such minute linear structure as in the case of *Morpho alga;* and as here the phenomenon is clearly a case of 'surface color,' so it is highly probable that the same cause is effective in the case of *Morpho*. Many other specimens were subsequently examined, but all fell into one or other of the two classes typified by these two.

"If a specimen of the beetle popularly known as the Diamond Beetle is examined with a low power under the microscope, the bright green dots on the wing-case are seen to consist of depressions from which spring brilliant and exquisitely colored scales; the colors varying throughout the range of the spectrum (green, however, predominating). The colors exhibited by these scales are so vivid and varied, and the changes so rapid with varying incidence, that it was at once evident that the effect must be due to diffraction from regular striations, which were accordingly looked for under a magnification of about 1000 diameters. There were occasionally faint indications of striated structure, but so uncertain that if other indications had been less decided it might have been concluded that some other cause must have been effective. But on putting the microscope out of focus a moderately pure *spectrum* was observed and by measuring the angles of incidence and diffraction of the various colors, the 'grating' space could be determined, and was found to be of the order of a thousandth to a two-thousandth of a millimeter.

"The specimen was next examined by reflected light[1]

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[1] The observation is somewhat difficult on account of the very small working space when using high powers.

and the striations at once appeared, the count of the striations giving numbers agreeing very well with the calculated values. Frequently a single scale showed two or even three series of striations, giving corresponding spectra in three different directions. Another important feature of these 'gratings' was shown in the fact that the light is all concentrated in a single spectrum, showing that the striations must have an unsymmetrical saw-tooth shape.[1]

"On immersing the specimen in oil or other liquid, little or no change is observed except in those specimens in which a small communicating aperture exists in the neck (point of support) of the scale. The oil can be seen to gradually fill the interior, and simultaneously all trace of color vanishes.[2] It appears then that the color in this case is due to fine striations on the interior surface of the scale.

"*Plusiotis resplendens* is a beetle whose whole covering appears as if coated with an electrolytic deposit of metal with a lustre resembling brass. Indeed it would be difficult for even an experienced observer to distinguish between the metal and the specimen. On examination with the Babinet compensator, it was found that the reflected light was *circularly polarized* even at normal incidence, whether the incident light was polarized or natural. The proportion of circularly polarized light is greatest in the blue, diminishing gradually in the yellow portion of the spectrum, and vanishing in the orange-yellow—for which color the light appears to be completely depolarized. On progressing towards the red end of the spectrum, traces of circular polarization *in the opposite sense* appear, the proportion increasing until the circular polarization is nearly complete in the extreme red.

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[1] It may be noted that the objection that the colors of birds and insects cannot be due to diffraction on account of the equalizing effects of the varying angles of incidence and diffraction, would not apply if the striations are so fine as to give practically a single spectrum extending over a range of 45°.

[2] Sometimes a faint indication of color remains (usually greenish) which shows the characteristics of surface color. It is probable that the surface color acts conjointly with the effect of diffraction, and indeed the character of the spectrum indicates an excess of green which may thus be accounted for.

"It was at first suspected that the phase difference (not always so great as one-quarter, but varying between 0.15 and 0.25) was due to linear structure, as in the case of *Morpho alga;* but on rotating the specimen about the normal no change resulted. The effect must therefore be due to a 'screw structure' of ultra-microscopic, probably of molecular dimensions. Such a structure would cause a separation of natural incident light into two circularly polarized pencils traveling with different speeds, and having different coefficients of absorption. Such cases have been observed in some absorbing crystals; but whereas in these the difference in absorption between the two circularly polarized pencils is quite small compared with the total absorption—here one of the two is almost totally reflected, while there is scarcely a trace of the other.

"If this hypothesis be correct, however, the selective absorption (or reflection) being reversed at the other end of the spectrum—then for the orange-yellow the resulting light should be compounded of these two; and the resulting light should be plane-polarized and not depolarized. The depolarization is in fact only apparent; for on using a moderately high power objective it is at once evident that there is a structure in the wing-case which causes a difference of phase between components varying very rapidly from point to point; and the resulting plane of the plane-polarized light varies with corresponding rapidity, leaving no trace of polarization when the observation is made with a telescope.

"The absorption coefficient for this specimen is quite of the order of that of the metals; and the thickness of the 'metallic' film is of the order of a ten-thousandth of a millimeter."

It will probably be simpler to consider the ordinary cases of metallic lustre before taking up the special case of binocular lustre, even though the two are intimately connected. Electrolytic silver is white and not metallic; polished silver is gray and metallic; while pulverulent silver is black and not metallic. The black of pulverulent silver is quite simple because the light is absorbed by multiple reflectors until no light comes out. As was shown by Wood,[1] the same phenomenon can be obtained on a large scale with a bunch of polished steel needles. We get the sensation of white only when we have diffused reflection. With electrolytic silver the innumerable facets scatter the light in every direction, without absorption of particular rays, and the metal appears white. In the case of the polished metal we have a high reflecting power but the reflection is specular and relatively little comes to the eye unless one happens to be in the direct line with the light. In other words we have very low diffuse reflection and consequently the metal appears gray and not white. Since the metals are opaque and have high reflecting power for the rays which they absorb, all the reflection is from a space bounded by two surfaces very close together, the outer surface and the inner surface to which the light penetrates. This double reflection is always associated with metals and is therefore called by us metallic. We get the same phenomenon with such solids as magenta, and we speak here of metallic lustre. In the case of total reflection at a glass surface we have high specular reflection and low diffuse reflection, so the surface appears gray. We are getting reflection from two surfaces close together and consequently we get the effect of a metal. We know that we are getting reflection from at least two surfaces because total reflection disappears completely if the film becomes too thin.[2] With the colors of thin films we have reflections from two surfaces very close together and consequently they are metallic; we have interference and consequently the reflected light is colored. The colors of thin films are more intense and more metallic when there is a dark background which prevents other light from being mixed with the colors of the thin films.

While we are not conscious of the reflections from the two surfaces, it is probable that the eye takes them into account subconsciously and that we do get a slight but per-

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[1] "Physical Optics," 449 (1911).

[2] Ibid., 374 (1911).

haps continuous change of focus. If this is the case, we should expect to get the effect of a metal whenever we had similar adjustment of focus. Helmholtz has applied this point of view to the case of solid metals where he is laying stress more especially on the differences in adjacent portions of the surface. A given portion of the slightly irregular surface will appear bright to one eye and dark to the other. The adjustment of these two impressions gives rise to a flutter effect which is the physiological significance of metallic lustre.

In stereoscopic or binocular lustre[1] the axes of the two eyes converge, while their normal position of repose is parallel. If the eyes get at all fatigued, they waver and do not hold their convergence. As soon as the error becomes noticeable, the brain brings the axes back again so that the pictures coincide once more. If the two pictures are colored or shaded differently, one eye will get tired before the other and the brain will momentarily give most of its attention to the second eye which is pointing in the right direction, while the first or fatigued eye will go more or less to sleep and will turn outward. After a short space of time, the second eye becomes tired and the first rested. The brain gives its attention now to the first eye, while the second turns outward. The result is that the brain gets a fluttering sensation superimposed on the perception of form and color. This flutter comes from the direction muscles and not from the retina. If the two pictures are of somewhat different brightness, the attention will shift from one to the other and the iris muscles will also flutter; the difference must not be too great or the brighter image will hold the attention all the time, so that there will be a more nearly steady state with less flutter. If the two pictures are of different colors there will be a flutter of color sensation through the optic nerve in addition to the flutter of the focusing muscles.

The impression of lustre is therefore due to the nervous flutter or unsteadiness of attention due to the brain from the

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[1] I am indebted to Dr. Edgar Buckingham of the Bureau of Standards for this suggested interpretation of binocular lustre.

directing muscles, the iris muscles, the focussing muscles, or the retina; or perhaps, in some cases, of all four. The cause of the flutter is a rapid shifting of the attention back and forth between the two eyes, probably as a result of fatigue. If fatigue is the cause, the eyes of different people would behave very differently. Some people would get the impression of binocular lustre when others would not. This seems actually to be the case, for Dove mentions that some of the phenomena are not very striking and many people do not see them. Brewster experienced no sensation of lustre when he combined in the stereoscope black and white surfaces having no geometrical form whereas Dove and Rood did perceive lustre under the same circumstances. Woolen goods striped black and white appeared lustrous to Burckhardt though they do not to most people. This seems to be an exaggerated case of the eyes wandering over the surface in a jerky manner.

Brewster says that lustre is due "to the effect of the eye in combining the two stereoscopic figures and to the dazzle occasioned by the alternating intensities of the two combined tints, the impression of one of the tints sometimes disappearing and appearing," which is practically the view advocated here though not put in quite so specific a form. In fact Brewster goes on to say that "the optic axes are in constant play, not only in varying the distance of their focus of convergence to unite similar points at different distances in the two diagrams, but in maintaining the unity of the picture by rapidly viewing every point of its surface." Where Brewster is wrong is in considering that binocular lustre has no relation to those varieties of lustre arising "from the combination of lights reflected from the outer and inner surfaces of laminated, transparent, or translucent bodies." Lustre is essentially a physiological or psychological phenomenon in all cases.

The more nearly the surface actually resembles a metallic surface, the easier it will be for the eyes to see it as metallic and the less fatigue will be necessary to produce the sensation of metallic lustre. This is brought out very clearly in Rood's experiments. Brücke points out "that we get the impression of a metallic surface even with substances which have in themselves no metallic lustre, provided we have simultaneously a roughened surface and a high reflection of light. The most familiar instance of this is the silvery streak which marks the reflection of the moon from a water surface rippled by the evening breeze. The wavelets make the surface of the water seem rough and the accompanying high reflection of light makes the water look metallic, more metallic than the disc of the moon itself."

Buckingham proposes distinguishing as follows between "glitter," "lustre," and "shine." When one looks at the moon as it is reflected from water that is not too smooth, one can distinguish the separate moving bright spots by looking carefully, and the effect is that of "glitter." If one looks farther out, there comes a point beyond which the separate moving bright spots are indistinguishable to the conscious mind, although they may still be there. This gives the impression of "lustre." From a quiet, clean surface of mercury or from a first-class optical mirror, one gets, not "lustre," but "shine." Shine is merely specular reflection. On this basis lustre is either an imperfect and irregular shine in which the irregularities are too fine to be noticed separately, or a fine-grained glitter—also too fine to be recognized consciously as composed of separate bright spots.

This seems to be a logical distinction. The only objection to it is that it excludes a mercury surface and the case of total reflection from being cases of metallic lustre and these are usually taken as our standards. On the other hand Brücke says: "In order to get the full extent of metallic lustre one must see the surface as such. If a metallic surface is ground and polished very highly, and if one is some distance away, the surface disappears completely and one sees only one's own image. It is doubtful whether a man who had never seen such a mirror would recognize it as a metal plate without further test even though he were otherwise familiar with metallic objects. If one sees the surface, owing to scratches from grinding or to defective polishing, the character of the defective spots shows one at once that one is looking at a metallic surface." The discrepancy between Buckingham's definition and the usual practice disappears if one speaks of metallic lustre only when one can see the mercury surface on account of dust, etc., or, in the case of total reflection, when the glass surface is not absolutely plane.

Buckingham raises an interesting point as regards the effect of spectacles with differently colored glasses. When looking at a landscape, the distance is so great that the eyes are pointed and focussed for infinity. Consequently a change of attention from one eye to the other does not cause any motion of the eyes, and consequently no special sensation of lustre. One might perhaps get an effect of lustre if one looked at an object closely—say 18 inches from the eyes, and it is also possible that some people might get an effect of lustre by looking even at a distant landscape. If they did, it would prove that a flutter of the directing muscles was not essential to the sensation of lustre. It might even turn out that the essential element was not a flutter of any particular set of muscles but a flutter of the attention. There is evidently room for a good deal of interesting experimenting here.

This hypothesis of Buckingham's regarding the production of the sensation of lustre seems to combine all the good points of the theories of Dove, Brewster, Rood, Brücke, Helmholtz, and Spring. It takes into account the possibility of great differences in individual observers, which has not been recognized specifically by the others, and it has the advantage as a working hypothesis of suggesting a great deal of research work which ought to be done.

Since metallic lustre of the ordinary type occurs when there is no light reflected back from any depth, we should get vitreous lustre when the transparency increases, which is what actually occurs. There is, therefore, no sharp dividing line between the two forms of lustre and there seem to be no quantitative experiments indicating at approximately what point most people would begin to differentiate between metallic and vitreous lustre. As a matter of fact it is very difficult to get people to commit themselves in any special case. Suppose one takes an electric fan with a light behind and a light in front. By varying the relative intensities of the two lights one can change from great opacity of the fan to great transparency and the lustre should apparently vary from metallic lustre to vitreous lustre. With an aluminum fan some people are willing to admit that this happens; but with a fan having brass blades, the color is so distinctive that most people insist that they see metallic lustre under all conditions. This seems to be an ideal case for a quantitative study of the difference between metallic and vitreous lustre.

It is not possible at present to give real definitions of the different types of lustre which have been distinguished by the people who write about gems; but the waxy lustre apparently occurs when we have a medium made turbid by a transparent phase. A suitable emulsion of oil in water is waxy. With increasing opacity it becomes opalescent. If too much fusible material is added in making porcelain, the mass becomes more transparent and we get a waxy porcelain. It is to be hoped that this whole question of lustre and of the types of lustre may receive more attention in the future than has been the case for a good many years. There seems to have been a wide-spread though erroneous opinion that we knew all about it.

Cornell University

THE ELECTROLYTIC PRODUCTION OF FLUORINE[1]

BY W. L. ARGO, F. C. MATHERS, B. HUMISTON AND C. O. ANDERSON

Fluorine was first prepared in quantity by H. Moissan[2] by the electrolysis of anhydrous hydrofluoric acid rendered conducting by the addition of potassium hydrogen fluoride. Moissan began with a platinum U-tube as his electrolyzing vessel, the openings in which were closed with fluorite stoppers in which the electrodes of platinum-iridium were set. Later he found that copper would serve equally well as an electrolyzing vessel but that platinum electrodes must be used, Fig. 1. With copper electrodes, polarization took place due

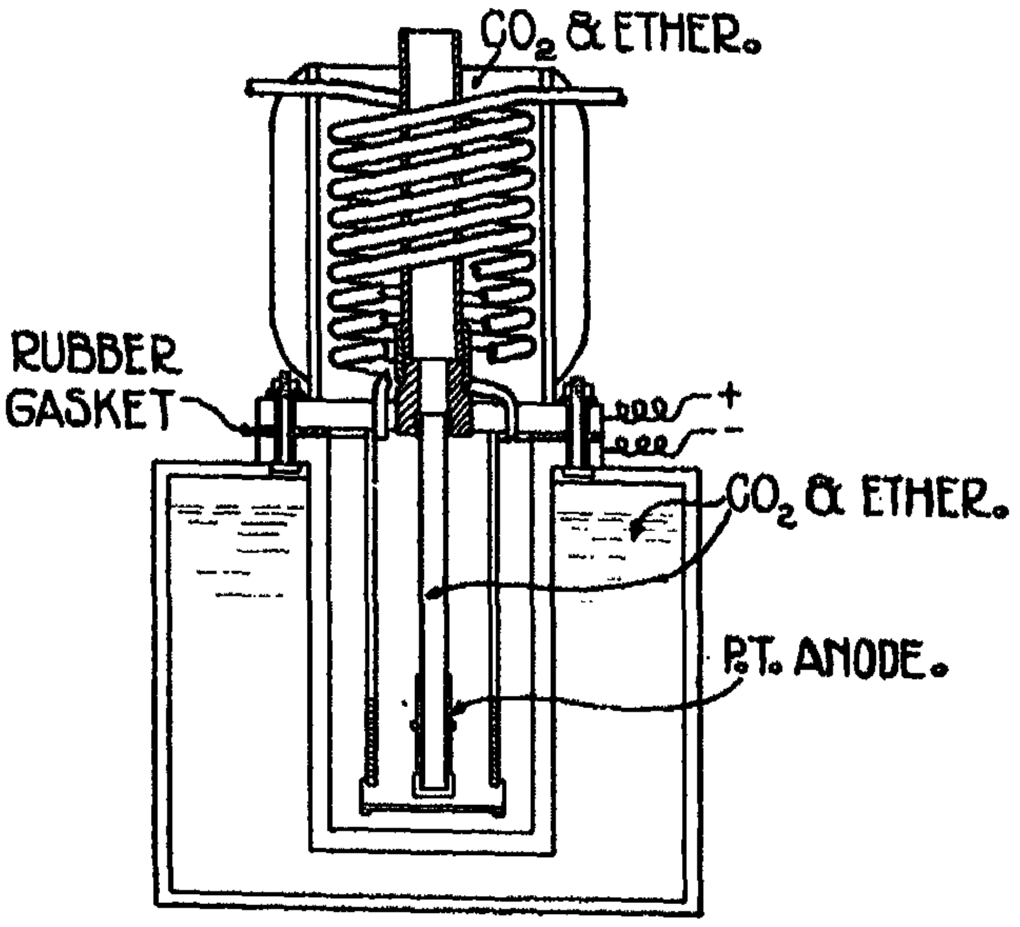

Fig. 1

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] Comptes rendus., 102, 1543 (1886); 103, 202, 256, 850 (1886); 109, 362, 637 (1889).

to the formation of a non-conducting film of copper fluoride on the anode. Owing to the heat generated in the electrolysis and the high vapor pressure of hydrofluoric acid under usual laboratory conditions, it was necessary to keep the cell well cooled. In his earlier experiments, Moissan effected the cooling by the evaporation of chlormethane. Later he used acetone containing solid carbon dioxide. Other investigators have used calcium chloride freezing mixture[1] and alcohol and solid carbon dioxide.[2]

The usual method of preparing anhydrous hydrofluoric acid was to heat potassium hydrogen fluoride.[3] Moissan decomposed the anhydrous salt in a platinum retort. Ruff and Plato,[4] and Goldschmidt[5] replaced the platinum retort by a copper one and found that this latter was not acted on appreciably. Ray and Banta confirmed this result.

Two explosions occurred at this laboratory while distilling the hydrofluoric acid from the double salt. The cause of the explosions was in both cases a clogging of the copper tubing leading to the condenser by particles of potassium fluoride carried along by the gaseous hydrofluoric acid. To avoid this, a copper retort was fitted with a distilling column an inch in diameter which was closed with a brass cap that served as a safety valve. Two tubes entered the distilling column near the top; one leading to the copper condenser, the other serving to admit air through a sulphuric acid wash-bottle. The condenser was joined by copper connections to a receiver also protected by a wash-bottle of sulphuric acid.

A very slow stream of air was caused to pass through the apparatus during the distillation. The absence of bubbles indicated that the pipe line was obstructed. The receiver and the condenser were cooled by an ice-salt mixture.

Experiments were made with the Moissan and with the Meslans type of cell, using platinum anodes. While some

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[1] Ruff and Ipsen: Ber. deutsch. chem. Ges., **36**, 1777 (1903).

[2] Cuthertson and Prideaux: Phil. Trans., **205**, 319 (1905).

[3] Fremy: Ann. Chim. Phys., (3) **47**, 6 (1836).

[4] Ber. deutsch. chem. Ges., **37**, 673 (1904).

[5] Monatsheft, **28**, 297 (1897).

fluorine was obtained, the platinum anodes were attacked even though the temperature of the cell was kept at —30° to —60°. It was quite evident that the corrosion of the platinum anode was so great that fluorine could not be made commercially in this way. An Acheson graphite anode containing 98 percent graphite was tried; but it swelled and disintegrated even when no current was passing. The action appeared to be due to the hydrofluoric acid rather than to fluorine.

Since potassium hydrogen fluoride melts at approximately 200° and decomposes but slightly at this temperature, it was determined to try to obtain fluorine by electrolyzing the fused salt. It was found that a graphite anode could be used. The final form of the cell is shown in Fig. 2. The electrolyzing vessel which served as cathode was of heavy copper, $3^{1}/_{2}$ inches internal diameter and 8 inches deep, surmounted by a heavy flange. The cell was wound with nichrome wire insulated from the wall with asbestos paper.

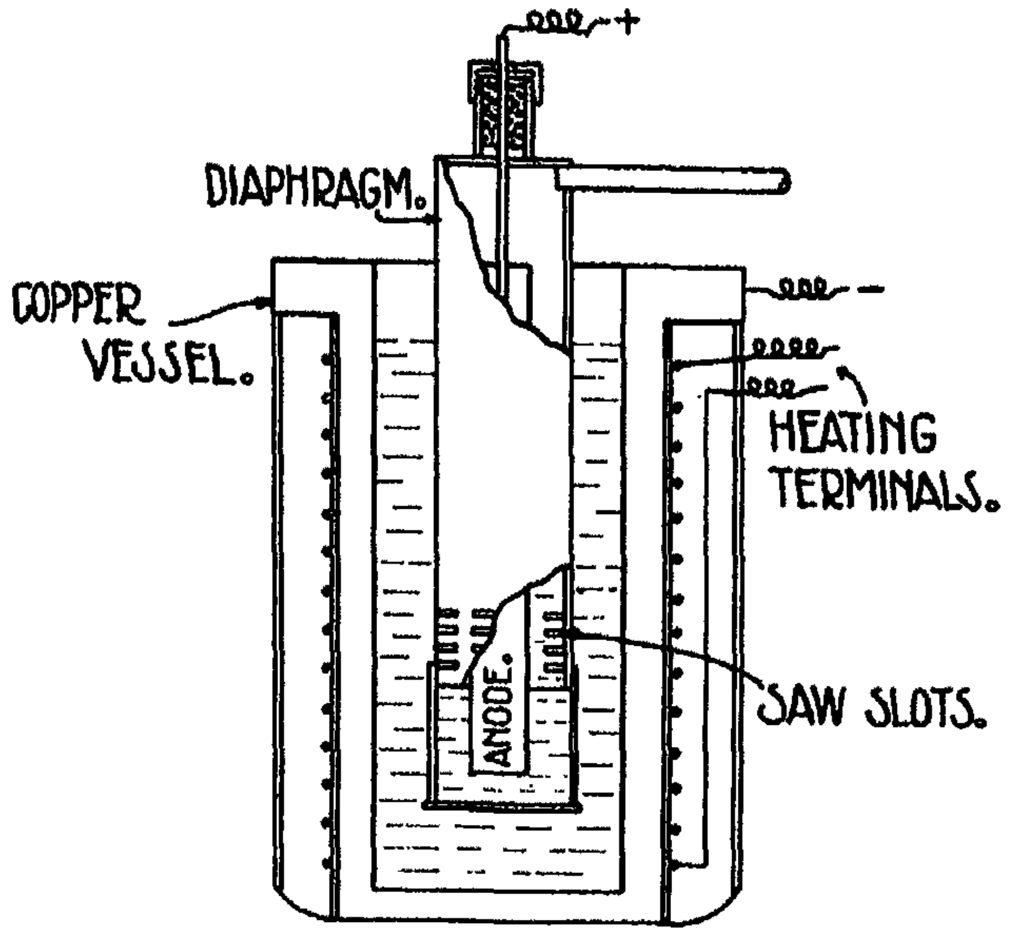

Fig. 2

To prevent loss of heat by radiation the wires were surrounded by asbestos wool and asbestos paper. The diaphragm was two inches in diameter. Near the bottom a number of slots were cut for the purpose of decreasing the voltage of the cell. Hydrogen evolved from the bottom of the electrolyzing vessel during electrolysis was prevented from rising to the inside of the diaphragm where it would unite with fluorine, by means of a false bottom which deflected the bubbles. Considerable space remained below the anode for potassium fluoride to collect. The graphite anode was insulated by packing it in a mass of finely powdered fluorspar, held closely and firmly round a copper bolt by means of a packing gland and nut. The copper lead was held in place by a washer of fluorspar while the finely powdered mineral was pounded in. Finally, a fiber washer was placed on top and the packing nut screwed down securely. The graphite anode was attached to the copper terminal by boring a hole in the former and pounding it firmly onto the latter.

The fused bath has a slight solvent action on copper vessels so that there is a gradual accumulation of copper fluoride in the bath. The solvent action increases with rising temperature and when there is a localized overheating such as is obtained with a Bunsen burner, it takes but a short time for a hole to be eaten through the vessel at the point it is heated. The local disintegration of the vessels has been overcome in large measure by electrical heating. In an electrically heated cell containing approximately 1500 grams of bath about 20 grams of Cu_2F_2 were formed in a week.

A fresh bath, prepared from potassium fluoride and commercial hydrofluoric acid, always contained some water which had to be electrolyzed out at a low current density before fluorine was obtained. If the current density was too high, polarization resulted and the voltage rose to 50 or 60 volts. There was sparking through the oxygen gas film that suffused the bath with a blue luminescence. A current density of 2 to 3 amperes per square decimeter was passed until a test of the anode gas showed the presence of fluorine, after which a much higher current was used without polarization resulting.

A difficulty which proved very troublesome indeed for a time was the foaming of the bath, particularly around the anode. This frothing carried up the electrolyte into the exit tube of the diaphragm where it froze and clogged up the system. Frothing resulted only after the bath had been electrolyzed for a considerable length of time so that the electrolyte had become viscous with the accumulation of potassium fluoride and copper fluoride. To prevent it, all that was necessary was to add hydrofluoric acid and regenerate the bath. Before it was found that regeneration would solve the difficulty, stirring the bath and shaking the anode by a motor were tried without avail. Simply grinding up the salt and adding hydrofluoric acid without filtering the solution to remove impurities serves to put the bath in good shape so far as frothing goes.

Since the electrolytic decomposition of potassium hydrogen fluoride results in a loss of hydrofluoric acid and the consequent formation of potassium fluoride it is necessary to regenerate the bath from time to time. Inasmuch as the potassium fluoride is not molten at the temperature of the bath it gradually settles to the bottom of the electrolyzing vessel. Attempts have been made to run anhydrous hydrofluoric acid into the bath under pressure but these have not proven successful since the acid is a gas and it merely bubbles through the molten double salt and reacts but slowly if at all with the solid on the bottom of the cell. Furthermore, in view of the fact that the bath dissolves copper slightly it is necessary occasionally to dissolve the electrolyte in water and filter off the impurities. During this operation the hydrofluoric acid can be added to the cell.

The procedure followed in this laboratory has been as follows: After using the bath until it becomes quite viscous as a result of the presence of considerable solid KF it is poured into a copper dish or on a sheet of copper. After cooling, the salt is crushed fine, placed in a copper vessel, and commercial hydrofluoric acid added. As a rule, the salt is considered as all KF and enough acid is added to form KHF_2. Inasmuch as there is always considerable KHF_2 present in the bath when poured out, a reasonable excess of acid is ensured. The bath with its excess of acid is heated slowly for several hours and finally brought to 225° when it is easily molten. It is then returned to the cell and a current of 2 to 3 amperes per square decimeter is passed for several hours to electrolyze out the water. It has been noticed that as the last traces of water are removed a temperature of from 240° to 250° is necessary to keep a molten electrolyte.

In order to prevent contamination of the bath by copper and the consequent necessity for dissolving up and filtering off the bath, a Dixon graphite crucible was substituted for the copper electrolyzing vessel. It was rapidly attacked, however, owing to the high percentage of clay in its make-up. A vessel made from graphite boards was next tried but the structure was such that it absorbed a large amount of hydrofluoric acid and so proved unsatisfactory. It is proposed to try a crucible of electrode graphite such as is used for the anode as soon as one can be secured. If this proves satisfactory the regeneration may be effected in the cell, without much difficulty. If anhydrous acid is used instead of the commercial product the period of drying and preliminary electrolysis to remove water will be materially shortened.

In the first cells used the voltage was 18 to 20 volts for a current of 3 amperes. This seemed higher than necessary. Accordingly the vessel was used as the cathode thereby decreasing the current density of this electrode; and the anode was dropped an inch below the diaphragm. With this arrangement it was found possible to pass 10 amperes at 12 volts. At a temperature of 240° to 250° a voltage of 15 was usual with a current of 10 amperes. At higher temperature the conductivity of the bath increased appreciably but loss of hydrofluoric acid offset this advantage. Working with ten amperes at 12 to 15 volts and a temperature of 225°–250°, the current efficiency is about 70 percent.

Among the tests for fluorine may be mentioned the following:

1. The not unpleasant odor of small quantities of fluorine is very characteristic. The odor reminds one somewhat of a mixture of ozone and chlorine but without the irritating action of the latter. This test readily serves for detecting leaks in the apparatus. Apparently fluorine possesses but little toxic action although long exposure to rather large quantities produces headache.

2. The unlighted gas mixture from a Bunsen burner is instantly ignited by fluorine. This test is delicate but less so than the odor.

3. Sulphur is ignited quickly by the gas. A soft charcoal, *e. g.*, a piece of charred wood glows brilliantly. Selenium reacts with fusion. Chloroform vapors react readily.

On account of the difficulties involved in the preparation of thoroughly dry potassium acid fluoride it occurred to us that the anhydrous acid could be prepared with considerably less difficulty if sodium acid fluoride were substituted for the potassium salt usually employed.

The following are among the more noteworthy advantages:

1. Sodium fluoride is not hygroscopic and hence overdrying of the double salt does not leave a material that has to be protected from the air; potassium fluoride on the other hand is very hygroscopic indeed.

2. The sodium salt decomposes below the fusion temperature while the potassium salt does not.

3. The sodium salt is cheaper.

4. The sodium salt contains a higher percentage of available hydrofluoric acid.

Two grams of sodium fluoride were treated with an excess of aqueous hydrofluoric acid. The reaction took place rapidly with the evolution of heat. The excess hydrofluoric acid was driven off, the product was dried at 260° for a few minutes and weighed. The gain in weight corresponded to 23.6 percent hydrofluoric acid. On heating again for a few minutes to 260°, a further loss of hydrofluoric acid to 20.9

percent was found. It was evident that 260° was too high a temperature for drying so the experiments were repeated at a temperature of 140° to 160°. The percentage hydrofluoric acid taken up was 32.3 which is theory. This percentage was reduced to 32.14 by drying a second time, at 140° to 160°.

With the present apparatus it is possible to show the properties of fluorine as a regular lecture experiment involving no especial difficulties. If one were to make fluorine on a commercial scale, it is quite probable that it would be desirable not to make the containing vessel the cathode and it is also probable that external heating would cease to be necessary.

This work was done in the Catalytic Laboratory of the Research Division of the Chemical Warfare Service under the general supervision of W. D. Bancroft.

THE COLORS OF COLLOIDS. VI

BY WILDER D. BANCROFT

Blue Eyes

Tyndall[1] pointed out that the blue color of eyes was undoubtedly the blue of turbid media, but this seems not to have been understood by the physiologists. Roberts[2] says: "The iris, on which the color of the eye depends, is a thin membranous structure composed of unstriped muscular fibers, nerves, and blood-vessels, held together by a delicate network of fibrous tissue. On the inner surface of this membrane there is a layer of dark purple pigment called the *uvea* (from its resemblance to the color of a ripe grape), and in brown eyes there is an additional layer of yellow (and perhaps brown-red) pigment on its outer surface also, and in some instances there is a deposit of pigment among the fibrous structures. In the albino, where the pigment is entirely absent from both surfaces of the iris, the bright red blood is seen through the semi-transparent fibrous tissues of a *pink* color; and in blue eyes, where the outer layer of pigment is wanting, the various shades are due to the dark inner layer of pigment—the *uvea*—showing through fibrous structures of different densities or degrees of opacity. The eyes of new-born infants of both white and black races (and I believe the new-born young of all the lower animals) are dark blue, in consequence of the greater delicacy and transparency of the fibrous portion of the iris; and as these tissues become thickened by use, and by advancing age, the lighter shades of blue, and finally gray are produced; the gray, indeed, being chiefly due to the color of the fibrous tissues themselves. In gray eyes, moreover, we see the first appearance of the superficial layer of yellow pigment in the form of isolated patches situated around the margin of the pupil, or in rays running across the iris. In the

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[1] "Fragments of Science: The Sky." See also Jour. Franklin Inst., 187, 250 (1919).

[2] Brit. Assoc. Reports, 50, 135 (1880).

hazel and brown eyes the *uvea* and the fibrous tissues are hidden by increasing deposits of yellow and brown pigment on the anterior surface of the iris, and black eyes result when this is very dense. It is very doubtful, however, whether the iris is ever so dark colored in the inhabitants of this country as to justify the term black being applied to it, and the popular use of the expression has reference to the widely dilated pupil common in persons with dark brown eyes. The nearest approach to a black eye among us is the dark blue or violet eye associated with black hair in some Irish adults; here the color is probably not due entirely, as in infants, to the greater transparency of the fibrous structures, but to interstitial deposit of black pigment, or to a layer situated on the anterior surface of the iris."

This view-point has been adopted in the other papers which I have read. Thus Darbishire[1] says: "When we speak of the color of the human eye, we are speaking only of the color of a particular part of it, namely the iris, which is the only part of the eye the color of which varies to any great extent. There is, of course, an almost infinite variety in the color of the eye; but the various types of color can be grouped into two large classes according to whether there is brown pigment on the outer surface of the iris or not. When the whole of the surface, which is the one that we see when we look at the eye, is covered with brown pigment on the outer surface of the iris the eye is generally brown. The word duplex has been coined to denote those eyes in which there is some brown pigment in front of the iris; and simplex to denote those eyes in which there is none.[2] Speaking generally, duplex eyes are brown, and simplex are blue. But as the two classes, duplex and simplex, include the whole range of human eye color it is evident that duplex does not simply mean brown and simplex blue, because they also include the green, the gray, and the hazel eyes.

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[1] "Breeding and Mendelian Discovery," 41 (1911).

[2] These terms were introduced by Mr. C. C. Hurst, who was the first to discover, investigate, and record the Mendelian inheritance of eye color in man.

"A duplex eye is, as we have said, any eye in which there is brown pigment in front of the iris. This brown pigment exists on the top of the fibrous tissue of the iris, which appears blue; so that if we could dissolve away the brown pigment from a dark brown eye the blue would appear underneath. There is every degree in the amount of this brown pigment. If there is very little indeed, it usually exists as a thin ring round the pupil, all the rest of the iris being blue. This has been called a ring-duplex, and if there is a mere trace of the brown pigment, a duplex eye of this kind would doubtless often pass as a gray or even blue eye. If there is more of the brown pigment a hazel eye is very often the result. In another form of duplex eye the brown pigment is distributed in patches over the blue ground color which can be seen between the patches; hazel eyes are also often the result of this arrangement. When there is a very thin uniform layer of brown pigment, the color of this (a sort of yellow ochre) blends with the blue of the background, which can be seen through, and a green eye is the result. And finally there are the self-colored duplex eyes in which the brown pigment is spread uniformly over, and completely concealing the blue background, giving the various intensities of the brown eye, according to its abundance.

"A simplex eye is one in which there is no brown pigment on the anterior surface of the iris. All the clear blue and gray eyes are of this class. The color of simplex eyes is not due to the color of the fibrous tissue of the iris itself, which consists of muscle fibers, nerves, blood-vessels, and so forth, but to a layer of dark purple pigment behind the iris, called the *uvea*. In the new-born infant the fibrous tissue of the iris is very delicate and transparent, so that most of the color of the uvea can be seen through it: that is why the eye of the new-born infant is dark blue. A clear blue eye is due to the delicacy of the fibrous tissue of the iris, which permits the color of the uvea to shine through. A pale blue or gray eye is due to the coarseness or 'stringiness' of the fibrous tissue, which prevents most of the color of the uvea from being seen.

Evidence that the color of very pale blue and of gray eyes is due to the color of the uvea which can filter through the fibrous tissue in front of it, and not to the color of the fibrous tissue itself, is afforded by the fact that in albinos, in whom the uvea is colorless, the iris appears pink, this color being given by the blood in the fibrous tissue. The various color of simplex eyes, namely, the different intensities of blue and gray eyes and the intermediates between these two colors, are therefore due to differences in the texture of the fibrous portion of the iris, which allow different amounts of the color of the purple uvea behind to filter through. A simplex eye, therefore, is one in which there is only one layer of pigment, the purple of the uvea; a duplex eye is one in which there are two layers of pigment, the purple of the uvea behind the iris and a varying amount of brown pigment in front of it.

"If the reader prefers the use of familiar terms, duplex may be spoken of as brown and simplex as blue, and in nine cases out of ten the application of these common words will be correct; but it must be remembered that there are some eyes which would be described as blue in common parlance, but which really fall into the duplex class because they possess a trace of brown pigment."

Davenport[1] quotes Roberts and then adds a paragraph of his own. "While in most races of the globe, brown pigment is heavily secreted in the iris, in northwestern Europe blue, gray, or yellow-blue eyes are found. It seems probable that, once upon a time, or perhaps at many times, an individual was born without brown pigment in the iris. The offspring of such prospered and spread throughout northwestern Europe and migrated thence to America and Australia. This defect, lack of eye pigment, has had a wonderful history. By noting its distribution the migrations of peoples can be traced. Thus Gray (1907) has shown that, in Scotland, pure blue eyes are most abundant in the coal and iron districts. This is probably due to the Irish immigrants, it being well known that blue eyes are very common among the Irish.

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[1] "Heredity in Relation to Eugenics," 27 (1911).

In the Spey valley of Scotland the density of pure blue eyes is high—probably owing to the Norse invasion at that point. So in our own country the pigmentation survey that will some day be made will show a high percentage of blue eyes where the Scandinavians and north Germans have settled."

The general point of view seems to me to be entirely wrong and I hope to be in a position before long to prove this experimentally. Roberts believes that blue eyes are due to the fact that the uvea is purple, and he considers that the marked blue in the infant's eye is due to the iris being more transparent and thus permitting the color of the uvea to show through. It seems to me much more probable that the blue is the color of turbid media as suggested by Tyndall, and that the eye of the infant is more blue than that of the adult because the suspended particles are finer and therefore give rise to a richer blue. The object of the uvea is to prevent the red color of the blood showing through, as happens with albinos, and to cut down reflections from the back of the eye. I believe it to be practically unimportant whether the uvea is purple, or black, or dark brown.

The development of pigment on the front of the eye will of course modify the color, a brown pigment giving all gradations between brown eyes and black eyes. If the brown pigment is yellow in very thin layers, we get a green eye. There should be no difficulty in duplicating this on a large scale in beakers or globes painted with a dark coating on the back, filled with a suitable turbid medium, and tinted to the desired extent in front. This should make a wonderful set of lecture experiments.

It is well known that most infants have blue eyes, which often change to other colors as the children grow up. This merely means that the pigment on the front of the iris usually develops quite a while after birth, just as do the teeth. The unpigmented eye is always blue and the change is therefore always from blue to some other color and not in the reverse direction. If the pigmentation is marked at birth, the child does not have blue eyes.

The general conclusions of this paper are as follows:

1. In blue eyes there is no pigment on the front of the iris.

2. The blue color is the color of turbid media and is richer, the finer the suspended particles.

3. When the uvea is lacking, the color of the blood shows through and we have albinism.

4. The function of the uvea is to prevent the red of the blood showing through and to cut down reflections from the back of the eye. This intensifies the blue, just as the colors of thin films are more intense when oil is spilled on an asphalt pavement. The blueness of the eye does not depend to any great extent on the color of the uvea, though this may play a part in certain special cases.

5. All other colors are due to pigmentation on the front of the eye which either modifies or masks the blue of the turbid media.

6. It should be a simple matter to duplicate experimentally on a large scale all the eye colors and thereby prove whether Tyndall or Roberts was right.

Cornell University

NEW BOOKS

The Treasures of Coal Tar. *By Alexander Findlay. 19 × 14 cm; pp. xiv + 137. New York: D. Van Nostrand Company, 1917. Price: $2.00.*— In the preface the author says: "In order that the effort now being made to promote the more widespread application of science and more especially to render this country independent of others for the supply of dyes necessary for the maintenance of our textile industry, shall not be relaxed, it is essential that the people as a whole should interest themselves in the work, and should gain some knowledge of what has been achieved in the past, and some understanding of the nature and complexity of the problems to be solved. As the matter is urgent, and of vital importance for the welfare of this country, the writer felt that, even in a time of much preoccupation, he could not refuse the invitation of the publishers to discuss in a readily intelligible manner the production and utilizations of coal tar, and to indicate sufficiently fully for the general reader, the almost infinite variety of material—dyes, drugs, perfumes, explosives—for the manufacture of which coal tar is the raw material.

"Based on this invaluable by-product of the manufacture of coke and of illuminating gas, an industry, or rather a series of industries, has been developed; but although Great Britain played a predominant part in the early stages of this industrial development, she failed to retain the great advantages she had gained, and the manufacture of synthetic dyes and drugs became increasingly a German monopoly. To such an extent was this the case that, before the outbreak of the war, Germany was producing more than three times the quantity of coal-tar product produced by all the rest of the world combined. It is true that dyes were manufactured in considerable amount in this country; but our manufacturers rested content, in too great a measure, with their dependence on German intermediates, which, instead of making, they imported and worked up into dyes. In spite of the warnings uttered by our foremost chemists during the past thirty years, in spite of the object lessons furnished by the destruction of the European madder and the decay of the Indian indigo plantations, this country failed to develop its coal-tar chemical industries on a material scale; and as a result of this failure she found herself, on the outbreak of war, placed in a position of great gravity. Perilously handicapped in our production of the munitions of war, threatened with the destruction of our textile industry through the cutting off of the German-made intermediates and dyes, and with the health of our people and army endangered through shortage of those synthetic drugs with which the German chemical industry had supplied us, we were brought face to face with our past neglect of chemical science and with our failure to encourage the application of that science in our industries. The chemists of the country were mobilized hurriedly and the production of the essential munitions of war and of a sufficiency of drugs was ensured; the Government came to the help of the dye-making industry, and in the past two years, in spite of many handicaps, great progress has been made.

"But, what of the future? Can we feel sure that the lessons of the war have been learned and that the loss and bitter experience of the past three years will be turned to permanent gain? Have our people acquired that new outlook, that new mentality, which is the only safeguard of our future? As I have written elsewhere, we are all prone to blame our manufacturers and directors of industry, and to place on them the responsibility for our backwardness in the recognition of the value of science, but we have to remember that they are themselves but a part of the national system, and their organization and outlook an expression of the national character and habit. Until we realize that our present unfortunate position is the result of a national defect which shows itself most glaringly in our lack of interest in education and of a desire for knowledge, and until we realize the necessity for each and all of us gaining a new standpoint and outlook, gaining a new ideal, we cannot hope for a permanent improvement in the attitude of the country and manufacturers towards science and its applications."

This has the right ring to it. The subject is discussed under the general headings: the production of coal tar; the distillation of coal tar; the constituents of coal tar and their applications in the raw state; molecular architecture; the production of dyes from coal tar; azo dyes; anthracene dyes and vat dyes; indigo and its derivatives; drugs, perfumes, and photographic developers; explosives. Like the other books of the same author, this one is well worth reading.

Wilder D. Bancroft

Stoichiometry. *By Sydney Young. Second edition. 22 × 15 cm; pp. xiv + 363. New York: Longmans, Green and Co., 1918. Price: $3.75.*—Owing to the change in the accepted atomic weight of silver, the author has rewritten the chapter on atomic weights, giving only a short summary of the work of Stas, and devoting more space to the more recent determinations of the atomic weights of silver, nitrogen, chlorine, and lead.

On p. 6 the author says: "In the light of our present knowledge it is almost impossible to give a satisfactory definition of the term 'element,' but perhaps the recommendations of Paneth may be adopted provisionally. The idea of elements previously held would be retained, and all the isotopes of any one element or a mixture of them would be spoken of as an element. The light and X-ray spectra would be the distinguishing criteria of a chemical element, which would be defined as a substance which cannot be decomposed by any chemical process. Atoms would be defined as the ultimate particles of matter, unchangeable by chemical analysis, which represent the limit of chemical decomposition. Elements might be defined as pure or mixed accordingly as they are made up of the same kind of atoms or of different kinds of isotopic atoms. Two elements should be denoted by the same name if, once mixed, they cannot be separated by any chemical process. But as Soddy points out in the Annual Report of the Chemical Society for 1916, difficulties must arise. Thus radium and mesothorium would be regarded as the same element, and should have the same name, as should also thorium and ionium."

The work of Morgan on falling drops is discussed in the new edition and so are the osmotic pressure data of Morse and Frazer and of the Earl of Berkeley. The section on the adsorption of gases by solids has been rewritten.

The present headings of the chapters are: fundamental law of chemical combination; general properties of gases; determination of atomic weights; accurate determination of atomic weights; the periodic law; the dissociation of gases and vapors; the properties of liquids; the kinetic theory of gases; properties of solids; mixtures; solubility and miscibility; properties of dilute solutions; dissolution and vaporization; the determination of molecular weight.

This is an admirable and valuable book; and the second edition is an improvement over the first.
Wilder D. Bancroft

A Handbook of Colloid-Chemistry. *By Wolfgang Ostwald. Translated by M. H. Fischer with notes added by Emil Hatschek. Second edition. 24 × 17 cm; pp. xvi + 284. Philadelphia: P. Blakiston's Son and Co., 1919. Price: $3.50.*—Owing to the impossibility of communicating with the author, the editors have left untouched large portions of the volume which contain the author's individual views. Numerous paragraphs have been added intended to bring to the reader various important advances in colloid chemistry made since 1912, more especially such as have to do with the viscosity of colloids.

Humphrey and Hatschek investigated a suspension of sifted rice starch grains (3μ average diameter) in a mixture of carbon tetrachloride and toluene having the same specific gravity, in concentrations of 2, 4 and 6 percent. They found that the viscosity for any given concentration varied with the rate of shear, being highest at the lowest rate of shear. To a much more marked degree, the viscosity of emulsoids is a function of the rate of shear. With an 0.5 percent gelatine sol the viscosity increases on standing and the change of viscosity with rate of shear is much more marked with a sol which has stood 72 hours than with one that is only 24 hours old. To make sure that the variation in the viscosity is really a function of the rate of shear and not due to a permanent destruction of structure, the series of measurements on the aged sol was repeated in the opposite sense, with increasing velocities. Marked hysteresis is shown and the curve thus obtained lies entirely above the one found with decreasing velocities, showing conclusively that no permanent alteration of the system has taken place.

"Arrhenius has shown on a large number of examples that his well-known logarithmic formula

$$\log \eta = Q\,C,$$

where Q is a constant and C 'the molecular concentration,' can be used for expressing the viscosity of emulsoid sols with remarkable accuracy. As the molecular weights of the dispersed phases are unknown, C can only be calculated by making simplifying assumptions, and the introduction of 'molecular concentrations' appears unjustified in the case of systems which we have throughout considered to be sub-molecularly dispersed. The formula can, therefore, hardly be anything but an interpolation formula; but for colloids in aqueous dispersion it leads to remarkably constant values both for Q and for the hydration factors, which latter are of the same order of magnitude as for hydrated salts. The formula, however, also fails entirely for the above-mentioned sols in organic solvents, the association factor becoming variable, and even negative in some cases. A generally valid formula—either rational or empirical—for representing the viscosity of emulsoid sols is, therefore, still lacking, and it may be worth mentioning that M. von Smoluchowski does not consider the prospect of deducing the former very hopeful."

These two paragraphs give a very fair idea of the added material. The rest of the book is practically what it was before and does not represent our present knowledge of the subject.
Wilder D. Bancroft

THE COLORS OF COLLOIDS. VII

BY WILDER D. BANCROFT

7

Blue Feathers

Newbigin[1] has given an uncritical but interesting discussion of the occurrence of structural colors in nature. This was written before Michelson's paper appeared on metallic lustre in butterflies.[2]

"Blue as a pigmental color is exceedingly rare among the more complex animals, but is not uncommon among plants and the simpler forms of animal life. Thus the blue colors of many butterflies, of the feathers and skins of birds, of the mandrill among animals, are all due to structural coloration, while the blue of hyacinths, of some jelly-fish, and of the lobster are pigmental colors. In flowering plants a blue color is in some cases associated with an alkaline condition of the cell-sap, but beyond this there is still much uncertainty. In animals a blue color occurs especially in surface forms, whatever their relations, *e. g.*, jelly-fish, molluscs as in *Ianthina*, and Tunicates. It is also remarkable as one of the conspicuous colors of coral reefs, where it occurs in corals, sea-anemones, Turbellarian worms, and starfishes; the blue colors of the cuttles and fishes of the same situation are no doubt optical.... In insects, where blue is very common, blue pigments have not yet been described, although it is improbable that the blue in all cases is structural.... Among Vertebrates blue pigments do not appear to have been as yet described, except in the case of the blue pigments of the eggs of many birds. These pigments are apparently derivatives of haemoglobin.

"A green color is of course almost universally distributed among plants, where it is due to the important pigment chlorophyll. Among animals, green like blue is rare as a pigmental color, except in simple organisms.... In Vertebrates green pigments are almost absent; as in the case of

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[1] "Colors in Nature," 41, 147, 153, 192, 219, 242, 262, 268, 287 (1898).

[2] Phil Mag., [6] 21, 554 (1911).

blue pigments, the most marked exception is probably the green pigment which colors birds' eggs, though according to Sorby the green color is here produced by a mixture of blue and yellow.... The yellow or tawny color of the hair in many mammals is not due to a special yellow pigment, but to the uniform distribution of a small amount of dark pigment....

"From the simplicity of the structures of the Coelentera it is naturally to be expected that true optical colors will be absent. These are not, however, quite unknown, for the calcareous axes of some of the Gorgonians display brilliantly iridescent colors. Agassiz[1] describes the species of Iridogorgia as having axes of a bright emerald-green or of burnished gold, while others have a lustre like mother-of-pearl. All the iridescent forms inhabit deep water, and the colors are probably due to the same cause as the colors of shells, which also tend to be especially iridescent when found in deep water....

"In butterflies the color phenomena are much more complex than in caterpillars, for while in the latter the color is a direct pigmental effect, in the former the two factors of structure and pigment occur in combination. In both kinds of color in butterflies the important elements are the scales of the wings. These are outgrowths of the chitinous cuticle and consist of a double membrane; the outer membrane is frequently much differentiated, and may display rows of blunt projections, which are thought to be of importance in color production. The two membranes are connected by bridges of chitin, and pigment granules may be deposited both in these bridges and in the outer membranes. Having regard to the small size of the scales, it will be readily understood that there is frequently great difficulty in determining whether a particular color is due to pigment or structure; the fact that a scale showing structural color frequently contains pigment in addition further complicates the matter. We thus find that there is much difference of opinion among observers as to the cause of particular colors. This occurs especially in the case of *dichroic* scales, those displaying one

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[1] "Voyage of the Blake," 2, 144.

color by transmitted light and the complementary color by reflected light. Some regard this effect as purely structural, others maintaining that the colors are due to dichroic pigments. Making due allowance for the difficulties of observation, it seems certain, however, that blue in butterflies is always a structural color, while green, black, and white are at least usually due to structure. Other of the structural colors are readily recognized by their metallic brilliancy and changing glow, which give to the butterflies possessing them an appearance of surpassing beauty. Many will recall Mr. Wallace's description of how his heart beat fast and his brain reeled when his perseverance was rewarded, and he captured with his own hands one of the finest of these living gems in the Malay Archipelago.

"In connection with these colors Urech (1893) notices one little point of some interest. He found that in some cases the scales display under the microscope a wonderful play of colors which is quite invisible to the naked eye. He suggests, reasonably enough, that it is in no respect improbable that these colors may be visible to other insects although not to us except by the aid of optical instruments, and that therefore they may quite alter the appearance of the insects as seen by other butterflies. Such observations are of interest as tending to exercise a check upon the purely subjective treatment of questions of color resemblance....

"Green in butterflies presents many difficulties. It may be entirely structural, and arise by surface markings or by the superposition of scales, as in the species of *Nematois* (Spuler). Again, from the green scales of *Papilio Eurymedes*, Urech extracted a yellow pigment which was almost insoluble in water but which dissolved readily in hydrochloric acid. He adds, as a note, however, that the scales retained their green color after treatment with ammonia. It is almost impossible to doubt that in this case the green color is structural, the part played by the yellow pigment being uncertain. Further, he found that the green scales of *Theda rubi* are yellow by transmitted light, and almost colorless when the light falls from the base of the scale upwards, while to hydrochloric acid they yield a yellow pigment. These two cases seem to suggest that in butterflies, as in birds, green may be produced by a combination of a yellow pigment and a structural modification. The dark pigments, as we have already seen, are probably identical in all butterflies; a pure black color is, however, in most cases due to the sculpturing of the surface....

"It seems probable that the pigments of cephalopoda are chiefly of the dark-colored nitrogenous type, though they have not been fully investigated. The beautiful changing colors are in large part due to the movements of the chromatophores, which alter the whole appearance of the animal as they expand or contract. So long ago as 1852 Brucke watched the color changes of *Sepiola rondeletii*, and noting how the tints varied in the order of the spectrum from blue to green, yellow, and red, came to the conclusion that the colors were optical. He thought that they were due to the colors of thin plates; but according to Krukenberg they are due to fine ridges in the surface of the cells....

"Among the colors of fishes, those of the forms inhabiting the neighborhood of the coral reefs of warm seas, must be especially mentioned. We have already seen how brilliant are the tints of the coral polypes themselves, and the same brilliancy seems to occur almost universally among the inhabitants of the waters round the reef. In fishes, however, the brilliant colors are probably produced not by pigments, but by structure. The colors fade with extraordinary rapidity after death or removal from the water, and according to those who have seen the fish in their natural condition, the coloration is at best quaint and striking, rather than beautiful....

"Birds resemble insects in displaying both types of color—the optical and the pigmental—to great perfection; but in marked contrast to the conditions which prevail in the Lepidoptera, we find that the bright pigments are usually lipochromes, never so far as is known waste products of the uric acid groups.... The dark melanin pigments are very widely distributed in birds as in all vertebrates. They occur in the form of minute amorphous granules in the epidermis of the cuticular structure, and not infrequently give rise to brilliant structural color or to very elaborate patterns and markings; in some cases they are uniformly distributed and give rise to plain gray, brown, black, and related tints. Structural colors in birds are abundant, and include, in addition to all metallic colors, blue, green, some yellow, white, and in part the glossy black colors. Blue, whether it occurs on feathers as in the jay, or on the beak, or the skin of the head, as in some birds of paradise, is always structural. The naked patches of skin in birds indeed exhibit the same tendencies with regard to coloring as are visible in the feathers....

"Feathers are outgrowths of the epidermis, formed like all such outgrowths of the substance keratin. They differ according to the function, and the part of the body in which they occur. Thus there are the quill feathers (which occur in wings and tail), the general contour feathers which cover the surface of the body, and the downs or soft under-feathers, which are often abundant on the breast. All these either contain pigment or are filled with bubbles of air and so display a white color... There are three great sets of color phenomena displayed by the feathers of birds: (1) The feathers may show beautiful and complex markings in brown, gray, and black; (2) they may display vivid optical colors; or finally (3) may contain brightly colored pigments, usually of the nature of lipochromes. Of these three, the first occur equally in long quill feathers and in the short contour feathers; they have no obvious relation to the structure of the colored parts, and as already seen, little is known of their meaning or course of evolution. The optical or structural colors are divided into subjective and objective. The changing subjective colors occur only in the barbules, and require the presence of a large amount of dark pigment for their full manifestation. Objective colors like green and blue are confined to the barbs and do not occur in the barbules; and the bright pigments occupy the same position. In general terms, therefore, we may say the barbules always contain a certain amount of dark pigment, and metallic colors arise when this is in excess and the structure is modified. The barbs, on the other hand, may contain a dark pigment, may show objective optical colors, or may contain bright pigments. The variations which produce these color phenomena are much commoner in the general feathers of the body than in quills; they do not usually occur simultaneously, and the appearance of any one set of colors is associated with an increased development of the special region of the feather with which the color is associated, as of the barbs, a portion of the barbules, and so on. It may be that from the development of markings, quill feathers are slow to vary in color, and are rarely brilliant. Color brilliancy is associated with a special development of some individual region of the feather, and it is essential for the purposes of flight that there should be a harmonious development of all the parts of the quills and no specialization of any particular areas. Therefore any tendency to the development of brilliant coloring in the wing quills would be checked by the resulting injury to flight, and so to the well-being of the species."

"The bright colors of the sun-birds are due either to lipochrome pigments or to metallic structural colors, belonging to Gadow's group of subjective structural colors.

1. *Pigmental Colors.*—The colors due to lipochrome pigments are either yellow or bright scarlet-red. Brilliant patches of red or yellow feathers frequently occur on the throat or on the ventral surface, or dorsally at the root of the tail. The feathers so colored are always short contour feathers and not quills. The bright color is confined to the apical part of the feather, the base being grayish or white, and the pigment occurs as usual only in the barbs. The barbules, if present, are grayish, but most frequently they are rudimentary or absent, so that the visible part of the feather consists of the diverging naked barbs, containing a considerable amount of bright pigment.

2. *Structural Colors.*—The metallic colors of the sun-

birds occur on feathers arranged in special patches on the head and throat, or as transverse bands near the tip of the general contour feathers, or as longitudinal bands at the edges of the quill feathers. In tint they are usually green, blue, violet, or reddish violet, yellow or red structural colors being absent. The colors are produced by a modification of the barbules of the metallic feathers. We have already described the general structure of barbules and noticed that each is divided into two regions—a proximal flattened region which may be called the lamina, and a distal slender region which, from its appearance, may be called the filamentous region. Now as in sun-birds the metallic colors are usually confined in quill feathers to a lateral stripe, it is obvious that it is possible to obtain a single barb which bears both metallic and non-metallic barbules. If we examine microscopically a non-metallic barbule, we shall find that it exhibits the ordinary structure of a barbule, and shows quite distinctly the division into two regions separated by a twist. The metallic barbules, on the other hand, are of quite different appearance, being broad, flattened, club-shaped bodies supported on a short stalk, and containing abundant dark pigment. Close examination of the barb shows that the metallic and non-metallic barbules are not perfectly sharply defined, but tend to pass into one another. Thus, as we follow the non-metallic barbules upwards, we find that the lamina diminishes in size, while the filamentous region becomes flattened, broader, and larger, at the same time losing its slender processes. Finally, the lamina becomes so much reduced as to form only the short stalk of the metallic barbules, while the distal region becomes modified into the club-shaped body, and is then completely devoid of hooklets or processes (cilia). These club-shaped barbules further exhibit a series of cross bars which, according to Gadow, are a series of compartments overlapping like the tiles of a roof. The ultimate causation of the physical color Gadow ascribes to the transparent sheaths of keratin covering these compartments, which he thinks act like a series of prisms. An important point in connection with these metallic barbules is, that they are so modified that both hooklets and folds are completely lost, and therefore there is no connection between the barbules or the barbs. Metallic feathers of this type have therefore a peculiar looseness of texture which is, for example, very obvious in the ornamental feathers of the peacock; the solidity of the flattened metallic barbules gives, however, to such feathers an appearance quite different from that of ordinary downy feathers, in which also the barbs are unconnected. The unconnected nature of the barbs is of especial interest, because it would render the feathers quite unfitted for purposes of flight if the variation were to occur in quill feathers. In sun-birds it is usually the contour feathers which are metallic, rarely the tail quills and apparently never the wing quills....

"The development of brilliant coloring in sun-birds is certainly associated with modifications of feather structure which cause the feathers to deviate more or less completely from the primitive type of feather structure. Turning now to humming-birds, we find that here pigmental colors are of relatively little importance, while structural colors attain an extraordinary beauty and brilliancy. Further, we find that the place of pigmental colors of sun-birds in contrasting with and showing up the metallic colors is taken in humming-birds by black and white. White especially is often of great importance in producing the general effect of beauty.

"In humming-birds metallic tints occur in both sexes, but are usually more brilliant in the male. They very frequently occur on the general contour feathers, the color being then often a bronze-green, which is not sharply confined to a transverse band, but fades away gradually behind. The metallic colors which are especially characteristic of humming-birds, however, occur, as is well known, in patches of extraordinary brilliancy either on the head as a crest, or on the lower surface, especially of the throat. The feathers forming these patches are peculiarly modified, and may display any of the colors of the spectrum including ruby-red and golden yellow—the colors which are so markedly absent from the metallic feathers of sun-birds. The rectioes of humming-birds not infrequently display metallic color, which may be distributed over the whole feather, or may be limited to a transverse band near the tip. Longitudinal bands of metallic color like those of the sun-birds do not seem to occur...."

Structure of Metallic Feathers.—The brilliant metallic feathers of the head region of many male humming-birds are in several respects very peculiarly modified. They are very short, much rounded, and overlap one another; the surface is strongly metallic and marked with deep ridges. A further point of interest is that the barbs, quite devoid of barbules, are prolonged as a delicate fringe beyond the apex of the feather. While for further details I must refer to my paper on the subject, we may simply notice that the metallic coloring is here not produced by a modification of the distal portion of the barbules, but by a deeper pigmentation and a structural change in the proximal region. The result of this is that the metallic color in humming-birds tends to appear first in the middle region of the body feathers—that is, the region where the barbules tend to attain their maximum development, and not at the tip of the feathers as in sun-birds. This primitive condition is well seen in the breast feathers of the female of *Eustephanus fernandensis,* and of both male and female of *E. galeritus.* Here we have white or dull-colored feathers, with a central spot deeply pigmented, and displaying a varying amount of metallic color. The increasing specialization of the metallic region is accompanied by a gradual retrogression of the apical region which is eventually represented only by the slender naked barbs.

"The metallic modification of the feathers in humming-birds is therefore not accompanied by any change which affects the locking together of the barbules and so the adaptability for purposes of flight; it differs in this respect sharply from the modification seen in the sun-birds where the metallic barbules are entirely unconnected. We can thus understand how it is that the quills of humming-birds may display structural color without their efficiency being in any way impaired. The fact is also readily explicable on structural grounds, if we recollect that it is the mid region of the feather which tends to become metallic, and it is this region which is most fully developed in quills. In humming-birds the color differences between the male and female, or between specialized and unspecialized species, are thus largely the result of an increased amount of melanin pigment in the brilliant forms, accompanied by a process of structural modification.

"The type of metallic color seen in the humming-birds is of much interest, because it has not been described outside of the family. In other cases we find that metallic colors in birds are of the type described in sun-birds, *i. e.*, are due to the conversion of the distal portion of the terminal barbules into a club-shaped body consisting of a series of overlapping compartments, the process being accompanied by the total suppression of cilia and hooklets. Such a modification of structure is apparently of very common occurrence in birds, but does not give rise to metallic color unless there is a simultaneous development of a large amount of black pigment....

"Blue and green structural colors are admirably displayed in the family of the kingfishers, which show also a gradual progression of color. Thus in *Ceryle rudis* the feathers are dark brown or black, more or less irregularly spotted with white, but with the white showing a distinct tendency to form a transverse band at the tip of the feather. In *Ceryle guttata* the feathers are regularly cross-barred with dull blackish brown and white. In *Carcinentes melanops* in the wing-coverts the covered part of the feather is striped black and white, but the terminal bar of white is replaced by blue. In the tail quills the under surface is usually black and white and the upper surface blue and black. Where there is a partial overlapping of the quills, one side of the vane may be black and white and the other exposed side black and blue. The blue patches occur in positions corresponding to the white ones, but are larger and show a tendency to fuse together. In the case of quill feathers, the blue is confined to the barbs but the barbules are still present, and their dull color somewhat diminishes the brilliancy of the blue. On the general contour feathers, on the other hand, the development of the blue color is associated with a suppression of the barbules, while the barbs as usual tend to become dilated and polished.

"While in many kingfishers blue and black are the dominant colors, in some the blue is replaced by green. Thus in *Halcyon lindsayi* a yellow color is common on various parts of the feathers, and where structural color occurs, it is here green and not blue. Many of the feathers of the back are black, cross-barred with yellow, and here the terminal cross-bar is wholly or in part replaced by green.

"These illustrations of color phenomena in birds, if they do not explain the development of bright color, may perhaps at least shed some light on the problem. They show that the development of brilliant color and structural modification go hand in hand; that brilliant pigmental colors tend to be confined to the barbs and are often associated with the suppression of the barbules; that melanin pigments may be present in large amount in both barbs and barbules; and that their presence in the latter is often associated with a structural modification which gives rise to optical colors; that the closeness of the association between the deposition of pigment in any region of a feather and the special development of that region is such as to prevent in the general case the feathers of flight acquiring great brilliancy of color. Facts of this kind surely tend to prove the definiteness of variation; they should, at least, be allowed for those who discuss the questions connected with the origin of color....

"Optical colors except white are rare in mammals, but true metallic colors occur in the Cape Golden mole (*Chrysochloris*). In this little insectivore the fur especially of the upper surface displays 'a brilliant metallic lustre, varying from golden bronze to green and violet of different shades' (Flower). The exact causation of the color appears to be unknown... Among the general color characteristics of mammals, we should notice the tendency of certain variations to recur constantly in many different orders; such are the deepening of the tint (melanism), the disappearance of the pigment (albinism), the prevalence of a sandy color in mammals inhabitating deserts, and so on. Melanic varieties are seen not infrequently in the leopard (*Felix pardue*), especially in Southern Asia; they seem to occur sporadically. A very interesting point about these leopards is that in certain lights, the markings characteristic of the leopards can be seen on the black ground like the pattern on watered silk. This shows that these markings are not wholly determined by the amount of pigment present in the hairs, there must be also some additional cause."

Altum[1] brings out a rather interesting point for which he offers no explanation. "In the case of the iridescent feathers with metallic lustre, the peculiar color is always accompanied by a peculiar structure. Wherever we find this type of color we find a feather structure, which feels hard, smooth, and metallic. It does not require a delicate sense to touch to distinguish blindfolded those parts of the feathers which show the metallic colors, if one runs the hand, for instance, up and down the back and breast of *Cuculus cupreus* or of the different red-breasted Trogons, etc. The metallic lustre is always associated with the peculiar, hard and smooth texture. A blind man could easily pick out all the birds with metallic lustre in a collection of any size. He would even be able to arrange them according to the intensity of the lustre and other peculiarities."

Bogdanow[2] points out that "feathers are to be divided into two groups: ordinary feathers, which are of the same color by transmitted or reflected light; and optical feathers, which show different colors depending on the way in which one looks at them. Ordinary feathers owe their color solely to pigments which are not attacked chemically by the sunlight. These pigments fall into two groups having quite different chemical properties: the first group comprises the yellow, red, lilac and green pigments, soluble only in alcohol and ether;

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[1] Jour. Ornithologie, 2, 19 (1854).

[2] Revue et Magasin de Zoologie, [2] 10, 180 (1858).

while the second group contains only the black pigment which is soluble only in ammonia or potash; and to a slight extent in water. The zoomelanin or black pigment of the feathers appears to be identical with the melanin found in the choroid. From the optical feathers one can extract brown and green pigments which are identical with those obtained from ordinary feathers. There is a distinct parallelism between the series of ordinary colors and the series of optical colors. Blue with all its shades must be considered an optical color in the feathers of birds."

Krukenberg[1] endorses this view. "My attempts to obtain a solution of a green dye from a green feather, of a blue dye from a blue feather, and of a violet dye from a violet feather, have been in vain so far; but there is some reason to hope for success in the case of the green feathers. Bogdanow seems to have been entirely right when he said that the light blue and the dark blue colors of feathers are optical colors, because the color disappears when one looks at the feathers by transmitted light.....

"All sorts of colors are to be found in the plumage of the parrots. In the same bird one may find the most intense greens, blues, reds, yellows, browns, and blacks; and in the case of *Sittace Macao*, all the colors are to be found on the same feather. If the feathers are chopped fine and extracted with boiling alcohol, only two soluble pigments [red and yellow] are found to give rise to all these colors in addition to one or more gray-brown to black pigments which are insoluble in water, alcohol, ether, chloroform, and in ethereal and fatty oils."

In experiments on the wings of Lepidoptera, Coste[2] concludes that "blacks and whites are not pigment but absorption and reflection colors, respectively. The great majority of blues are also physical colors—chiefly, if not entirely, interference colors; and it is doubtful if there be any pigment blues at all. Some greens are also physical colors, very

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[1] Vergleichend-physiologische Studien, 1, V, 98 (1881); 2, V, 154 (1882).

[2] Nature, 45, 541 (1892).

similar to the blues; the character of another group is somewhat ambiguous, although probably these, too, are physical. A third group is pigmental, and probably derived from yellow. All reds are pigmental... The greater majority of yellows are pigmental, of various degrees of solubility or insolubility; but a few cannot at present be decisively pronounced either physical or pigmental, and the same remark applies to chestnut."

Gadow[1] has discussed in detail the application of the laws of colors of feathers. "*Pigment Colors.* It has long been a matter of discussion whether or not pigment exists in feathers on account of its never having been successfully extracted. Recently, however, various pigments have been discovered. What we know at present about pigment in feathers is almost entirely the result of the investigations of Bogdanow and Krukenberg.... We may be almost certain that, wherever we have feathers with the various shades of black, brown, red, and yellow, if these feathers do not change their color in different positions of the eye, their color is merely due to a pigment. But there may be complications; if, for instance, the deeper strata contain a black, and the upper ones superimposed red pigment, the whole will appear dark red. Or if we take red with a superimposed yellow layer, the result will be orange. The richness of colors will often depend entirely on the amount of the pigment, *e. g.*, grey.

"*By diffraction and reflection* we can explain the following phenomena in feathers:

"1. *White.*—There is no white pigment or white objective color in natural objects, and wherever we have a white object, its color is due to there being an innumerable number of interstices between its molecules, or air-cells in its substance. The whole substance of a white feather, the ceratinine, is colorless, but its texture forms a fine network.

"2. *Simple Reflection of Light.*—The gloss of feathers, independent of the color itself, is the result of their surface being smooth and polished: if the surface is rough, the colors

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[1] Proc. Zool. Soc. London, 1882, 409.

given to the feather by pigment appear more or less dull; but if polished, they will appear with a more or less strong gloss, and they will look much more saturated, *e. g.*, brilliant red. The polished surface is produced by the horny substance of the feathers.

"3. *Interference of Colors and Color of Thin Plates.*—The thin plates are represented by the extremely thin laminae of the radii or by a thin coating of the transparent ceratinine. These parts appear with a certain color simply because they are thin; but instances of this are very rare, although the planes of the barbules are certainly thin enough to allow the application of colors of thin plates. In *Galbula tombacea*, for instance, the thickness of such a barbule plane, where it contained little or no pigment, was certainly less than 0.0006 mm [0.6μ]. The so-called iridescence of feathers might be thus explained. An underlying pigment complicates the problem a little. A smooth glossy surface may likewise be produced by a fine film of oil on the surface of the feathers, *e. g.*, in water-birds.

Application of the Theory of Colors Which Are Produced by a Series of Narrow Ridges

"Almost every fine feather exhibits a sort of iridescence if we look through it towards the light. The system of fine lines is then represented by the series of radii or barbules on either side of the rami or barbs. That these parts are minute enough for this is proved by observation. We know that diffraction colors begin to be visible to the naked eye if there are about twenty interstices to a millimeter. Now in a feather taken from the neck of *Pitta* (in the green part of the feather), I found the distance between the top of the two neighboring barbules equal to 0.05 mm, or at another part = 0.04 mm.

Explanation of the Objective Structural Colors

"Objective structural colors are due to particular structure of the feather substance which contains a pigment differently colored from the color actually observed, and which is not variable.

"*Blue Feathers.*—All attempts made by chemists to find a blue or violet pigment in feathers have been unsuccessful. Such feathers contain only a black-brown to yellow pigment. The simplest proof of this astonishing fact is that such feathers, if examined with transmitted light under the microscope, invariably appear brown. The blue feathers of parrots lose this color if held against the light, *i. e.*, if examined under indirect [transmitted] light. Moreover we can make a crucial test. If certain colors result from a particular surface structure of the feathers, these colors must disappear if we destroy the supposed color-producing parts. This can actually be done. If we press one of the deep-blue feathers of a macaw between two hard planes, so as to squash or smash the stratum of prismatic cones, or if we hammer it carefully, the blue immediately disappears, and the injured part looks grey or brownish according to the underlying pigment. The same is the case with the beautifully blue feathers of *Artamia*. Green parrot feathers, when treated in a similar way, become yellow, since this is the color of their pigment. Thus structural or optical color may, so to speak, be knocked out of a feather. (Fatio observed that blue disappears after injuring the surface by scratching off some of the enamel.) This explains the dark appearance of the abraded parts of feathers of parrots and other vividly colored birds. Again red, orange, brown, black, and most of the yellow feathers (*i. e.*, such which owe their color directly to pigment) do not lose or change their color under any physical treatment.

"The explanation of the *blue* color is the most difficult of all in those feathers where the blue is independent of the position of the eye, *i. e.*, in which the blue does not change. In most cases the blue is confined to the rami, which, for instance in *Coereba* and in *Artamia*, in the blue parts of the feather are devoid of cilia and radii, and are broader and flattened out. With a magnifying power of about 640, we first observe that the whole ramus is covered by a transparent, slightly yellowish or perhaps quite colorless, sheath or coating, the thickness of which is not more than 0.0014 mm [1.4μ]. The surface of this sheath is uneven and granulated. Immediately under this sheath we find one continuous layer of prismatic polygonal (frequently hexagonal) cells or cones. Most of these cones are broadest at their apices, and become smaller towards their bases; others have nearly parallel walls or may be broadest below. (This layer of cones has been called '*émail*' by Fatio, its discoverer.) The space between their apices seems to be filled up with the same matter as the coating. The color of the cones is pale yellowish, or, if this is only the reflection of the underlying pigment, they are colorless. The distance between the middle of two neighboring apices I found equal to 0.005 mm [5μ]; this would also be their breadth at the base. Their height seems to be slightly larger. No actual measurement, however, could be obtained, as I did not succeed in getting a clear side view of them. As to the structure of these little cones themselves, it is very difficult to arrive at a satisfactory conclusion, considering the minuteness of the subject. However, in *Pitta moluccensis* and in *Artamia* I observed a system of extremely fine lines running parallel with the long axes of the cones, *i. e.*, transverse or vertical to the long axis or surface of the ramus. These lines themselves do not seem to be straight, but irregularly waved. The breadth of each bar I calculated to be less than 0.0006 mm [0.6μ].

"Below this stratum of polygonal prisms or cones lies brownish yellow pigment, near the middle of the barb; where the layer of pigment is thicker it looks black-brown. This pigment, of course, together with the proper substance of the feather, occupies the rest of the barb. Thus we have, if proceeding from the surface to the middle of a blue barb, the following structure:—

1. A transparent, apparently homogeneous, sheath of ceratinine.
2. One layer of prismatic cells.
3. A brownish pigment.

The sheath may vary in thickness and surface structure from about 0.0014 to 0.0043 mm. In *Pitta* I calculated its thickness to 0.0016 mm, and the surface appeared to be quite smooth; whilst in *Coereba* each top of a cone corresponded with a slight elevation of the sheath. The breadth or diameter was calculated to about 0.006 mm; it agrees very closely with that of *Coereba* and *Ara*.

"Fatio, who examined the structure of blue feathers, also says that under the prismatic layer there are 'de grande cellules polygonales à noyau coloré.' But I suppose this is an optical delusion, and that the large polygons (generally hexagons) which we see while looking vertically down upon the surface of the rami are the lateral outlines of the prismatic columns. Therefore what he figured as polygons are simply the foreshortened columns, and the underlying pigment gives them the appearance of cells with a dark nucleus.

"The thickness of the surface coating of blue feathers varies considerably in different birds, and even in different feathers of the same bird. Differences between 0.0016 and 0.0043 mm cannot be put down as mistakes of measurement. Again, we know that the thickness of color-producing plates varies from about 0.00006 to 0.0004 mm [60–400$\mu\mu$], giving bluish white or pale orange light, respectively. And if the plates in question are thicker than about 0.005 mm [5μ], they cease to produce color, and the law of colors of thin plates is not applicable to them. Now our surface coating of 0.004 mm is about ten times as thick as the thickest of color-producing plates; consequently, this surface coating cannot be the cause of the blue color. Moreover, we find quite a similar sheath surrounding red and black feathers; and therefore the function of this sheath will be, besides merely protecting the feather, to give the blue color, produced by other parts, a glossy brilliant appearance. This, however, does not mean that this transparent sheath is superfluous or unimportant to the appearance of blue; since, supposing the blue is produced by the underlying cone stratum, there must be some material to reflect this blue to our eye, in a similar way that a piece of wood shows its color up much better when polished or varnished.

"We must therefore look for other reasons for the appearance of blue. It is true that all blue feathers contain a yellowish to brown pigment; but the same is the case with many others, like yellow and green feathers, and, besides this, a yellow pigment alone can never produce blue. The most essential part of blue feathers is the layer of prismatic columns; but as these vary considerably in size, from 0.011 to 0.003 mm, they alone cannot be the essential part, nor can it be the thickness of the transparent coat of the little columns themselves, since even this extremely thin coating is sometimes too thick to allow the application of 'thin-plate colors.' As the primary cause, we have to consider the fine ridges which we observe on the outer surface of all these prismatic columns. Many of them are so fine that they are even narrower than the length of one wave of light (the length of one wave of red light being 0.0007, that of violet being 0.0004 mm). As they form a system of ridges, I am inclined to apply to them the theory of 'diffraction colors' and to explain the blue color of feathers by this theory.

"The color produced by thin plates depends entirely on the proportion of the thickness of the plate to the length of the waves (w); consequently if this proportion is equal to x, and y is the plate when first looking red, this same color will appear every time when the thickness of (y') of the plate has increased to an odd multiple of wx. But after a certain thickness is obtained, the plate loses the power of producing color. Very similar conditions apply to the theory of colors produced by a system of narrow ridges. However, as these ridges in the cones are so minute that a cipher generally does not appear before the fourth decimal, we are unable to measure them with exactness. Moreover, these ridges do not appear always as straight lines but appear to be waved; to measure the length and deviation of these waves would be mere guesswork. Whether this system of ridges is the only cause of the blue color is doubtful; very likely the transparent coating and the cones themselves will considerably influence the light passing through them. The production of blue therefore in a feather would be the result of a very complicated process.

"Let us throw only a furtive glance at some of the changes which the light falling upon and passing through a blue feather is likely to undergo. First, part of the rays will be simply reflected from the outer surface [of the sheath of creatinine]; secondly, the rest, before passing through this stratum, will be variously broken and reflected *before* reaching the coating [of the prismatic columns], since the stratum of [creatinine] is not homogeneous, but consists apparently of several irregular scales and secondary strata; thirdly, the coating [of the prismatic columns] breaks the rays again and partly reflects them, and, if it is only 0.0006 mm thick, as in *Pitta*, it is thin enough to allow the application of the theory of thin-plate colors; fourthly, the system of ridges; fifthly, some rays will reach the layer of brownish pigment. How much of them is absorbed, how much reflected as brownish light, and what the changes are of this brown light before it comes up again to the surface, we cannot tell. Again rays striking in different places will be under different conditions. To follow and to calculate all these changes would be almost a superhuman task. We know only the result, namely blue color.

"By the application of the theory of colors of narrow ridges we are enabled to explain several other colors, fortunately under less difficult circumstances. We have seen before that many yellow feathers owe their color to a yellow pigment. But several of them do not contain any pigment. The thin rami and radii of the downy part of a feather of *Pitta*, for instance, appear colored (yellow) only under direct [reflected] light, but they are colorless if examined under the microscope with transmitted light. Now in yellow feathers, no matter if they contain pigment or not, the surface shows very fine, longitudinal ridges, which are more or less parallel to one another, and which appear as straight lines. This I found was the case in the yellow feathers of *Pitta*, *Psittacula*, *Arachnothera*, *Picus*, and *Parus*. The distance between the tops of two neighboring ridges varied from 0.001 to 0.0005 mm [1.0–0.5 μ]. That there are real ridges on the surface we can see on a transverse section of a yellow radius. The radius of a yellow pectoral tuft-feather of *Arachnothera* had a diameter of 0.007 mm; as there were about twelve such ridges, their distance could not be greater than $0.007\pi/12 = 0.0018$ mm. In *Pitta* the radius of half-downy feather had a diameter of 0.012 mm. All round there were about twelve ridges, and the breadth of one ridge was rather smaller than the interstices; therefore the breadth of one ridge must be smaller than $12.0\pi\ (12 + 12) = 0.0015$ mm. Another method of calculating gave 0.0012 as the breadth of one ridge."

Violet feathers.—Similar ridges exist on the surface-coating of metallic feathers, as, for instance in *Aethopyga* and in *Sturnus;* but the ridges do not appear to be quite straight, moreover they are much finer; in *Sturnus* only 0.00085 mm.

Green feathers.—Green pigment has been found only in the *Musophagidae*. All other green feathers contain only either zoofulvin [a yellow to greenish yellow pigment] or a black-brown pigment. Krukenberg suggested therefore that the green appearance is the result of a mixture of the yellow pigment color and of a blue-optical structural color. However, this cannot well be always the case, since most green feathers do not show that peculiar structure which we meet with invariably in blue feathers.

"All the green feathers which I have examined show the following structure: Generally a transparent smoothly surfaced sheath surrounds the rami and the radii, which are both green. Between this sheath and the invariably present yellowish, brownish, or pinkish pigment one sees a system of ridges and fine pits. These ridges are shorter and less regular than those observed in yellow feathers, and the little pits are rather irregularly dispersed over the shaft and plane of the barbs and barbules. As we know of no green feathers without any pigment, and always with such an irregularly ridged and furrowed surface structure, we cannot say that this structure directly produced green, nor that it produces blue. We must accept that they break the yellow light issued from the yellow pigment, into green.

"Red feathers are frequently surrounded with a thick, transparent sheath, for instance those of *Ramphastus;* but they have no peculiar or particular surface structure, and the large wrinkles which we observe in them seem to be merely the result of a drying-up process of the horny feather-substance. In orange or orange-brown feathers, however, we frequently find a dark red pigment and yellow surface structure."

Explanation of Subjective or Metallic Colors.—We speak of metallic colors if the feathers under reflected light appear with a metallic gloss, and if their glossy color changes into another one according to the position of our eye. If we look in a position nearly parallel to the plume of the feather, it will appear black. This can be done in two ways: first with our eye between the object and the light, a position which I propose to call A; secondly, with the object between the light and the eye, position C. By passing the eye from position A to position C, we notice the gradual appearance of all the various metallic colors which the feather is able to display. We further observe that these colors do not appear at random, but, and this is of the greatest importance, that they begin with the colors nearest to the red side of the spectrum, and end with the violet. The position just intermediate between A and C is that in which we look vertically down upon the plane of the feather, with the object turned fully to the light. This position we call B.

In order to ascertain this fact, I have examined, under these three positions, about eighty birds of all orders, wherever metallic colors were present, and did not find one single exception to the rule. With the exception of two particular cases, which I shall explain later on, the metallic parts of all these birds look perfectly black in position A; if we turn the bird to position B it will, let us say, look green; and halfway between B and C this bird will assume a blue color, which again passes into violet before appearing black again in position C. If the bird begins with bronzy red, it will change through golden green to pure green, then through bluish green to blue and violet. There is not a single feather which, if moved from B to A, changes from green to blue, in other words, from the violet to the red end of the spectrum. Thus we are able to predict into which color a bird will change if we know its color in position B. Thus a blue feather can only become purple or violet; a green one has more changes; and a golden green one still more. It is, however, very rare that a feather changes through more than half the spectrum; a coppery red feather will generally cease with green; a violet feather cannot change at all, except into black, since beyond the violet there are no visible colors in the spectrum.

"Another important factor is that metallic feathers can appear in any color which is represented in the spectrum, but not in any which, like brown or grey, are not spectral colors. All these circumstances induce me to explain the changeable metallic colors as prismatic; and in order to prove this we have to examine the feathers for their prismatic structure. In any metallic feather, the metallic color is confined to the radii which are entirely devoid of ciliae, and consists of a series of variously shaped compartments which overlap one another like tiles of a roof.... As every metallic feather shows precisely the same phenomena as a prism under similar circumstances would show, we have every right to consider the explanation of metallic varying colors as proved. There are, however, several *observed facts* which need an explanation, since they seem to rather upset this theory.

"First, why does not every metallic feather display all the colors of the spectrum? And why do they generally range over not more than a few neighboring colors? Of course any prism, however small it be, displays all the colors of the spectrum; but this does not mean that all of them *reach* our eye! Part of the spectrum might be hidden by some other object standing between it and our eye; for instance we can easily cut off either end of a spectrum by a screen.

In the feathers the screen would be represented by a neighboring radius," so that the yellow may be concealed, in which case the feather would only vary between red and greenish. "Or two neighboring prisms, even if they belong to the same radius or barbule, may be so situated that their spectra partly overlap one another. This would have a double result: first, that where two complimentary colors fall upon each other, they would simply produce white light; secondly, that through the combination of two different colors, as, for instance, yellow and blue, there would appear a third one, in this instance green." If the blue of one prism covers the yellow of another, we should probably see only the red and orange colors produced by the second prism because yellow and blue make green, and red and green make white.

"Another circumstance, which might make this process very complicated, is implied in the consideration that the surface of the prismatic sheath is frequently uneven. How many different systems of prisms result from this arrangement, and how in the purple feathers of an *Aethopyga* the rays of light become broken by the surface ridges into blue and violet, we are unable to explain.

"A third phenomenon which needs explanation is that some of the most gorgeously metallic feathers cannot be made to look black in position A or C. An example of this is the beautiful coppery red to deep blue of a jacamar. Under the microscope the compartments of such a feather are extremely convex; consequently there will always be some part of such a compartment which presents a vertical plane to the eye, and which therefore is always more or less in the position B."

"Now to sum up. We have to distinguish between several categories of colors in feathers.

1. *Objective chemical colors* directly produced by pigment. To these belong *black*, *brown*, *red-orange*, and *yellow*.

2. *Objective Structural Colors.*—The feathers may contain no pigment at all, and the color be produced solely by a special structural arrangement of the feather substance, for instance *white* and frequently *yellow;* the latter if the surface is com-

posed of very fine and narrow longitudinal ridges. Or the feather contains a yellow to brownish black pigment, and the color actually observed, as *green, blue*, and *violet*, is produced by a specially produced and particularly constructed transparent layer between the pigment and the surface. Of nonchanging colors *blue* and *violet* are always structurally objective. *Green* seems to be only in a few cases the results of yellow pigment combined with blue surface structure. In most cases it seems not to be a mixture of two colors, but due to yellow pigment light being broken into green. A green pigment seems to be very exceptional.

3. *Colors which change and which depend entirely on the Position of the Light and Eye.*—They are produced by a transparent sheath, which acts like a prism. Any changing color represented in the solar spectrum may be thus produced in feathers."

Haecker[1] takes quite a different view of the subject. "According to Krukenberg the yellow, yellow-red, and red (ordinarily diffused) pigments belong to the class of lipochromes or fat dyes, while the brown and black granular ones are melanines.... The brown pigments, which form the basis for all brown, gray, black, and blue colors, always occur in the form of grains.... In the definitive feather the pigment is chiefly in the cortex and in the barbules (radii) when the color is brown... When the dark brown pigment grains are packed very closely in the cortex and in the barbules a black color is produced, while gray occurs when there is relatively little pigment in the front part of the cortex and when there is a marked increase in the metameric arrangement of the pigment in the barbules. The pigment in the barbules is of great importance in causing a dark or a light tint, as is shown well in the light gray and dark gray feathers of *Columba palumbus*. Really black pigments are rarely found in birds' feathers and gray pigments never. A close packing of the dark brown pigment grains often produces the effect of black; but whenever the pigment is isolated it proves to be dark brown.

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[1] Archiv. mikr. Anatomie, 35, 68 (1890).

"Both from a phylogenetic and from a purely histological viewpoint, the gray color is connected closely with the blue color. At least production of gray involves two of the conditions for the formation of blue, namely the unpigmented cortex and the dense layer of pigment in the medullary cells. The third requisite is the occurrence between these two films of a layer of thick-walled box cells,[1] which are more or less polygonal when seen from above. Fatio had already recognized in them the cause of the blue color, without having recognized the finer structure. He accounts for the blue and green colors of the 'enamelled feathers' by the passage of rays reflected at the center of the feather through an upper transparent layer which is colored differently and is also reflecting. Gadow has later studied the blue feathers with care and has tried to account for the blue color by the theory of diffraction colors. With *Pitta moluccensis* and *Artamia* he found a system of very fine grooves which run parallel to the long axis of the prismatic box cells. In the course of the discussion he says: 'As the primary cause we have to consider the fine ridges which we observe on the outer surface of all these prismatic columns.' He is doubtful whether this is the only cause of the blue color for he says that 'very likely the transparent coating and the cones themselves will influence the light passing through them. The production of blue therefore in a feather would be the result of a very complicated process.'

"Against this view of Gadow's the following points may be urged:

1. The invariable occurrence of the following arrangement: *Epitrichium;* rind layer with no pigment; a layer of regular, air-filled, thick-walled box cells with pores in the walls; dense, granular, or fibrillar pigmented background. It is quite inconceivable that the real cause of the blue color is not to be found here.

2. The ridges, which Gadow mentions explicitly only in the cases of *Pitta moluccensis* and *Artamia*, are not an ab-

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[1] This term is suggested by Haecker instead of "Schirmzellen."

solutely necessary phenomenon. I, myself, have found elements, which corresponds approximately with Gadow's ridges, only in *Pitta maxima*, and though I have found, on the outer cells in a cross-section of a Cotinga feather, ridges which correspond in position with Gadow's ridges, their occurrence in the horny and bent outer cells might easily be the result of mechanical strain or pressure.

3. If the existence of these ridges was proved everywhere, their position, more or less parallel to the incident light, is not what it should be for the production of diffraction colors. Besides, it is inconceivable that such ridges could suffice to produce a uniform blue color.

"In order to determine the relative importance of the different constituents of the arrangement cited under (1), I have made a few simple experiments. (A) A blue feather from *Ampelis cotinga* L. (*Cotinga cayana* Geoffr.) was fastened with the lower side on the object carrier and the *Epitrichium* shaved off carefully together with the horny film which is only slightly developed in this case. By reflected light the highly developed intercellular substance of the box cell layer appears dark brown on account of the underlying dark pigment; the surface of the box cells sends back blue light chiefly at the edge, while in the middle of the Oberhaut the underlying dark pigment begins to count.

(B) The green feathers of *Calyptomena viridis Raffl.* show the box cells structure but the cortex contains a dissolved yellow dye. When the cortex is removed, the underlying box-cells send back blue light.

"The conclusion to be drawn from these two experiments is that the cortex and the *Epitrichium* play no part in the formation of the blue color; but, owing to their high refractive index, spread the blue rays in such a way that blue light is also seen above the intercellular parts. This is confirmed by the following two facts:

(1) In cross-sections of the Cotinga *feather* the cortex appears colorless, while the box-cells show their characteristic color provided they have kept their air-content.

(2) In the banded wing covert feathers of *Garrulus glaudarius* L. the cortex developed just as much in the dark places as in the light ones.

(C) If a feather of *Pitta cyanoptera Temm.* is fastened with its upper side to the object carrier, and the *Epitrichium* and pigment layer are shaved off the under side, those portions (now seen from below) where the actual box-cells are not injured, show in transmitted light a yellow color and in reflected light a blue color, the intensity being low owing to the absence of the pigmented background. The same occurs in the uninjured feather in the extreme outer cells where there is no underlying pigment layer. Finally, the same effect is often produced though to a very slight extent in the cells of the marrow substance having no thickened walls.

"It follows that the chemically modified substance in the typical box-cells with thickened cell walls—and to a lesser extent the other narrow cells—have the property of reflecting blue light and of letting yellow through. The thicker the cell walls the more marked is the color.

"To repeat, there are three factors essential to the production of the blue color:

(1) The air in the cells.

(2) The thickened walls of the box-cells.

(3) The numerous pores which can often be detected in the cell walls.

"In cross-section only those cells which contain air show markedly the typical color of blue by reflected and yellow by transmitted light. This appears very beautifully in cross-sections of the feathers of Cotinga. Wherever the air has not been driven out by the impregnating material, *i. e.*, wherever the air fills the whole cells and especially the numerous pores, which are especially easily seen in Cotinga, the color appears. If the impregnating material (Venetian turpentine or glycerine) has displaced the air, the color disappears while the outlines become more marked. Dilute or concentrated sulphuric acid, when warmed, destroys at once the slightly resistant horny film and permits the escape of the air bubbles, thus causing the disappearance of the color.

"The phenomenon is to be explained as follows: the absolute index of refraction of air is very different from that of the modified substance constituting the cell wall. The difference between the two is especially marked for blue and violet light. Consequently when light passes through the cell walls which contain numerous pores, the blue light is scattered the most. Assume that a beam of light consists of 100 rays of blue light and nine hundred rays of other colors. When passing the surface separating the cell walls from the air-filled canals, there may be for instance 50 percent of the first and 30 percent of the second reflected back. In other words, at the first surface of separation there will be sent back 0.5 × 100 blue rays and 0.3 × 900 other colored rays. At the next surface the amount will be $(0.5)^2 \times 100$ blue rays and $(0.3)^2 \times 900$ of the others. The oftener a reflection takes place at a dividing surface, the greater will be the ratio of the blue rays to the others and the more marked will be the blue color. The absolute index of refraction of glycerine, Venetian turpentine, etc., is not very different from that of the horny layer. Consequently much more light will pass through unchecked and the ratio of the reflected blue rays to the others will be smaller.

"The last factor to consider in connection with the blue color is that due to the layer of pigment. Its effect is shown most clearly by the 'Häher' feathers. At the black places the box-cells are not yet developed; the walls have the same thickness as those of the marrow cells; and the pigment fills the cells. In the blue places the grains of pigment are either on the back of the box cells (dark blue) or are outside these cells (bright blue), while at the same time a thickening of the cell walls takes place. In isolated cases there is a difference in tint due to differences in the heights of the cells, the blue being brighter the higher the cell layer. A similar effect can be produced by doubling the cell layers."

"The significance of the dark pigment layer is shown by the following experiments:

(D) If the *Pitta* feather is prepared as in (C) and the carrier laid on the dark stand of the microscope, the blue remains in reflected light; but if it is laid on white paper, the blue color disappears because the white light, which is sent out from the paper, masks the blue light completely.

(E) Treatment with chlorine converts the black-brown color of the pigment into a light brown or a yellowish brown, whereupon the characteristic blue color disappears.

The dark layer of pigment protects the blue light reflected back from the box-cells from admixture with light of other wave-lengths which might be reflected from beneath the screen cells.

"The results of the investigations on the blue color are as follows:

(1) The *Epitrichium* and the cortex spread the reflect blue light and thereby cause the effect of a uniformly-colored blue surface.

(2) The blue light is reflected chiefly from the surfaces between the modified cell walls and the air channels.

(3) The pigment layer protects the blue light from admixture.

"I will now discuss some of the more important shades of blue.

(1) *Type of the pure blue wing covert feathers* (*Häher type*).—There is no change to greenish or violet.... In the cortex one finds colorless grains, which are to be considered as altered pigment granules, in which the dark, granular pigment has been destroyed in some way, since they correspond in position to the pigment grains still in place on the back side of the barbs. In some of the grains there is a little pigment. A similar structure is to be found in the blue wing-covert feathers of *Platycercus Pennanti* Vig., which belongs to the Sittacinae.

Next in order come two variations of the pure blues:

(2) *The blue of the Irene type with a peculiar gloss.*—This occurs in some of the most different species (*Irene, Pitta, Malurus, Halcyon*). The glossy effect is due to the broadening of the cross-section just as in the case of *Bombycilla;* the *Epitrichium* forms the mirror surface. A single layer of

thick-walled cells containing air covers the dense underlayer of pigment. In the simplest possible, but most complete, way a saturated blue is obtained. The cross-section of a *feather* from a male *Irene malayensis Horsf.* does not show a completely symmetrical structure; the edge which is outermost from the shaft of the feather is easily bent back; the cells are flatter at this point, their tangential diameter is larger, and the inside of the cell is decreased by the presence of knobby excrescences on the cell walls. The arrangement of the box-cells reminds one of the peculiar increase of surface in the palisades of the phaenorogamous leafs.

(3) *Blankehlchen type* (*cobalt blue*).—In the few cases where blue occurs in the feathers of our song-birds (*Sylvia succica* L., *Parus coeruleus* L.) it is a dull cobalt blue and not very brilliant. The barbs have a simple, oval cross-section with a well-developed box-cells system. The pigment is partly in lumps in the thickened rear wall of the box-cells, and partly it fills the lumen in spindle-shaped grains. The refracting media here are the front wall and part of the side walls of the box-cells. The barbules are slightly developed and without pigment or structure color. In the case of the North American blue-bird, *Siala*, the cross-section of the barbs has the form of an I-beam.

(4) *Eisvogel type.*—The clear (azure-blue) feathers of the "Eisvogel," which vary markedly towards the green when viewed at certain angles, have a very remarkable cross-section in the case of the barbs. Under the layer of 3–4 thick-walled box-cells there is a dense layer of dark brown, pigmented marrow cells so arranged that only a small portion of the outer cells of the box-cell layer have a dark background. A precisely similar arrangement is to be found in the cross-section of the *feathers* of *Cotinga cayana* Geoffr., previously mentioned. The blue feathers of this latter bird also have a greenish tint, which is almost the same as that of the "Eisvogel." Since the much rumpled barbules, containing no pigment, have no effect on the color, the greenish tint must either be due to the insufficient under-layer of pigment or

perhaps to the approximately identical curvature of the cross-section in the two cases.

(5) *Blauracken type.*—The pale sea-green feathers on the under side of *Coracias garrula* owe their greenish tone chiefly to the yellowish barbules and perhaps also to the under-layer of pigment which is scanty on account of the great depth of the cells.

(6) A change of the blue by reddish to cornflower and lilac occurs in the wing covert feathers of *Coracias garrula* and also in the tuft of *Palaeornis haematodus.* The form of the cross-section is astonishingly like that of a round horseshoe. The pigment occurs in the upper film. Both circumstances may play a part in the change of tint. An argument in favor of the second is furnished by the lilac feathers of the *Coracias Eurystomus afer,* in which the lilac color is evidently due to the disturbing secondary rays reflected back from the light brown pigmented under-layer.

"Green colors can occur in various ways:

(1) Through green pigment....

(2) The olive green of our song-birds is due to a clouding of the yellow feathers. The barbs of the green feathers of our "Meisen" for instance show a non-granular yellow coloring of the medullary cells and of the walls of the air-containing medullary cells. The change to green is caused by the small amount of brown pigment in the air-cells and through the barbs. In *Motacilla flava* L. there is the unexpected phenomenon that the quill even in cross-section shows highly developed box-cells while the previously described simple structure occurs in the barbs. The green tint is therefore strengthened by the quill sending out blue light which mixes with the yellow light from the cortex to form green. In this way a beautiful green feather is produced.

(3) *Calyptomena viridis Raffl.*—The completely developed box-cells are covered by the yellow-colored cortex. Experiment B shows that this is actually the way the green is produced, while the conditions for the blue are given by

the presence of pigment in the thickened medullary cells, this is not so in the next case.

(4) *Tanagra lutea.*—The golden yellow, shining feathers of the "Bürzel" have narrow cells with much thickened cell walls; but there is no pigmental under-layer to isolate the blue rays. So long as these golden yellow feathers lie one upon another they show the color of the yellow dye; but the rear ones, which rest on the black tail feathers, appear green because the box-cells and the dark background give rise to blue beneath the yellow rind.

"Pigment is always present in yellow, orange, and red colors. It is true that Gadow found a different type of yellow in the yellow feathers of *Pitta moluccensis*, for he says that the thin rami of a downy part of a feather of *Pitta* appeared colored (yellow) only under direct light, but they are colorless if examined under the microscope with transmitted light." This statement is certainly an error in case Gadow was really studying *Pitta moluccensis* Müll *cyanoptera Temm.* (unfortunately he does not characterize the bird sufficiently definitely). Both barbs and barbules appear quite intensely yellow even in transmitted light. On the barbules I have not been able to find the usual cross-section which Gadow describes. Instead of the regular toothed-wheel structure, I find, common to all the barbules and unsymmetrical cross-section, in which the thinner part corresponds to the back edge, which is usually curved. I conclude therefore that Gadow did not study *Pitta moluccensis* Müll.

"If we consider the relation of the yellow and red pigments (lipochromes) to the brown ones (melanines), it is unquestionable that the latter are phylogenetically older. Not only are they the only ones yet found in the embryonic covering, but the primitive markings (longitudinal spottedness, cross-bands) are due almost exclusively to a regular distribution of the brown pigments. In the most advanced forms there can be noted a gradual displacement of the brown pigments by the lipochromes in accordance with Eimer's law of the posterior-anterior and inferior-superior development, in other words, a change of the brown color (pigment in the cortex) to gray (brown granular pigment in the medullary cells), green (brown granular pigment in the medullary cells and diffused yellow in the cortex) and yellow (diffused yellow pigment in the cortex). An instance of this is *Motacilla flava* L., where the crown of the nape of the neck is still ashy gray with a few green feathers, while the lower portions, which are the most developed, are a pure yellow.

"The chemical conditions for the occurrence of the two types of pigments are different, as Krukenberg also points out, so that in animals which are partial albinos, melanism may be absent though the lipochrome colors have developed normally. Considered from this point of view, the colors of partial albinos are easy to understand. I mention two striking illustrations of this since Krukenberg has not done so. I saw an albino "Distel" finch (*Fringilla carduelis* L.) in which the red patch at the bill and the yellow wing barbs (lipochrome) had kept their original color, while the brown pigment had disappeared from all parts where it occurred normally. There is also a pure yellow form of "Blaumeise" (*Parus coeruleus* L.) in which the yellow pigment has developed and this has not been the case with the brown pigment which causes the blue color. While this albino is an ontogenetic variant of the "Blaumeise" with exclusive development of the yellow (lipochromatic) pigment, the "Lasurmeise" (*Parus cyaneus* Pall.) is a phylogenetic modification of the same with sole development of the brown (melanic) pigment. The "Lasurmeise" is a "Blaumeise" in which the yellow pigment has not developed and constantly it is blue on the back instead of green (blue plus yellow) and white on the under parts instead of yellow.

"The gloss on the yellow and red feathers always occurs in connection with a marked development of the keratified cortex substance with simultaneous crumpling of the air-filled medullary cells and of the barbules. The keratified part is thus the effective reflecting portion. This shows up extraordinarily well with *Phasianus pictus* L. and with different species of orioles, especially with *Oriolus regeus Gainard* from New Holland... "

"Our present optical methods do not enable us to determine in what way the gloss and the color of the metallic barbules are produced. In favor of the color being produced like that in iridescent plates (Knöpfe) and of the phenomenon being a matter of interference is the regular occurrence of fine longitudinal stripes, which can be seen very well in the white but metallically lustrous neck feathers of the ring-dove. In the case of *Lamprocolius splendidus* it is also not possible to cite the highly developed *Epitrichium* of the barbules as an illustration of the action of thin plates as Brücke has done; the relatively great thickness of the highly refractive epithelial layer causes Gadow to assume the refraction of the light by prisms, saying that 'the colors which change and which depend entirely on the position of the light and the eye are produced by a transparent sheath which acts like a prism.' This explanation is by no means convincing. The question as to the cause of the metallic colors cannot be considered as answered definitely.

"If we summarize the points brought out in this paper, we may draw the following conclusions:

1. According to Krukenberg the pigment in birds' feathers can be divided into lipochromes (red and yellow pigments) and melanines (brown pigments). In partial albinos one or the other group disappears, thus showing that the conditions of formation are different. The melanines are the older phylogenetically and give rise to the most important markings characteristic of the families. In many cases (songbirds) the lipochromes move from the back to the front.

2. The brown color is due to the deposition of granular pigment chiefly in the cortex; gray is produced when this pigment draws back into the barbs and when it is massed in groups in the barbules, while black color arises from a high concentration of a dark brown pigment and only occasionally is it due to a black pigment.

3. The conditions for a blue color are: an *Epitrichium*

and cortex containing no pigment; box-cells with thickened walls and filled with air; dark under-layer of pigment. From experiments A and B on the removal of cortex, the importance of the latter is shown; through its high refraction it spreads the blue light. The blue light rays are emitted from the air-filled box-cells. The blue light is produced at the surfaces of the cell walls. If the cell walls are in contact with impregnating substances such as Venetian turpentine and glycerine, with refractive indices more near to that of the substance forming the cell wall much less blue light is produced.

4. The gloss is due to an increase in the cross-section. With greenish blue and violet (lavender) feathers the blue light is modified by the presence of other wave-lengths in consequence of a too scanty underlayer of pigment to the presence of a yellow or brown color.

"Green is due to green pigments (*Musophagidae, Eurylaemus, Somateria*) or through a change in the yellow due to the presence of brown pigment or to the occurrence of yellow pigment in the box cells (*Calyptomena*). A green color may also occur if there are black feathers under the yellow ones. The yellow and red colors are due to yellow and red pigments which may be either granular or diffused.

"The gloss on the feathers is due to the development of the rind substance together with a simultaneous decrease in the marrow substance and a crumpling of the barbules. The peculiar gloss on the plate feathers of *Bombycilla* is due to a broadening of the reflecting *Epitrichium* surface and to the marked development of the colored cortex. The plates are caused by the fusion of the end barbs. In metallic feathers the barbules are the ones that produce the metallic effect. There are always longitudinal ridges and grooves on these which appear to cause interference phenomena."

Strong[1] gives some additional data without doing anything towards clearing up the general theory. "The researches

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[1] Bull. Harvard Museum of Comparative Zoölogy, 40, 147 (1902).

of Altum,[1] Bogdanow,[2] Brücke,[3] Gadow,[4] Krukenberg,[5] and Haecker[6] have shown that the colors of birds may in general be divided into two classes, (1) those due simply to the presence of a pigment, and (2) the so-called structural colors. Under simple pigment colors they have placed red, yellow, orange, black, and brown, whereas white, gray, blue, the so-called metallic colors, iridescent phenomena, and lustre are called structural colors. According to Haecker, green is structural color, except for the single case of turacoverdin, a pigment described by Krukenberg.

"The production of structural colors has been variously explained as due to either (1) light interference phenomena or (2) diffraction or dispersion of light rays. Except for white, however, a dark granular pigment (melanin) has always been found associated with such effects. Peculiar modifications in structure are associated with blue colors. Altum observed that feathers giving bright blues have the barbs isolated, *i. e.*, not connected with each other by barbules. Haecker considered as necessary for the production of blue: (1) a thickened unpigmented cortex, (2) a deposit of brown pigment in the medullary cells of the barb, and (3) the occurrence of more or less polygonal, porous-walled box cells.

"I have examined blue feathers from the indigo bird (Passerina cyanea), the blue bird (Siala sialis), Pitta sordida, Pitta moluccensis, Cotinga cayana, and the blue-jay (Cyanocitta cristata). The brilliant blue feathers furnished by Pitta and Cotinga have the barbules rudimentary or of insignificant size where the color is most intense. The lateral diameter of the barb is also greater than in the more proximal and less brilliant portion. Such feathers never appear blue

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[1] Arch. Ornithologie, 1854, 293; Jour. Ornithologie, 2, 19 (1854).

[2] Rev. et Mag. Zoologie, [2] 10, 180 (1858).

[3] Sitzungsber. Akad. Wiss. Wien, 43, II, 177 (1861).

[4] Proc. Zool. Soc. London, 1882, 409.

[5] Vergl. physiol. Studien (2) Part 1, 151; Part 3, 128 (1882).

[6] Haecker: Arch. mikr. Anatonie, 35, 68 (1890); Zool. Jahrbuch, Abt. Syst. Geog. Biol. Thiere, 15, 267 (1901).

except when seen from above. Their ventral surface gives a dull brown color. The box cells are conspicuously developed. The cavities of the ordinary medullary cells have a thick peripheral layer of dark brown pigment. In Cotinga I found no ordinary medullary cells, but the ventral cortex was thickened and appeared black from a rich supply of pigment. Blue feathers from the blue jay, the blue bird, and indigo bird show no box cells, but there is a pigmentation of the central medullary cells similar to that observed in the Pittae. The distal portions of blue feathers from the blue bird which I examined gave a much more brilliant blue than the proximal portions. The transition from bright to dull blue was abrupt. With the aid of a microscope, it could be seen that a light blue of uniform intensity was given by the barbs in both proximal and distal portions. Where the feather appeared bright blue, *the barbules were absent*. A similar relation between brightness of color and the absence of barbules has been noticed by other writers for other birds.

"A variation from the conditions described by Haecker for the production of blue is found in the blue feathers of the indigo bird. I have never seen any pigment in the medullary cells; but heavily pigmented barbules occur and they are not reduced in size. A section of a barb from the dark brown tertiaries of the "homer" pigeon shows little, if any, more pigment than is found in gray feathers of Sterna hirundo. The distal as well as the proximal barbules are liberally supplied with brown pigment, however, whereas in Sterna, only the more proximal portions of the distal barbules have an appreciable amount of pigment. The wing feathers of the *juvenal* plumage vary from plain gray to brownish gray. When the latter color occurs there is a noticeable pigmentation of the proximal barbules....

"While a deposit of melanin pigment in the more central of the medullary cells of the barb is usually associated with the production of blue, as described by Haecker, the pigment may occur in the barbules and not in the barbs. This is the case in the indigo bunting (Passerina cyanea)."

In a paper published in the same year, Haecker and Meyer[1] really give a consistent theory of the blue color. "Different kinds of Parrots of the Species *Sittace* and *Platyercus* display in their plumage the whole color scale in the order in which it occurs in the spectrum: red, yellow, green, and blue. A well-known instance is one of the common Aras, *Sittace macao* L., in which the red of the upper body comes next to the yellow, green and blue patches of the wings exactly in the spectrum order; in fact single wing-covert feathers show in small compass the whole four-colored scale. It has been known for a long time that these gradually blending colors are not formed, as one might expect, by successive changes in a single color factor; but that there are two distinct methods of formation. The red and the yellow in birds' plumage are pigment colors while the blue and, to some extent, the green are so-called physical or structural colors in which the coloration is not due to a pigment of the same color but depends on the histological structure of the feather. It is also known that blue pigments have not yet been found in the feather of any bird and green pigments only occasionally. On the other hand, the blue structural color is widespread and shows a more or less high degree of development, not only among the parrots but among the most different, and in no way related, families of birds. These different facts make it seem interesting and important to seek a definite solution of the cause of the blue color and, above all, to determine whether the typical structure of the feather is sufficient to account of the appearance of a blue color, and to see what further conditions are necessary in order to cause the development of blue in any family of birds....

"If a sky-blue feather of *Cotinga* or *Malurus* is examined in the dry state with a high magnification (Seibert 2 mm, for instance), the barbs of the feather appear chiefly a dull grayish blue and a dull yellow or reddish yellow color is shown only by cells at the edges, through which the light can pass unchecked from below owing to a too scanty underlayer of pig-

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[1] Zool. Jahrbücher. Abt. Syst. Geog. Biol. Thiere, 15, 267 (1902).

ment. If one removes some of the rind layer at any point by scraping, so that liquid can enter unchecked, and if one puts a drop of Canada balsam on the edge of the cover glass, the following effect is to be noted in the border cell: In the enamel or box-cells,[1] which were colored uniformly yellow or reddish yellow, the colored substance seems to contract, at first to an aproximately spherical mass with serrated edges. After some time the single cell seems like an entirely colorless box, with the round, hollow space in it filled by an air bubble, while the walls often contain dark granules. Finally the air bubble itself disappears and some still darker points are to be seen in the walls of the box-cell. This phenomenon can be explained only on the hypothesis that the liquid gets in through the damaged portions of the rind and displaces the air gradually from the single box cells. The process takes place with different degrees of rapidity, probably because of the special structure of the single cells, so that in a Canada balsam preparation, which has become hard, or even in sections, one may find different stages of the change fixed.

From what one sees through the microscope, it is clear that the walls of the box-cells are penetrated by a large number of radial pores, through which liquid passes into the box by capillary action. The projections in the serrated edges mark the places where the air content is displaced by the liquid, in other words, the pores in the walls, while the dark points at the end of the operation are small traces of air left in the pores.

"In the completely soaked cells it is usually not possible, at least with *Cotinga*, to detect any signs of porosity in the cell walls, which can be explained by the cell wall and the Canada balsam having the same refractive index. In some cases, for instance with *Malurus*, in points on sections where the cut has not damaged the box-cells, there can be detected some points on the surface of the cell walls, and these are probably the outer ends of the pores.

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[1] Instead of the unfortunately chosen term Schirmzellen, we suggest the strictly morphological term of box-cells.

"Even though the pores in *Cotinga* and other instances can be detected only while the air is going out and the liquid coming in, there can be no doubt as to their regular distribution, since the whole course of the decolorization indicates their presence with certainty. In addition one can do a similar thing synthetically by drying the frames of certain perforated thalamophores, especially the Textularia, which are easily raised in salt-water aquaria, and then watching them under the microscope while they are being wetted by a liquid. When Canada balsam is used and, still more, when using the substances, to be mentioned later, which have a lower index of refraction, the displacement of air gives results similar to those described. There can be no question but that the air in the box-cells and especially in the pores in the walls is the cause for the phenomenon that the cells in question are reddish yellow by transmitted light and sky-blue by reflected light.

"The objection might be urged that all this was true for air-dried feathers of old bird skins; but that the important factors might be different for feathers taken freshly from the living birds. While this objection seems an unreasonable one in itself, it was tested by making the same experiment on a blue feather plucked freshly from a living *Ara* (*Sittace macao* L.). The displacement and disappearance took place in the same way and was accompanied by the same color changes as with the *Cotinga* feather.

"In connection with this fundamental experiment it will be well to discuss the experiments with other liquids. Liquids with about the same refractive indices as Canada balsam, such as xylene, benzene, and cedar oil (immersion oil) give the same phenomena as Canada balsam. Since these liquids are much less viscous, the changes take place more rapidly and sometimes almost instantaneously. The final result was great transparency and complete lack of color in the impregnated parts of the feather. A different phenomenon occurs both with liquids having a smaller index of refraction and with those having a larger one. On treating with alcohol, which wets the walls very readily, the border cells in the places where the rind has been damaged by scraping, become instantaneously a transparent golden yellow by transmitted light and a bright blue by reflected light. The air bubbles remain for perhaps ten minutes in the hollow spaces inside the box-cells. When they disappear, the places in question become pale yellow by transmitted light and pale blue by reflected light if one uses a low-power objective.... The color is more marked with water than with alcohol. When water flows into the border cells at the damaged places, the cells appear chiefly reddish yellow by transmitted light and marine-blue or sea-green by reflected light. When a Seibert 2 mm objective is used, the cell walls appear a full yellow by transmitted light and distinctly granular, while the lumina of the cells are orange. The pores thus remain permanently visible when filled with water.

"If one changes to substances which have higher refractive indices than Canada balsam, xylene, etc., and takes, for instance, mixtures of benzene and carbon bisulphide, one finds at first no more color effect than with Canada balsam. If the amount of carbon sulphide is increased to a ratio of $CS_2 : C_6H_6 = 3 : 1$, traces of color appear; when the ratio is 7 : 1 or with pure carbon bisulphide, a marked color effect is produced. With low magnification (Seibert objective 16 mm, Oc 8), the scraped portions are distinctly yellow by transmitted light and distinctly blue by reflected light.

"Since experiments, made one after another with the same feather, always gave the same results, it is clear that the color disappears when the box-cells and their pores are filled with a liquid having the same index of refraction as the cell wall. The color appears as soon as the refractive index of the imbibed substance is markedly different from that of the cell wall, regardless of whether it is smaller (alcohol or water) or larger (carbon bisulphide).

The data are given in Table I, the first color being for reflected and the second for transmitted light.

TABLE I

	Refractive index for Na light	
Pure CS_2	1.627	Distinct color, pale blue and pale yellow
$CS_2 : C_6H_6 = 7 : 1$ by volume	>1.558	Distinct color, pale blue and pale yellow
$CS_2 : C_6H_6 = 3 : 1$ by volume	>1.558	Traces of color
$CS_2 : C_6H_6 = 1 : 1$ by volume	1.558	No color
Canada balsam, Av.	1.54	No color
Cedar oil	1.515	No color
Xylene	1.502	No color
Benzene	1.501	No color
Alcohol	1.362	Distinct color, light blue and golden yellow, changing to pale blue
Water	1.333	Strong color, sea-green and reddish yellow. Great transparency but pores visible
Air	1.000	Strong color, cloudy blue and cloudy reddish yellow. Not transparent

"This table shows that the feathers are colorless when the box-cells are filled with a liquid having an index of refraction for sodium light of about 1.52 and that color appears when the imbibed liquid has an index of refraction markedly greater or smaller than 1.52. We therefore conclude that the index of refraction of the cell substance for sodium light is 1.52.

"Starting with the fact that the wall of the cells are broken up by the radial canals into small pieces surrounded by air, the simplest assumption[1] to make is that the cell substance has the same refractive index as air for yellow light, the complementary color to the blue of the feather, while there are considerable differences in the indices of refraction of the two substances for the other rays of the spectrum. In this case the yellow light would pass unrefracted through the mixture of cell substance and air and would be absorbed by the black

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[1] Cf. Christiansen: Wied. Ann., 23, 291 (1884); 24, 439 (1885).

pigment layer, while the rays of all the other colors would be refracted and reflected until they finally reached the eye of the observer, who would see the color complementary to the absorbed yellow. This hypothesis requires that air and cell substance have the same index of refraction for yellow, namely 1.0003, that of air for sodium light. The experiments on the color phenomena when the air is displaced by liquids, show that the index of refraction of the cell substance for white light, which corresponds with that for greenish yellow, is about 1.52. The two values are so far apart that this hypothesis as to the blue color is quite untenable.

"A more general hypothesis was made in 1890,[1] that the difference between the refractive indices of cell substance and air increased toward the blue end of the spectrum. Blue light would then be reflected relatively more strongly than the other colors. It will now be shown that this hypothesis did not account for all the facts and that the blue color is due to:

(1) The difference between the refractive indices of the cell substance and air without involving the hypothesis that this difference is distinctly greater for blue than for red.

(2) The small size of the pores whose diameter is small in comparison with a wave-length of light.[2]

"According to observations made with the highest power, Seibert and Zeiss objectives, the diameter of the pores in a *Malurus* feather is about 0.3 μ, while that in a *Cotinga* is certainly smaller. The observed diameter of the canals is thus smaller than the wave-lengths of red light (0.8 μ) and lies close to the limit of what we can detect optically. It is possible that the canals have still finer branches which are too small to be detected under the microscope. The walls of the cell substance are thus pierced by air-filled tubes having a diameter less than that of the wave-length of light. In other words, we have a transparent medium in which are embedded transparent substances having dimensions small in comparison

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[1] Häcker: Archiv. mikr. Anat., 5, 35 (1890).

[2] Cf. Rayleigh: Phil. Mag., [4] 41, 274 (1871); [5] 47, 375 (1899); Bock: Wied. Ann., 68, 674 (1899).

with that of wave-length of light, and having an optical density different from that of the medium. The refractive index of the medium is about 1.52 and of the transparent embedded substance about 1.0003.

"It has been shown by Lord Rayleigh that if white light penetrates such a combination of two transparent substances differing in optical density, a diffuse reflection of light takes place at the embedded bodies, the blue light being scattered the most. Since the intensity of the reflected light of any color varies inversely as the fourth power of its wave-length ($I = \text{Const}/\lambda^4$), the scattering of the short-waved, blue rays will be relatively large while the red and yellow rays will predominate in the transmitted light.[1] In our case the development of the blue is favored by the fact that the red and yellow rays which pass through the cells are absorbed by the black layer of pigment and therefore cannot be seen by the observer. The best way to determine whether this hypothesis applies is to compare the blue light reflected from the feathers quantitatively with the light reflected from a white surface. If the blue feather behaves like Rayleigh's medium there will be a relative increase in the blue rays [which can be calculated], while in the reflection from a white substance, the ratio of the intensities of the single colors will remain the same as that in the incident light.

"The measurements were made by projecting the light from the blue feathers of a stuffed *Malurus* skin on one-half of the slit of a new model König spectrophotometer while the light from a piece of white paper was projected on the other half of the slit. Both bird and paper were illuminated by an electric arc light, the rays from which had been made parallel by a suitable arrangement of lenses. In a second series of observations the bird-skin was replaced by a piece of white paper and the reflection of the blue feather compared with that of the white paper. For the sake of completeness a spectroscopic examination was made of the light

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[1] Lord Rayleigh considers the blue color of the sky as due to light scattered by particles suspended in the air.

reflected from a shiny, blue paper and from a pigmented paper, the blue color of which was as much like that of the feather as possible. The data are given in Table II. Column 1 gives

TABLE II

Wave-length 1	*Malurus* 2	$1/\lambda^4$ 3	$\frac{1/\lambda^4}{I} = 1/C$ 4	Shiny, blue paper 5	Blue pigmented paper 6
	%			%	%
0.656	20.6	5.40	26.2	28.2	21.1
0.630	21.7	6.35	29.3	19.1	16.5
0.604	23.5	7.52	32.0	16.3	16.6
0.581	26.2	8.77	33.0	16.4	17.1
0.566	27.4	9.74	35.5	17.1	18.5
0.548	28.8	11.09	38.5	21.6	23.8
0.531	34.2	12.58	36.8	26.6	27.7
0.516	39.3	14.11	35.9	31.8	32.2
0.505	43.3	15.37	35.5	39.8	38.4
0.492	—	17.06	—	45.1	41.4
0.481	47.6	18.69	39.3	56.7	52.6
		Av., =	35.6		

the wave-length to which the photometric measurement relates. In columns 2, 5 and 6 are given the intensities I of the light reflected from the blue *Malurus* feathers, the blue gloss paper and the paper containing the blue pigment, expressed in percentages of the intensity of light reflected from white paper the same conditions. The numbers in the third column are proportional to $1/\lambda^4$ and column 4 gives the quotients

$$\frac{1/\lambda^4}{I} = 1/C,$$

which must be constant if the box-cells behave like Rayleigh's medium. As a matter of fact, marked variations from the average $1/C = 35.6$ occur only in the extreme red and the extreme blue, where the experimental error is large owing to the lack of sensitivity of the eye to these colors. When column 2 is plotted against column 1 the resulting curve of the *Malurus* feather coincides very well with the theoretical in the region from 0.6 to 0.5μ....

"This hypothesis also accounts for the previously mentioned fact that when liquids are sucked up which have a greater or a smaller refractive index than that of the cell substance, the same blue is obtained as when the pores are filled with air. According to Lord Rayleigh the intensity of the reflected light varies with the square of the difference between the refractive indices of the medium and the embedded substance. It is thus independent of the sign of the difference and therefore independent of whether the pores are filled with carbon bisulphide or with water. If the difference in the refractive indices is very slight, as when the canals are filled with water, the blue will be less predominant than when the pores are filled with air. As a matter of fact the water-soaked feather is somewhat more green than the unchanged feather.

The hypothesis calls for a predominance of yellow and red in the transmitted light and this can be seen with the box-cells after removing the pigment layer and with the border cells where the course of the rays does not carry them through the pigment layer. All the color phenomena observed with blue feathers can thus be accounted for satisfactorily and it has been possible to show that the box cells have the required characteristics of canals with a diameter less than a wave-length of light and an index of refraction differing from that of air."

The fact that green may be the result of a yellow film superposed on a structural blue is shown very clearly in some experiments by Gadow.[1] "One of the most interesting colors is green. It is not only very common in many frogs, especially such as lead an arboreal life, but it strikes us by its vivid, saturated tints, and last, not least, by the changes which creatures thus endowed can exhibit in their coloration. If you examine the skin of a green tree-frog under transmitted light by holding it against the light, it does not look green at all, but more or less black-brown. The same piece when examined under low power and direct light, shows a mosaic

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[1] Proc. Roy. Inst., 16, 587 (1901).

of green polygonal areas, separated by black lines and interrupted by the openings of the skin glands. Seen from the under surface, the skin is black. Under strong power the black layer is seen to be composed of ramified black pigment cells, and where the light shines through the skin appears yellow. The mosaic layer is composed of polygonal cells, each of which consists of a basal half, which is granular and colorless, while the upper half is made up of drops of yellow oil interspersed in the cell plasma. Since these cells interfere with the light, they are called the interference layer. A vertical section through the skin shows the following arrangement. Below are the black chromatophores, looking rather like the roots of a tree-stump turned upside down. More black is distributed in the upper strata of the cutis near the interference layer. The superimposed protective epiderm may be left out of account, although its condition influences the whole phenomenon somewhat.

"The presence of the layer of interference cells upon the underlying dark background produces the well-known phenomenon of the color of dense media—namely blue. Only the rays of short wave-length are reflected, while those of greater length are absorbed by the black background. Consequently the skin would appear blue, just as the sky is blue, or diluted milk becomes bluish, and the veins of thin and white skinned people appear bluish. But in our frogs' skin the blue light is mixed with the yellow coming from the upper half of the cells, from the yellow oil, and the result of blue and yellow is green. This can be shown experimentally. Application of a drop of caustic potash dissolves the guanine crystals and the skin at once appears black. On the other hand, remove the yellow oil by extracting it in alcohol, then the green frog looks blue. An instance of this is the scientific name of the grass-green Australian tree-frog, *Hyla coerulea*, so-called because it is always blue in our spirit collections. A scratch in the skin of a living green tree-frog, just deep enough to injure or disarrange the yellow layer, appears at once deep blue. If the lesion penetrates the crystal layer, it looks black.

"When, by the action of the chromatophores, the black pigment is shoved towards the surface, the green becomes more saturated. When the pigment is pushed still further, between the interference cells, or even enveloping them partly, then the skin assumes a dull, dark brown to black color. Tree-frogs sometimes do this when they feel dull and cold. Again, when the black pigment is withdrawn from the surface into the deepest strata, and when the chromatophores themselves are much contracted, the skin becomes yellow. Lastly when the chromatophores are more or less contracted, and when the yellow color, instead of being diffuse, concentrates into small drops, our tree-frog assumes a leaden gray or silky whitish hue."

There are apparently two ways in which a structural blue can be obtained. We may have suspended particles as in the case of the blue sky and the blue eye. This is apparently what happens with the tree-frog because Gadow believes that the turbidity is due to suspended particles of guanine. We may also have air bubbles suspended in a transparent solid medium, instead of solid or liquid particles suspended in a transparent gaseous medium. This is Haecker's theory in regard to blue feathers and it is evidently a perfectly legitimate one, which accounts for the facts as presented so far. With both types of structural blue a dark background is desirable to intensify the color by cutting off reflected white light, and actually a dark pigment is found wherever there is a structural blue in nature. Haecker's theory cannot be considered as proved definitely until we have made in the laboratory structural blues of this type and have shown that they do rival in color the blues of the blue jay, the blue bird, the kingfisher, and the indigo bunting. It seems to me that it ought not to be difficult to do this; but I cannot find that anybody ever has done it. Until this has been done experimentally, it is always possible that some point has been overlooked.

Given a structural blue, the structural green is simple enough. We have this in the green eye and in the green frog. It is still an open question whether the metallic blue of the peacock and the metallic greens of the humming birds are structural colors or whether they are like the butterfly colors studied by Michelson. The fact that nobody has ever isolated a blue pigment is not conclusive, because the color in question is the surface color of the pigment and not the color of the solution. Assuming for a moment that the green of the humming bird was due to solid magenta, we should get a red solution and not a green one on extraction. This point has not always been kept in mind by the people who have studied the pigments in birds' feathers.

The general conclusions to be drawn from this paper are:

1. A structural blue may be obtained when we have finely divided particles of liquid or solid suspended in a gaseous medium (blue of the sky) or a liquid medium (blue of the eye or the tree-frog); or when we have finely divided air-bubbles suspended in a liquid or solid medium (blue feathers).

2. A dark background intensifies the blue in all three cases.

3. A structural green may be obtained by combining a structural blue with a pigment yellow.

4. Haecker's theory in regard to blue feathers cannot be considered as proved until similar blues have been obtained synthetically in the laboratory.

5. It is an open question whether all blues in feathers are due to structure alone.

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PREPARATION OF TETRACHLORETHYLENE[1]

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BY H. B. WEISER AND G. E. WIGHTMAN

Tetrachlorethylene was prepared by Faraday[2] and by Regnault[3] by passing CCl_4 through a heated tube. Regnault describes the method as follows:

"I prepared this chloride of carbon (C_2Cl_4) according to Faraday's method by passing the vapors of carbon tetrachloride through a glass tube filled with fragments of glass and heated to redness. A large amount of chlorine is liberated and a liquid condensed which is the chloride C_2Cl_4, colored yellow by the dissolved chlorine. This liquid is far from being pure. It contains a large amount of CCl_4 undecomposed by the action of heat or which is reformed in the cooler portions of the apparatus. One can decompose a part of the remaining CCl_4 by passing the materials through the tube again and again, but not all of it can be decomposed in this way. The liquid is shaken with mercury to absorb the free chlorine and is then distilled under a low pressure and as low a temperature as possible."

Later on, in the same paper, Regnault describes the action of heat on C_2Cl_4.

"This chloride (CCl or C_6Cl_6) was formed incidentally by Julin d'Abo in a nitric acid distillation. Faraday and Phillips, who analyzed Julin's product, have tried to reproduce Julin's results but without success. This compound can be secured by passing the chloride C_2Cl_4 a great many times through a tube heated to a good red heat. In the cooler portions of the tube there condenses a substance in very fine needles which can be taken up with ether and which can be obtained entirely pure by subliming a second time."

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] Faraday: Trans. Roy. Soc., p. 47 (1821).

[3] Regnault: Ann. Chim. Phys., [2] 70, 107 (1839).

In a later paper, Regnault[1] discusses the effect of varying temperature on the decomposition of CCl_4.

"Carbon tetrachloride, when heated, undergoes decomposition with a loss of part of its chlorine and gives rise to a number of chlorides of carbon, the decomposition of which varies with the temperature at which the decomposition takes place.

"If a tube through which is passed the vapors of CCl_4, is heated to a bright red, the chloride C_2Cl_4 is obtained chiefly. After having passed three times in succession a definite amount of carbon tetrachloride through a tube filled with particles of glass and heated to a red heat, the liquid obtained after distilling over mercury to remove the dissolved chlorine showed the following composition:

1.012 gms. gave 0.518 gm. corresponding to 14.15 percent of C (C in C_2Cl_4 14.15 percent).

A determination of the density by Gay-Lussac's method gave the value 5.58.

"The preceding values approach very near to those which obtain for C_2Cl_4 so that there is no doubt that the compound analyzed was formed almost altogether.

"If the temperature of the tube is higher some small crystals of the chloride of Julin $CCl(C_6Cl_6)$ are formed. By holding the tube below a red heat, I believe that the chloride C_2Cl_4 changes to a chloride of carbon, C_2Cl_6 isomeric with Faraday's perchloride but with a density a little less. Unfortunately, the experiment was carried out with too small amounts of material to study the reaction sufficiently and the season was too advanced to enable me to procure a new supply of C_2Cl_4, the preparation of which requires a very intense sunlight."

Löb[2] has shown that when carbon tetrachloride vapor is heated by a platinum wire, the first reaction is the splitting off of chlorine with the intermediate formation of dichlormethylene which is then converted into tetrachlorethylene. Tetrachlor-

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[1] Ann. Chim. Phys., [2] 71, 385 (1839).

[2] Zeit. Elektrochemie.

ethylene may react with some of the chlorine to form hexachlorethane or it may be converted into hexachlorbenzene and chlorine, presumably with dichloracetylene as an intermediate stage. There is usually a certain amount of charring, due either to the direct dissociation of carbon tetrachloride into carbon and chlorine or to the dissociation of one of the decomposition products of carbon tetrachloride. The reactions may be written:

1. $2CCl_4 = 2CCl_2 + 2Cl_2 = C_2Cl_4 + 2Cl_2$.
2. $C_2Cl_4 + Cl_2 = C_2Cl_6$.
3. $3C_2Cl_4 = 3C_2Cl_2 + 3Cl_2 = C_6Cl_6 + 3Cl_2$.
4. $CCl_4 = ? = C + 2Cl_2$.

The directions given by Regnault are not sufficiently explicit to enable one to determine the best conditions for obtaining a high yield of C_2Cl_4 by decomposing CCl_4. Accordingly, in preparing 50 pounds of C_2Cl_4 for research purposes, it was endeavored to ascertain the best conditions for decomposition and condensation of the resulting products, with the end in view of securing quantity production of tetrachlorethylene.

The work done to date consists of the following stages:

I. Decomposing CCl_4 in a quartz tube heated in an electric furnace.

1. Decomposition as done in the apparatus designed and assembled by E. M. James of the Catalytic Unit.

2. Decomposition, using electric furnace; condenser with inner and outer cooling system.

3. Decomposition, using electric furnace; iron condenser with inner and outer cooling system; NaOH in the receiver for the distillate.

II. Decomposing CCl_4 in a quartz tube in a brick furnace heated with illuminating gas.

1. Quartz tube; iron condenser; quartz to wood joint.

2. Quartz tube embedded in fire clay within iron pipe; iron to iron joint with a union.

3. Double length of quartz tube; same assembly as II (2).

4. Single length of quartz tube; exit of tube within the furnace; longer inner iron condenser.

III. Decomposition in a quartz tube, heated electrically by means of nichrome wire wound on tube and covered with heat insulator.

1. Quartz to iron joint, using a packing gland.
2. Same assembly as III (1) with a CO_2-ether bath at —75° C around a condenser in the chlorine stream.
3. Same assembly as III (2) with a CO_2-ether bath at —30° C to —35° C around the receiver.
4. Same assembly as III (1) with a scrubbing tower and a CO_2-ether bath at —75° C interposed in the chlorine stream beyond the scrubbing tower.
5. Quartz to iron joint, using a packing gland, with an upright condenser of iron.

I (1). The first run was made in the apparatus designed and assembled by E. M. James. The purpose of this run was to become familiar with the technique of the operation and the general behavior of the reaction. Carbon tetrachloride was distilled into a horizontal quartz tube, filled with broken quartz and pumice and kept at about 800° in a tube furnace. It was evident from the first run that the main difficulty lay in the clogging of the apparatus by a solid, assumed to be C_2Cl_6. Evidently, too great a time elapsed between the time the gases issued from the furnace and the time these same gases entered the condenser. In other words, the cooling was sufficiently gradual to allow the reactions expressed above to proceed in the reverse direction, resulting in the formation of C_2Cl_6. It seemed the obvious thing, therefore, to shorten the distance between the point of outlet of the gases from the furnace and the point of their entry into the condenser. It was further thought that if one could secure a sufficiently sudden cooling from the temperature of the furnace to the temperature of the condenser, the unsaturated compound would not have time to pick up chlorine to form the saturated compound C_2Cl_6, as shown above. A new type of condenser was designed, therefore, to meet these requirements.

I (2). The new condenser, referred to, consisted of a pyrex tube about 1.5 inches in diameter, into which was inserted a smaller pyrex tube 0.5 inch in diameter and closed at one end. The quartz tube was connected with the outer condenser by means of a rubber stopper through which passed the inner pyrex tube. The glass tube assembly passed through the ends of a tin box through cork stoppers. The space in the tin box around the glass assembly was filled with cracked ice and salt. Water was passed into the inner smaller tube. In this manner a condenser was secured which gave inner and outer coooling. In addition there was not more than two inches between the point at which the gases issued from the furnace and the point at which these gases met a surface at the temperature of tap water. The time consumed by the gases in covering these two inches of space was further reduced by constricting the end of the quartz tube to a $^1/_{16}$ inch opening. The issuing gases were thereby literally shot against the end of the cold tube at a fairly high velocity.

Before starting the runs in this assembly, it was decided to determine whether or not an iron condenser instead of glass would stand up under the chlorine, inasmuch as glass would be impracticable in a commercial process, due to its fragility and its comparatively poor conductivity of heat, as compared with metal. Before beginning the first run therefore, a small iron pipe plug was placed in the outer glass condenser at the end of the inner condenser and immediately in the path of the gases issuing from the furnace, *i. e.*, in the chlorine stream. The plug was left in this position during three runs, and when it was examined there were no visible evidences of corrosion. This showed the feasibility of using an iron condenser in the presence of dry chlorine.

The results of the three runs made in this apparatus showed no deposits of any account in the condenser or in the train employed to carry the chlorine evolved to the outside air. This was an improvement over the apparatus described in I (1), in which clogging with solid was a constant source of delay and annoyance. The distillate from three runs was collected in one receiver and was allowed to stand 24 hours. During the course of the day following the runs, the receiver was removed from the ice-salt bath and was placed on the desk top. After several hours the cork stopper was blown out with great violence and on investigation it was found that the flask was too hot to handle with comfort. Copious fumes of chlorine were evolved, with effervescence of the contents of the flask. This indicated that the distillate contained dissolved chlorine, and at the temperature of the room, reaction was taking place between the unsaturated compound and the chlorine. When the distillate was treated with NaOH to neutralize the chlorine, washed with water, dried with $CaCl_2$ and distilled, it gave a yield of only 46 percent and a considerable amount of solid (presumably C_2Cl_6). This suggested the possibility of improving the yield by removing the chlorine from the distillate immediately upon its entry into the receiver. To accomplish this it was proposed to place about a liter of 1 : 1 NaOH therein, before commencing the run.

I (3). A new condenser was now built consisting of a 0.75 inch iron pipe passing through a threaded cap on the lower end of 1.5 inch iron pipe closed with a 0.75 inch cap at the upper end. The iron pipe assembly was partially enclosed in a water-tight wooden box. The quartz tube was connected to the iron pipe by means of an asbestos-sodium silicate joint.

In the two subsequent runs made in this apparatus, solutions of 1:1 and 1:10 NaOH, respectively, were used in the receiver. When the first run was complete the distillate seemed lost in a yeasty-looking mass from which no smell of chlorine was obtained. When water was added and the mass shaken, the yeasty character disappeared and a 2-layer system was formed with the alkali in the upper layer. In this run the rate of passing the vapors through the furnace was very rapid, being 2 liters per hour. There was no C_2Cl_6 after the distillation was complete. The yield of C_2Cl_4, however, was small, being only about 31 percent. It was thought that the speed at which the vapors were passed through the furnace allowed too short a time for the CCl_4 to be sufficiently decomposed.

In the second run a 1:10 solution of NaOH was used in the receiver and the rate of passing the vapors of CCl_4 was reduced to 1 liter per hour. At the end of the run, when the receiver was disconnected, a strong evolution of chlorine was observed, thus showing the employment of too weak a solution of alkali. There was no solid formed, however, at the end of the distillation, and a yield of 53 percent indicated the efficacy of longer submission of the CCl_4 vapors to heating in the furnace.

In the run just described, an attempt was made to determine the temperature maintained in the furnace. A pyrovoltmeter was used with a Pt-Rh couple. The couple was placed in a quartz tube of small bore, and this tube was placed in the quartz tube of the reaction furnace. When no vapors were passing through the tube the temperature remained about 900° C and when the vapors were passing the temperature registered was about 750° C.

At this point in the investigation serious trouble began to develop due to an imperfect joint between the quartz and the iron. Quantities of chlorine escaped into the room and into the furnace, which was ruined by the gas attacking the hot nichrome wires and disintegrating them thus destroying the circuit. The ruined units of the furnace were replaced and the whole apparatus moved outside where one or two more runs were made. In these runs the rate of passage of the CCl_4 vapors through the furnace was still further reduced by filling the tube with quartz which was more finely broken than that employed in the previous runs. This made a more compact mass through which the gases had to pass. The redistilled distillate showed an increase of about 15 percent in the volume of C_2Cl_4 produced and there was also a great increase in the amount of the C_2Cl_6, so that the net increase in the yield was only about 3 percent.

The work up to this time seemed to indicate:

1. That a temperature of 900° C to 1000° C is conducive to good decomposition.

2. That a slow rate of passing of the vapors of CCl_4 tends to increase the decomposition desired.

3. That the greater the concentration of Cl_2 and C_2Cl_4 in the furnace the greater the tendency to form C_2Cl_6.

4. That in order to keep the apparatus as thus far designed from clogging with C_2Cl_6, enough undecomposed CCl_4 must pass through to dissolve out the solid and keep the tube open.

5. That there is a balance between the amount of decomposition and the speed of passage of the gas, that makes for the easiest operation and the best yields.

6. That there is a definite concentration of Cl_2, C_2Cl_4 and CCl_4 beyond which one cannot work efficiently unless Cl_2 be removed from the sphere of the reaction.

II (1). The next stage in the development of the work consisted in endeavoring to use the illuminating gas flame to accomplish the heating of the furnace. It was also attempted to design a different type of joint between the quartz tube and the iron condenser. The first attempt was made using a bare quartz tube in a brick furnace, and employing a quartz to wood joint.

The furnace was built of one thickness of 8 inch × 4 inch × 2 inch fire brick set on edge. The baffle plates were four in number, placed alternately in the furnace. The furnace was maintained at a cherry-red heat by the use of two blast lamps. On attempting to make a run, the heat of the gases issuing from the furnace was such that the wood charred beneath the asbestos-sodium-silicate cement and shrank away from the tube, thus liberating clouds of gas. The joint was thus an instant and complete failure.

II (2). The next trial was made with an iron to iron joint, the quartz tube being embedded in fire clay within an iron jacket. The fire clay was made of sticky consistency, a 1.5 inch pipe was filled with it and the quartz tube was forced down therein. After clearing the mud from the interior of the latter the whole was baked in a slow flame. The iron-jacketed assembly was then joined to the condenser assembly by means of a 1.5 inch union with a lead washer. The same kind of brick furnace was employed as described in II (1).

Two runs were made with this assembly. The vapors were passed through quite rapidly, as there seemed to be a tendency for the apparatus to clog up, as shown by the height of liquid in the pressure column. The results of both runs were somewhat disappointing, being 56 percent and 59 percent, respectively. It was thought that the reason for the comparatively low yields was to be found in the rapid rate of distilling the vapors through the furnace. After the first run a leak developed around the union. The assembly was dismantled and the union was soldered to the iron pipe. This effectively stopped all leakage. On dismantling the apparatus it was found that the fire clay in the union had become sodden with the condensed vapors from the furnace. This caused a muddy mass which flowed into the narrow portion of the channel, and this accounted for the stoppage and the building up of the pressure mentioned above.

II (3). The next development consisted in increasing the length of the furnace. The only stock of quartz tube available was of a maximum length of 30 inches. Accordingly, two tubes were embedded end to end in fire clay within an iron pipe as described above. A longer brick furnace was necessary. This was made, in the main, similar to the original brick furnace, the only difference being the construction of four ports for blast lamps, one lamp for each baffle chamber, and the putting of the outlet for the flue gases at the in-take end of the furnace. By this means the principle of counter flow was employed, in the hope that a more uniform temperature might be secured within the reaction chamber where decomposition was to occur.

When the first run was made in this assembly several things were at once apparent.

1. Copious clouds of vapor, strongly tinged with yellow, filled the receiver (a 10-gallon carboy) showing a much higher

chlorine concentration than had been formerly obtained, and hence a better decomposition of CCl_4.

2. In addition to the yellow tinge there was a strong tinge of reddish brown, probably ferric chloride. This suggested the possibility of the chlorine getting in contact with the hot iron, as it was shown in I (2) that cold iron is not appreciably attacked by chlorine. This reaction was probably taking place at the point of union of the two quartz tubes within the iron jacket. It was presumed that some of the fire clay had oozed through the joint into the channel of the tubes, thus falling away from the iron wall and leaving it exposed. This supposition was subsequently confirmed.

3. There was a constant tendency for the tube to clog. On opening the condenser there was invariably found a muddy sludge which completely blocked the outlet. This was thought to be solid chloride of iron, mixed with CCl_4, C_2Cl_4 and C_2Cl_6.

Though three runs were made in this assembly, the difficulty of securing continuous operation was such that complete data were obtained in only one run. It was evident from these data, however, that a very material improvement in the decomposition had been obtained. The ultimate yield was poor due to the formation of very large amounts of C_2Cl_6, again bearing out the theory of balance between amount of decomposition and rate of distillation. It might be possible, however that a more efficient method of instantly chilling the gases issuing from the furnace would obviate the difficulty due to the formation of C_2Cl_6. During the third run, the iron jacket in the furnace burned through at the point of union of the two quartz tubes and clouds of chlorine poured forth.

II (4). The next modification was an assembly differing from that described in II (3) only in the point at which the quartz tube ended. It was planned to have the hot gases emerge at a point just beyond the sphere of active heating in the furnace, and it was further planned to accomplish chilling of these gases immediately at this point, by extending the inner tube of the condenser through the union and on into the brick furnace. By this means, gases at furnace heat would be made to impinge upon a surface at the temperature of tap water, without any time being allowed for the interaction between chlorine and C_2Cl_4.

This run began splendidly, but unfortunately the end of the quartz tube was a little too far within the furnace. About an inch of the iron pipe jacket was left exposed to the direct action of the gas flame and this portion of the tube burned through under the action of the chlorine within two hours. It is assumed that the assembly would give good results if the quartz tube ended at a point just within the brick wall of the furnace, in such a manner that the chlorine would be unable to reach any portion of the iron tube heated directly by the gas flame. It is thought that the temperature of the iron would not be sufficiently high at such a point to cause any troublesome reactions between the chlorine and the iron. It was now decided to abandon this type of heating, and the type of quartz to iron joint.

III (1). The investigations up to this point revealed the fact that too little was known concerning the temperatures at which the most efficient operation could be secured. The mode of heating by gas did not lend itself to a ready means of varying the temperature. In addition it was felt that the method of joining the quartz to the iron had not proved satisfactory. Since the electric current lends itself to very ready control through the medium of suitable resistance, it was decided to employ electrical heating. A new kind of joint was suggested that seemed very feasible. These new features will now be described.

The joint employed was in effect an ordinary stuffing box usually found on machines to produce a joint with the minimum of leakage around a moving part. Although this type of joint was suggested at the beginning of the investigations, it had never been attempted because it was felt that the extremely brittle character of the quartz tube would not permit the degree of compression incident upon using a packing gland. The joint in question has solved the difficulty beyond question, as all the succeeding runs in the investigation were made without the suspicion of a leak.

After the quartz tube was joined to the condenser the tube was wound with four lengths of number 10 nichrome wire, each length being 8 feet long. Each length of wire formed a heating unit. All four units were connected in parallel in a 110 D. C. circuit. A resistance and an ammeter were placed in series in the circuit.

In the first furnace thus constructed, a thin sheet of asbestos paper was wrapped on the quartz tube and the nichrome wire was wound thereon. In this manner the wire was prevented from slipping, short-circuiting being thus avoided. The spaces between the coils of the winding were filled in with coils of 0.25 inch hard asbestos cord. The nichrome-asbestos cord winding was then covered with 0.25 inch of alundum cement for insulation purposes. When the connections were made and the tube was carefully heated, the alundum baked to a very hard protective coating. A current of 20 amperes heated the tube to a bright cherry-red heat. After heating for a period of three or four hours, however, the ammeter failed to register the current, and on investigation it was found that the nichrome wire had failed under the high temperature.

In the next furnace, a heavy cardboard wrapping of asbestos was placed next to the quartz tube, and only three units of 8-foot lengths of wire were employed. The spacing of the coils was increased from $^1/_2$ inch as in the first furnace to $^1/_4$ inch. A current of about 12 amperes was used. In this furnace the asbestos board on which the wire was wrapped proved itself such a good insulator that the interior of the quartz tube failed even to glow.

Another furnace was constructed in which the wire was wound directly upon the bare quartz tube, the winding being covered with alundum cement as formerly. Two units of 12-foot lengths of wire were used and a current of 10 to 12 amperes. As in the first case, the interior of the furnace heated to a bright glow, but the nichrome wire again failed under the heat.

It was now evident that a heavier nichrome wire must be employed. A number 18 wire was secured and a single unit of 12-foot length was wrapped upon the bare tube with approximately 0.5 inch spacing of coils. The tube was thus wrapped close to the packing gland at one end and to within three inches of the intake end. The alundum cement supply had become exhausted, so no insulator was baked on the tube as formerly. Instead, the tube and wire were wrapped with three layers of soft 0.5 inch asbestos rope ordinarily used for packing. This proved the best insulation thus far employed and the furnace stood up for a considerable number of runs. Eventually, however, the wire burned out, and on the removal of the wrappings of asbestos, it was found that a slight corrosion seemed to have occurred in the wire an inch or so on each side of the point at which it had burned out. It was suggested that the iron in the asbestos had become alloyed with the nichrome wire, thus causing it to fail more readily. In order to protect the wire from this possible source of trouble, the wire was coated with $^1/_4$ inch of plaster of Paris, which was thoroughly dried out by gentle heating. The asbestos rope was wrapped thereon. This type of furnace lasted through the rest of the runs made in the investigation and proved highly satisfactory.

In the apparatus just described, 16 runs were made. The current and the rate of distillation of the CCl_4 were varied at will and at the date of writing a yield of 92 percent on the basis of the amount of CCl_4 decomposed, has been obtained. By employing a current sufficient to give a temperature of 1200° to 1300° (with no vapors of CCl_4 passing through the tube) and by distilling at a rate of about 1 liter per hour, a decomposition of 76.4 percent resulted.

III (2). Up to this point in the work the method of computing the yield was as follows: The volume of CCl_4 put through the furnace was noted. The distillate was redistilled and the amount of CCl_4 recovered was subtracted from the volume put through the furnace. The difference represents the amount of CCl_4 decomposed. The theoretical amount of C_2Cl_4 obtainable from this amount of CCl_4 was computed and the amount actually obtainable from this amount of CCl_4 was computed and the amount actually obtained was expressed as a fraction of the theoretical yield. A little consideration will reveal the fact that the difference between the actual and the theoretical yield ought to represent the amount of C_2Cl_6 or such other chlorides of carbon as may be formed in the reaction and which ought to be left as a residue in the distilling flask at the end of the distillation of the products of decomposition. Inasmuch as the residue left in the flask (usually called C_2Cl_6) in the majority of runs made in the furnace described in III (1) did not exceed 2 percent by volume of the amount of CCl_4 passed through the furnace, it seemed clear that some loss was occurring. Since there were no leaks in the system that could be detected, and since the furnace did not clog up run after run, thus indicating that there was no loss due to carbonization or polymerization in the furnace, it seemed very probable that the vapors of CCl_4, C_2Cl_4, and possibly C_2Cl_6, were being carried out in the chlorine stream which was sent up the ventilating flue. It was now decided to liquefy the chlorine stream and determine the loss if any.

The chlorine and the vapors escaping from the receiver were led into a receiver surrounded with a CO_2-ether bath at —75° to —80°. After a run was complete the liquid chlorine was allowed to boil off at room temperature and the redistilled chlorine was again liquefied. In this manner it was found that 150 cc of liquid smelling strongly of CCl_4 went over in the chlorine stream.

III (3). The question now arose as to whether or not those volatile vapors could be stopped in the receiver attached to the furnace-condenser assembly. To determine this point, the receiver in question was surrounded by a bath at such a temperature that the volatile products in question would not vaporize, and the chlorine would not liquefy. By this means it was hoped to secure a separation of the vapors, formerly lost, from the chlorine which had carried them off. The temperature employed in the distillate receiver was —30° to —35°

C, obtained by CO_2 and ether. When the liquid chlorine was redistilled, not more than three or four cubic centimeters of liquid remained, thus showing that most of the vapors that were formerly lost might have been retained by a more efficient system of condensation.

III (4). Since the employment of CO_2 and ether as a cooling medium would be impracticable on a commercial scale, it was decided to try if the vapors suspended in the chlorine stream could be removed by means of a scrubbing device. The delivery tube from the condenser was tapped to allow the passage of chlorine directly into the tower instead of through the receiver as in the former runs. A trap was interposed outside the receiver to divert the chlorine, and by a by-pass from the receiver to the main stream provided for the escape of the chlorine dissolved in the distillate. The amount of water passing through the scrubbing tower was regulated by the manipulation of the cock on the water line. A CO_2-ether bath was placed in the line beyond the scrubbing tower to condense the chlorine as heretofore described.

When this run was complete, 20 cc of liquid smelling strongly of CCl_4 were obtained from the flask from which the liquefied chlorine was redistilled. This showed that this type of scrubber was unsatisfactory.

The resistance to the free passage of the gas caused by the interposition of the scrubbing tower, bubblers, etc., was sufficient to cause a virtual stopping up of the furnace. Just at the end of the run the pressure was sufficient to cause the quartz tube of the furnace to explode with violence, thus ruining the furnace for further use.

III (5). An attempt was now made to improve the condenser, in the hope that something could be devised which would permit of a faster rate of distillation of CCl_4 and at the same time condense the finely divided material which was carried out in the chlorine stream as described above. It was thought that if the vapors after emerging from the furnace could be made to slow down, time would be given them to condense, provided there were a sufficient amount of cold condensing surface. To accomplish these ends, a condenser, in principle identical with that already employed but differing in size and arrangement, was designed. The outer condenser, which was formerly a $1^1/_2$ inch pipe, was changed to a 6 inch pipe. The inner condenser which was formerly a $^3/_4$ inch pipe was changed to a bundle of $^1/_8$ inch pipes connected with return bends. The interior of the 6 inch pipe was thereby filled with a considerable amount of condensing surface. The condenser was longer than that formerly employed.

When this apparatus was set up and the water was passed through the inner condenser coils, a leak developed as was shown by the drip out of the delivery pipe. This meant that the surface of the condenser was moist and as chlorine attacks moist iron, the apparatus was impossible for continuous use. One run was made, however, but the data were not complete enough to warrant an opinion as to the efficiency of the apparatus.

Inasmuch as this investigation was concerned mainly with temperature and rate of distillation of CCl_4 it was thought that it would be advantageous to assemble the data in tables in order that one might compare the results side by side. Accordingly, four tables have been prepared. In Table I are given the data as secured. In Tables II to IV, inclusive, the data are given as they would appear if the runs had been made with 100 cc volumes of CCl_4 in the distilling flask.

Before passing to a study of the data, a sample computation of the yield will be given. For this purpose the data of any run may be taken.

RUN NO. 15 (TABLE IV)

Compound	Mol. Weight	Sp. Gravity
CCl_4	153.84	1.58
C_2Cl_4	165.81	1.61

$$2CCl_4 \longrightarrow C_2Cl_4 + 2Cl_2$$

$$307.68 \longrightarrow 165.81$$

$$307.68 : 165.81 = \text{Weight of } CCl_4 : \text{Weight of } C_2Cl_4$$

$$= \quad G \quad : \quad x$$

$$x = \frac{(165.81)G}{307.68} = 0.539\ G$$

$$G = (\text{Vol. } CCl_4 \times 1.58) \text{ gms.}$$

$$x = 0.539 \times 1.58 \times \text{Vol. } CCl_4$$

$$\text{percent yield} = \text{Weight } \frac{C_2Cl_4 \times 100}{X}$$

$$= \frac{\text{Vol. } C_2Cl_4 \times 1.61 \times 100}{\text{Vol. } CCl_4 \times 0.539 \times 1.58}$$

$$= \frac{161 \times \text{Vol. } C_2Cl_4}{0.539 \times 1.58 \times \text{Vol. } CCl_4}$$

$$= 189 \times \frac{\text{Vol. } C_2Cl_4}{\text{Vol. } CCl_4}$$

$$= 189 \times \frac{13.3}{43.3} = 58.1.$$

As explained earlier in this report, the investigations were carried out.

1. In a quartz tube heated in an electric combustion furnace.
2. In a quartz tube heated in a gas furnace.
3. In a quartz tube wound with nichrome wire heated electrically.

The data for the runs made in each type of furnace appears in Tables II, III, and IV, respectively.

Runs 1–3 were made in an electric combustion furnace, runs 4–6 in a gas furnace, and runs 7–23 with nichrome wire on tube.

In run 20 no NaOH was used in receiver and distillate was allowed to remain over night in contact with chlorine dissolved in it. This accounts for high yield of C_2Cl_6.

Average rate of passing CCl_4 vapors through the furnace 20.5 cc per minute.

Average percent yield—43.1 percent.

TABLE I. DATA AS ACTUALLY SECURED

Run No.	Vol. CCl_4	Time Min.	Temp. Approx.	Vol. CCl_4 recovered	Vol. CCl_4 decomposed	Vol. C_2Cl_4	Vol. C_2Cl_6	Percent Yield
1	2000	80	900	470	1530	370	155	45.7
2	4000	225	900	1275	2725	450	10	31.3
3	4155	240	900	1360	2795	790	15	58.3
4	2700	195	1000	910	1790	535	55	56.5
5	2550	105	1000	600	2150	700	45	61.4
6	2500	125	1000	550	1950	460	35	44.6
7	3000	100	1150	1664	1336	330	10	46.7
8	3000	105	1150	1635	1365	430	10	59.4
9	3000	120	1150	1500	1500	445	10	56.0
10	3000	220	1150	1675	1325	400	150	57.0
11	3000	80	1050	2050	950	275	15	54.9
12	3000	135	1050	1675	1325	500	15	71.5
13	3000	120	1050	1400	1600	500	50	59.2
14	3000	225	1050	1050	1950	675	200	65.4
15	3000	160	1050	1700	1300	400	20	58.1
16	3000	130	1050	1800	1200	390	5	61.5
17	3000	185	1050	1200	1800	585	20	61.4
18	3000	230	1200	950	2050	800	25	74.0
19	3000	210	1200	1100	1900	820	30	81.6
20	1000	160	1200	1155	1845	375	700	38.4
21	1500	75	1300	520	980	400	20	77.3
22	1500	90	1325	355	1145	560	25	92.4
23	1500	75	1300	660	840	320	20	71.9

TABLE II. DATA OF RUNS MADE IN ELECTRIC COMBUSTION FURNACE

Run No.	Vol. CCl_4	Rate in cc min.	Approx. Temp.	Vol. CCl_4 recovered	Vol. CCl_4 decomp.	Vol. C_2Cl_4	Vol. C_2Cl_6	Percent Yield
1	100	25	900	23.5	76.5	18.5	7.7	45.7
2	100	17.8	900	31.8	68.2	11.3	0.3	31.4
3	100	18.9	900	32.7	67.3	19.0	0.3	53.3

TABLE III. DATA OF RUNS MADE IN FURNACE HEATED BY GAS

Run No.	Vol. CCl_4	Rate in cc/min.	Approx. Temp.	Vol. CCl_4 recovered	Vol. CCl_4 decomp.	Vol. C_2Cl_4	Vol. C_2Cl_6	Percent Yield
4	100	13.7	1000	33.7	66.3	19.8	1.3	56.6
5	100	26.2	1000	21.8	78.2	25.5	1.1	61.4
6	100	20	1000	22	78	18.4	1.4	44.6

Heated in a gas furnace.

Average rate of passing CCl_4 vapors through the furnace 19.97 cc per minute.

Average percent yield—55.8 percent.

TABLE IV. DATA OF RUNS MADE IN FURNACE WOUND WITH NICHROME WIRE AND HEATED ELECTRICALLY

Run No.	Vol. CCl_4	Rate in cc/min.	Approx. Temp.	Vol. CCl_4 recovered	Vol. CCl_4 decomp.	Vol. C_2Cl_4	Vol. C_2Cl_6	Percent Yield
7	100	30	1150	55.5	44.5	11	0.3	46.7
8	100	28.6	1150	54.5	45.5	14.3	0.3	59.4
9	100	25	1150	50	50	14.8	0.3	56
10	100	13.7	1150	55.8	44.2	13.3	5.0	57
11	100	37.5	1050	68.3	31.7	9.2	0.5	54.9
12	100	22.5	1050	55.8	44.2	16.7	0.5	71.5
13	100	25	1050	46.7	53.3	16.7	1.7	59.2
14	100	13.5	1050	35	65	22.5	6.7	65.4
15	100	18.9	1050	56.7	43.3	13.3	0.7	58.1
16	100	23.6	1050	60	40	13	0.2	61.5
17	100	16.2	1050	40	60	19.5	0.7	61.4
18	100	13	1200	31.7	68.3	26.7	0.8	74
19	100	14.3	1200	36.7	63.3	27.3	1.0	81.6
20	100	18.9	1200	38.5	61.8	12.5	23.3	38.4
21	100	20	1300	34.7	65.3	26.7	1.3	77.3
22	100	16.7	1325	23.7	76.3	37.3	1.7	92.4
23	100	20	1300	44	56	21.3	1.3	71.9

In run No. 20 the distillate was left over night without neutralizing the chlorine dissolved in the distillate. This accounts for the high yield of C_2Cl_6.

A study of the above tables shows the following average yields according to the temperature:

900–1000° (Runs 1–3)	43.1 percent
1000–1100° (Runs 4–6, 11–17)	59.2 percent
1100–1200° (Runs 7–10, 18–19)	63.5 percent
1200–1300° (Runs 21–23)	80.5 percent

In computing these averages run No. 20 was disregarded.

It will be noticed that the average rate of passing the gases through each type of furnace was practically constant.

Hence the only factor materially changed was the temperature. It will be observed that as the temperature of the furnace was increased, the average yield was increased. This result was predicted early in the investigations. It was expected, however, that the quantity of C_2Cl_6 would increase more with the increase of temperature than actually proved to be the case. This seems to be an indication that the formation of C_2Cl_6 could be practically eliminated with a proper system of "quenching" of the products of decomposition.

In Table IV, it will be noticed that the amounts of CCl_4 recovered are higher than one would expect in view of the fact of increased temperature. A possible explanation may lie in the fact that in the runs tabulated in Tables II and III, a small receiver was used for the distillate. In the runs 7–18, a large receiver (a 10-gallon carboy), was used. This provided an expansion chamber for the gases, thereby causing a drop in their velocity. Consequently, the CCl_4 vapors suspended in the chlorine stream had time to condense, instead of being carried rapidly out as was the case with the small receiver. In fact, one could observe small streams of condensed material flowing down the sides of the large receiver during the course of the run. Hence, more CCl_4 was recovered in runs 7–18 than in runs 1–6. That is, the values for CCl_4 recovered in the first six runs are probably too low. In the runs 18–23 the amount of CCl_4 recovered drops again. This result was to be expected, due to the higher temperatures employed in the furnace. It does not follow, however, that increase of temperature could be used indefinitely to improve the yield. Experience proved that a temperature can be reached at which CCl_4 seemed to be completely dissociated into carbon and chlorine. In preparing for one of the later runs, the furnace was inadvertently heated for the space of an hour or so before commencing the run. Accordingly when the vapors were started through, the furnace was at a maximum heat. (Estimated at about 1500° C). Very dense clouds of chlorine were emitted from the delivery tube along with a cloud of very fine black dry dust which proved to be carbon. Within the space of a minute so much carbon had collected that the delivery tube and the receiver were completely blocked up. During all this time not a trace of liquid distillate appeared, showing that there were no vapors able to be condensed at the temperature of the condenser. Had any CCl_4 or C_2Cl_4 been present the carbon would have been moist, or indeed would not have appeared at all as it would have adhered to the sides of the condenser until it washed down sufficiently to clog the delivery tube with more or less sludgy material. This result seems to indicate that the best temperature for decomposition must lie between 1300° and 1500°.

IV. In view of the fact that the formation of C_2Cl_6 is avoided with difficulty, the question arose as to whether or not it would be easier to make C_2Cl_6 and then reduce the hexachlor compound to tetrachlorethylene. It was decided to try some experiments on the reduction of C_2Cl_6. The following statements in the literature bear on the subject of reduction of C_2Cl_6:

"If[1] one brings this C_2Cl_6 into a flask with granulated zinc and water and then adds H_2SO_4 from time to time so that there is always a moderate evolution of hydrogen taking place, there results after several hours' action a complete reduction of the same into C_2Cl_4. A lower temperature appears more favorable to the change and completes it more quickly, probably because the hydrogen evolution is less violent under these conditions."

"One allows the gas evolution to go on some time after only liquid C_2Cl_4 is present and then distills the product with steam. It is good for the purpose of a rapid reduction to use considerable zinc and to shake frequently. In this way the solid C_2Cl_6 may be kept between the single particles of zinc, for it is only where the zinc touches it that the removal of chlorine with the formation of HCl appears to take place."

"Since the preparation in this way goes quite rapidly, neatly, and without loss, it is to be preferred to the other previously known methods; to the Faraday method, in which

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[1] Geuther: Liebig's Ann., 107, 212 (1858).

the vapor of C_2Cl_6 is conducted several times for complete decomposition through a weakly glowing tube filled with pieces of porcelain to the Regnault method[1] in which one decomposes it to the afore-mentioned C_2Cl_4 with the help of KHS solution."

"It is very remarkable that the formation of C_2Cl_4 results only by using H_2SO_4 for the hydrogen liberation and not by using HCl."

The following work on the reduction of C_2Cl_6 was carried out:

1. Preparation of C_2Cl_6.
2. Reduction of C_2Cl_6 with zinc dust and H_2SO_4.

(1) The residues had been saved which were left after the distillation of the products of decomposition obtained by the treatment of CCl_4 in the hot tube, as previously explained. The residues were of a dirty brown or black color, due no doubt to the carbonization of part of the material in the distilling flask. These were now placed in an Erlenmeyer flask, which was laid on a wire gauze on a retort stand so that the mouth of the flask pointed downward. A second flask was placed with its mouth against that of the first flask and the joint was wrapped loosely with a roll of cloth. The flask with the residues was then gently heated. The C_2Cl_6 sublimed beautifully and the material being quite heavy, it flowed very rapidly into the second flask. The entire material on hand was sublimed three times in this manner and the resulting product was a snow white powder with a strong tarry odor.

(2) 100 grams of C_2Cl_6 were placed in an Erlenmeyer to which was added 500 cc of water. The flask was closed with a two-holed rubber stopper in which were fitted a dropping funnel and a long glass tube which was intended to act as a return condenser. The flask was placed in a water bath at 20° C. Concentrated H_2SO_4 was now placed in the dropping funnel and was added to the contents of the flask a few drops at a time. The flask was shaken constantly. A rapid evolution of hydrogen took place on the addition of the acid. In about

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[1] Regnault: Ann. Chim. Phys., [2] 71, 377 (1839).

three minutes after the first acid was added, the white crystalline character of the C_2Cl_6 had entirely disappeared and a rather heavy looking oil, clear and slightly tinged with yellow, appeared in its place. To all appearances the reduction seemed to be complete at this time. The addition of acid and the shaking of the flask were continued for about 15 minutes longer. The reduction flask was then connected with a steam generating flask and a condenser, and the products of the reduction were steam distilled. The oil came over in the first 100 cc of distillate but the distillation was continued until about 500 cc of water had collected in the receiver. The oil was then separated from the water and was fractionated. The results of the experiment follow:

Vol. distilled up to 121° C.	37 cc
Actual weight of distillate	58 grams
Calculated weight (Vol. × 1.61)	59.12 grams
Calculated yield for complete red'n	70 grams
Percent reduction	82.85
Weight of the residue	7.5 grams
Percent not converted to C_2Cl_4	7.5
Weight of residue remaining liquid	5.4 grams
Vol. of liquid	5 cc
Approx. sp. gr. of liquid residue	1.08

The residue was considerably carbonized and remained for the most part liquid, a few crystals appearing here and there. The odor of the residue was at the same time strongly garlicy, and very biting and penetrating.

This experiment seems to indicate that C_2Cl_6 could be reduced to C_2Cl_4 with the greatest ease.

A similar experiment to that just described was carried out with CCl_4 instead of C_2Cl_4. When the products of the reduction were fractionated, chloroform and CCl_4 were obtained. The reduction flask smelled quite strongly of $CHCl_3$, and in fractionating about 10 cc of this product, boiling at 60.65, were obtained.[1]

The results of the investigations may be summed up as follows:

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[1] Cf. Regnault: Loc. cit.

1. CCl_4 may be decomposed at a temperature as low as 600° C to give C_2Cl_4 and Cl_2.

2. Decomposition increases with the temperature, the maximum decomposition (to give C_2Cl_4 and Cl_2) being secured at 1300° to 1400°.

3. The products of the decomposition must be cooled very rapidly to prevent the chlorine from reacting with C_2Cl_4 to form the solid C_2Cl_6.

4. The decomposition of CCl_4 can be secured very rapidly in a quartz tube, and the condensation of the products of decomposition may be accomplished in an apparatus of iron, provided that the iron surfaces in contact with the chlorine be dry and comparatively cool (not above 150° C).

5. The difficulty of joining quartz to iron, due to the brittle nature of the quartz and the difference in the coefficient of expansion of the quartz and iron, may be readily overcome by the use of a proper packing gland.

6. The yield may be materially affected by the type of condenser employed. In order to eliminate losses due to uncondensed material being carried out with the chlorine a large amount of condensing surface must be available.

7. It seems advisable to avoid too efficient decomposition of CCl_4. Otherwise solid C_2Cl_6 forms in the condenser, thus clogging up the apparatus. Excess CCl_4 dissolves out such solids and keeps the condenser tube open.

8. C_2Cl_6 can be reduced easily to C_2Cl_4.

The following suggestions were made in regard to future work:

(1) Arrange the assembly in a vertical position so that the flow of the distillate will wash down any solid that tends to form. In addition, the entire condensing surface tends to function, instead of the lower half of the condenser in the case of the horizontal assembly.

(2) Provide a condenser of such a capacity that there is a large expansion of the gases immediately upon their emergence from the furnace. This would tend:

(a) To lower the temperature of the gases and make more difficult the formation of C_2Cl_6.

(b) To slow up the rate of flow of the gases and thus give the products more time to condense.

(3) Fill the condenser with condenser coils to give a large condensing surface.

(4) Equip the decomposition furnace with a thermocouple so that the temperature of the reaction may be registered continuously.

(5) Introduce an inert gas, such as air or nitrogen, at room temperature, into the products of decomposition at the point of their emergence from the furnace. This would tend:

(a) To cool the gases rapidly.

(b) To dilute the gases in such a manner that the concentration of Cl and C_2Cl_4 conducive to a ready formation of C_2Cl_6, is avoided.

NEW BOOKS

The Elementary Nervous System. *By G. H. Parker. 21 × 15 cm; pp. 229. Philadelphia: J. B. Lippincott Company, 1919. Price: $2.50.*—In the preface the author says: "The dependence of human affairs upon the nervous system of man is so absolute that it was inevitable, as soon as the relation was understood, that the activities of the simpler animals should be interpreted as though these creatures were miniature human beings. That such interpretation was carried far beyond its legitimate bounds, even by the scientifically trained, is now admitted on almost all sides, but it is no easy or simple task to ascribe to this movement its proper bounds. That these bounds are vastly more restricted than has usually been supposed is certain. An approach to a clearer understanding of what they are is assured through the application of experimental and quantitative methods to the questions concerned rather than by a continuation of the older more purely observational procedure. It is from this standpoint that an attempt has been made in this volume to portray the elementary nervous system as it exists in the simpler animals and in the simpler parts of the more complex forms. It is believed that this treatment of the subject may help in the solution of the general problem by removing once and for all some of the old misunderstandings concerning the nervous system and by inviting the student's attention to new methods of attack."

There is an introductory chapter and then the subject is treated under the three general headings: effector systems; receptor-effector systems; central nervous organs. The neuromuscular system probably did not originate primarily as a nervous structure. The first trace of this system is to be seen in independent effectors, the smooth muscle of the lowest multicellular animals. This tissue, as seen in the oscular and pore sphincters of sponges, represents muscle unassociated with nerve and acting under direct stimulation from the environment. Such independent effectors are apparently open only to a limited range of stimuli; particularly to those of a physical type and are relatively slow and sluggish in response. The second step in this series is seen in the receptor-effector system of such animals as the coelenterates. This step has been accomplished by adding to the independent effector of the lowest forms a receptive element in the nature of a sensory surface. The receptor-effector system in its simplest conceivable form consists of a patch of sensory cells attached to a group of muscle cells, but practically every instance illustrative of this particular combination is complicated by the fact that the central branches of the receptive cells are not only applied to the muscle cells but form among themselves a network of communication whereby the impulses that arise from a few receptive cells may be transmitted to many muscle cells instead of being limited to a restricted group. Here is to be seen the first trace of the nervenet, an organ that in present forms makes the receptor-effector system immensely more responsive and in past forms harbored the germ of a central nervous or adjustor apparatus that in the end profoundly affected the whole scheme of neuromuscular organization. The most highly differentiated type of neuromuscular system in which an adjustor or central organ has arisen between receptors and effectors represents the final step in the growth of this group of organs. The novel element in this particular combination is the central organ or adjustor, and this arises in the region between the receptor and the effector and out of that material which in the elementary system constituted the nervenet. Its growth is associated with an inward migration whereby it retreats from the surface of the animal to a deeper situation and comes thus to gain what is significant of its growing importance, a certain degree of protection.

To the layman one of the very interesting facts given in the book is as to the amount of water which a sponge causes to pass through its body. The author estimates, p. 46, that for an ordinary *Spinosella* the flow may be about 1575 liters per day with a head of 1.3–2.9 millimeters of water.

Wilder D. Bancroft

Colloid Chemistry. *An Introduction with some Practical Applications. By Jerome Alexander. 17 × 12 cm; pp. vi + 90. New York: D. Van Nostrand Company, 1919. Price: $1.00.*—The author intends to give within a very limited space the most important general properties of colloids, and some of the practical applications of colloid chemistry. The titles of the chapters are: introduction; classification of colloids; consequences of subdivision; the ultra-microscope; general properties of colloids; practical applications of colloid chemistry.

In the chapter on practical applications of colloid chemical principles, the sub-heads are: astronomy; meteorology; geology and mineralogy; clay and ceramics; agriculture; electroplating and electrodeposition of metals; metallurgy; dyeing; soap; ice cream; confectionery; brewing; tanning; photography; boiler scale; cement, mortar and plaster; filtration; chemical analysis; pharmacy; foods and their preparation; physiology and pathology; digestion; absorption, secretion and excretion.

Under astronomy the author shows that the streaming of the tails of comets away from the sun may be due to the ionization of the constituent colloidal particles and their consequent electrical repulsion; or, more probably, it may be due to the sun's rays, as was pointed out by J. Clerk Maxwell. "The intensity of the sun's rays on a particle depends upon its surface which varies as the square of its diameter, whereas the gravitation of the same particle to the sun depends upon its mass which varies as the cube of its diameter. Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm. As the diameter diminishes, the repulsive force gains the ascendency, soon reaching a maximum and again diminishing until the two forces again balance each other when the particle has a diameter of only 0.00007 mm."

In the section on foods, the author says: "It is a serious error to judge foods upon the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate, and calories are not alone the criteria of food value—the physical condition of food largely governs its usefulness to the organism. The experiences of centuries has taught us the value of 'light' bread or cake leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; unleavened bread was eaten only in time of stress, as we learn from the Bible. The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter are formed from tissues partially dehydrated by age."

The book is interesting and should convince people that colloid chemistry is an extraordinarily important branch of chemistry There are very few slips. The reviewer does not believe crystallization from a saturated solution when this is centrifuged is a proof that the original solution was not strictly homogeneous, p. 8; but then he also does not believe that one ever passes continuously from a colloidal to a true solution, and yet this latter is a dogma cherished by everybody else who writes on colloids. *Wilder D. Bancroft*

Mining and Manufacture of Fertilizing Materials and their Relation to Soils. *By Strauss L. Lloyd. 19 × 14 cm; pp. vi + 153. New York: D. Van Nostrand Company, 1918. Price: $2.00.*—The chapters are entitled: chemistry of fertilizers; origin and composition of soils; the relation between soils and fertilizing materials; pebble phosphate ore dressing and milling; hard rock phosphate ore dressing and milling; phosphorus; artificial manure manufacture; manufacture of superphosphate; compound manures nitrogenous manures; the fixation of atmospheric nitrogen; potassic manures; the examination of commercial fertilizers and materials; the examination of soils.

It is interesting to note, p. 4, that the chief function of lime is to improve the mechanical condition of the soil by loosening heavy clay soils and also by holding together and giving body to light sandy soils.

On p. 33, we read: "It is a fact of great interest and importance that one form of a fertilizing constituent is preferred by some plants to the same constituent in another form. This preference is indicated by greater yield or better quality of product or by both. Thus, wheat seems to give better results when nitrogen is applied in the form of nitrate of soda than in any other form. The quality of tobacco is injured by potash in the form of muriate and, hence, only sulphate of potash should be used for fertilization purposes. The quality of sugar beets and of potatoes appears to be better when sulphate of potash is used."

There is a considerable loss of phosphate when mining hard rock phosphate ore, p. 43. "Practically all of the deposits contain, with other material, more or less phosphate in a soft or pulverulent condition. Under present methods of mining and treatment this 'soft' phosphate is necessarily lost in the process of washing, being carried to the dump along with the sand, clay, and other constituents of the matrix." The author found in one case that "of this material taken from the pit three-fourths, carrying about 27 percent calcium phosphate, goes to the dump, while one-fourth, carrying 77 percent calcium phosphate, is saved; thus of the total phosphate ore taken from the pit, in this instance at least, one-half goes into the dump. From these data it is apparent that a large amount of phosphate ore is being lost annually in this section and that any economical method of reclaiming this waste or of utilizing the floats, if such be devised, are clearly of the greatest importance to the phosphate industry, and ultimately to the agricultural interests of the whole country."

On p. 99, the author says: "Cyanamide does not suit humic acid soils, where its action is uncertain and where it may poison plants. For the same reason its use is not recommended in light, sandy, somewhat torpid soils, especially those with an acid reaction. All other soils, especially loose friable soils, which contain enough lime and are regularly manured with farmyard dung, may be manured with cyanamide." *Wilder D. Bancroft*

Surface Tension and Surface Energy. *By R. S. Willows and E. Hatschek. Second edition. 19 × 13 cm; pp. viii + 114. Philadelphia: P. Blakiston's Son and Company, 1919. Price: $1.50.*—In this new edition there are a number of changes, the most important being the addition of an extra chapter on complex phenomena. In this the authors discuss the concentration of a solid at a dineric interface, the formation of emulsions, dyeing, tanning, and ore flotation. It is all a little bit vague because the authors apparently consider only the occurrence of a solid film in the formation of an emulsion and they speak of the solid as not being wetted at all by the emulsified liquid, quite overlooking that in this case, the solid would not pass into the interface at all. They also speak of lamp-black as not being wetted by water, whereas purified lamp-black is wetted extraordinarily readily by water. Even in a brief sketch it is well to stick to facts.

In the case of dyeing they have overlooked the fact that direct dyes do not behave like acid dyes in presence of electrolytes. A colloidal solution of a dye does not behave exactly like a true solution. In the case of ore flotation, the authors do not take into account the stabilizing action of the adsorbed solid particles on the bubbles. In fact they are a bit shaky on the whole question of froths. When discussing surface tension, p. 2, they speak of forming a thin film of a pure liquid on a wire frame and finding that a given weight will just stretch the liquid film definitely—within certain limits. There is nothing in the text to show that this is not a real experiment.

It is not strictly accurate, p. 29, to say that "in the etching of a highly polished metal surface, such as is used in photomicrography, it is the amorphous phase which is dissolve readily, leaving the crystals in relief." In many cases, it is possible to etch either one of the two phases depending on the reagent used.

Books like these are interesting and worth while; but condensation seems to lead more often than is necessary to inaccuracy of statement.

Wilder D. Bancroft

Catalytic Hydrogenation and Reduction. *By E. B. Maxted. 19 × 13 cm; pp. viii + 104. Philadelphia: P. Blakiston's Son and Co., 1919. Price: $1.25.*—In the preface the author says: "The present volume has been written with the object of presenting in an easily accessible form the numerous examples of catalytic hydrogenation which have been published from time to time. Special attention has been given to experimental methods and, in addition to the simple hydrogenation of unsaturated linkages, such as the conversion of ethylene to ethane or of benzene to cyclohexane, various catalytic reductions of a less simple nature usually involving the splitting off of water or of a halogen acid, have been included.

The subject is treated under the general heads: introduction, preparation of catalysts; the method of catalytic hydrogenation; the hydrogenation of unsaturated chains; the hydrogenation of unsaturated rings; miscellaneous reductions dehydrogenation; technical hydrogenation of unsaturated oils.

This sort of compilation is very well worth while. No matter how well one may think one knows a subject, there are always things that one has overlooked, there are always things that one has forgotten, and there are always things that one reads from some other point of view. A little book like this, which one can glance through in a short time, is a great help. The things that happened to interest the reviewer especially this time were the paragraphs on the reduction of acetylene to ethylene, p. 40; the reduction of nickel and copper oxides at room temperature in presence of colloidal palladium, p. 71; the inability as yet to split off hydrogen from such compounds as hexane, o. 73; the reversible equilibrium with quinone and hydroquinone, p. 77; the reaction between carbon monoxide and water in presence of palladium, p. 79, and the removal of carbon monoxide from hydrogen, p. 90. *Wilder D. Bancroft*

The New Science of the Fundamental Physics. *By W. W. Strong. 24 × 16 cm; pp. xi + 107. Mechanicsburg: S. I. E. M. Co., 1918. Price: $1.25.*—"The new science is essentially a more complete application of laboratory methods to the basic units, measurements and laws of science. It aims to apply the empirical method and eventually the same method units and apparatus to all phenomena." We can all agree with this programme and the author has made an interesting presentation. While this is a carefully written book in the main, it is marred here and there by rather unfortunately worded paragraphs which inevitably prejudice the reader and consequently put the author on the defensive when he should not be. The reviewer is glad to bear witness that the book seems better every time he looks it through anew. *Wilder D. Bancroft*

The Preparation of Substances Important in Agriculture. *By Charles A. Peters. Third edition. 19 × 14 cm; pp. vii + 81. New York: John Wiley and Sons, Inc., 1919. Price: 80 cents.*—"It has been the aim in this manual to select substances of agricultural interest, adapt them to laboratory preparation and explain their chemistry to the best of our present knowledge, not overlooking their practical significance." The substances studied are superphosphate, sulphate of ammonia, potassium nitrate, sulphate of potash-magnesia, sulphate of potash (high grade), muriate of potash, lead nitrate, lead arsenate, lime-sulphur, copper sulphate, Paris green, Bordeaux mixture, emulsions.

Lead arsenate is the standard arsenical poison for chewing insects and kerosene emulsion is an old remedy for insects that do not chew and consequently cannot be poisoned. Such sucking insects have to be attacked through their breathing apparatus. The aphis is an example of this.

One reason for the particular form of this manual appears to be that only about half of the students entering the Massachusetts Agricultural College have had farm experience and it is difficult to interest a student in the preparation of superphosphate or Bordeaux mixture unless he knows something of its use. A few simplified spellings have been used. *Wilder D. Bancroft*

THE COLORS OF COLLOIDS. VIII

BY WILDER D. BANCROFT

Metallic Colors

The data given in the preceding papers has made it seen practically certain that many of the colors observed in birds and animals were structural colors. These conclusions are controverted strongly by Walter,[1] so far as the shimmer colors are concerned.

"When light falls perpendicularly on a plane, polished surface of a practically transparent surface, the amount reflected increases with decreasing wave-length. The light reflected vertically from a water surface is 0.0202 of the original intensity in the case of red light and 0.0212 in the case of the violet. While there is a relative increase of five percent in favor of the violet light, this would not be detected by the unaided eye...The difference is greater when the difference in the indices of refraction increases. With cassia oil, the relative intensities of the two sets of rays is 0.0534 for the red and 0.0630 for the violet, an increase of about 16 percent in favor of the violet. Even this cannot be detected directly. If the same beam of light is reflected a number of times alternately from the surface of the liquid and from a metal mirror, it comes out a beautiful sky-blue. Check-tests with two metallic mirrors show that the color is really due to the reflections from the cassia oil.

"Total reflection at the surface separating glass and a liquid will not take place for the rays for which the index of refraction is the same for the two media. If this is true for blue in a certain liquid mixture measured against crown glass, the reflection color for perpendicular reflection from the crown glass will begin with yellowish brown (only to be seen subjectively). With increasing angle of incidence the color will become more intense but practically unchanged in tone until

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[1] "Die Oberflächenfarben oder Schillerfarben," 6, 20, 41, 78, 93 (1895).

at the angle of total reflection for red, it changes suddenly to a beautiful bright red, passing through golden yellow, lemon-yellow to bright green at grazing incidence where the angle of incidence is 90°. If the agreement is in the green, the reflection color changes only to citron yellow at grazing incidence. If the agreement is in the yellow, the final color is the first bright red, so that the color which shows at the grazing incidence gives quite a clue to the portion of the spectrum for which the refractive indices of glass and liquid are exactly equal. One can find the point accurately by decomposing spectroscopically the light reflected from the surface separating the two media, when the incident angle is very large. In the reflection spectrum one sees the totally reflected rays at the end of the spectrum in full strength. Passing toward the violet end of the spectrum there is a rapid decrease in brightness....If the point of agreement of the two indices of refraction is in the green, this part of the spectrum will be completely dark, while the color will increase in intensity as one passes on to the blue owing to the increasing difference of the indices of refraction.

"The iridescent substances are without exception highly colored substances which absorb certain portions of the visible spectrum very markedly and other portions very slightly or not at all. The consequence is that the coloring matter behaves to the strongly-absorbed colors like a metal and reflects them markedly and acts towards the slightly-absorbed colors like an ordinary colorless body and reflects them but slightly. When white light or sunlight falls upon such a substance, the reflected light has a different composition, in other words it is colored. A sufficiently plane surface of such ean iridescent substance shows a colored lustre in addition to the brilliant lustre of the metals.

"The rays which predominate in the reflected light and which give it the characteristic color are those which are most absorbed by the substance. On the other hand with transmitted light which gives rise to the so-called body color, it is clearly the portions of the spectrum which are not absorbed which determine the tint, and the body color must therefore be to some extent complementary to the reflected color. That this is the case for surface colors was pointed out by Haidinger[1] more than forty years ago in the law which bears his name and states that the body color and the surface color of iridescent substances are complementary. This law holds almost always approximately. The red-dyeing substances usually have a greenish surface color, and the blue-dyeing substances a yellowish one, while the reverse is true and the green-dyeing and the yellow-dyeing substances have red and blue surface colors respectively. It was pointed out by Stokes,[2] however, that this law cannot be accurate if one uses the word 'complementary' in a strict sense, because the body color of a substance is not a definite thing and varies with the depth of the layer.[3] It may also be urged against Haidinger's law that the surface color of a given substance is by no means definite, for it depends upon the angle of incidence and on the optical properties of the medium in contact with it, two values which are independently variable. Thus magenta appears a beautiful bright green in the air, but bluish green if spread upon glass and looked at from the glass side. In fact in contact with the diamond it appears a pure blue, a color which of course in no way complementary to the almost pure spectrum red transmitted by a rather thick layer of magenta, nor is it complementary to the pink, or mixture of red and violet, which is characteristic of a thin layer. Therefore one must limit Haidinger's law to the surface color of an iridescent substance in contact with a medium of very definite optical properties and to the body color of a layer of definite thickness. The surface color should be determined

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[1] Sitzungsber. Akad. Wiss, Wien, 8, 97 (1852).

[2] Phil. Mag., 6, 393 (1852).

[3] For instance a chlorophyll solution is green in thin layers and red in thick ones. In the first case green and red light are both let through and in the second case only red. Since the human eye is much more sensitive for green than for red, the green predominates in the thin layer even though it is absorbed more by it than is the red. In a thicker layer the green is extinguished completely and there is left only the less strongly absorbed red.

in contact with a phase of medium refractive index such as crown glass, while the body color should be determined in a film having about the thickness of the average wave-length of light.

"The fact that the surface color of an iridescent substance varies markedly with the index of refraction of the medium in contact with it shows that the absorption alone is not sufficient to account for the manifold phenomena. The degree of reflection of a given ray of light from a given substance depends not merely on the degree of absorption or on the value of the absorption coefficient, but also on the value of its index of refraction and this latter factor is more important the less the absorption is. For colors which are absorbed very slightly, the index of refraction is the sole factor in determining the strength of the reflected light. This is of great importance with the iridescent substances because the study of the abnormal dispersion of these substances twenty years ago, brought out the fact that there were great differences in the indices of refraction for the slightly absorbed rays on either side of the absorption maximum, differences of a magnitude hitherto unknown in any one substance. Carbon bisulphide has about the highest dispersing power of any of the colorless substances and the indices of refraction for the visible spectrum all lie between 1.6 and 1.7. With magenta the index of refraction for the violet rays near the G line is about that of air ($n = 1$) while some of the red rays in the neighborhood of the C line are refracted more than by the diamond ($n = 2.4$), the most strongly refractive of all the colorless substances.

"These two sets of rays are absorbed so little by magenta that we may consider them as not absorbed at all and may therefore apply Fresnel's reflection formulas to them. It follows that the violet rays will not be reflected at all when the light passes through the air to the dye because no light is reflected at the surface between two colorless substances having the same index of refraction. On the other hand magenta must reflect the red rays practically as completely as diamond and consequently the surface color of magenta will be distinctly yellow instead of the bluish green required by Haidinger's law because the whole red side of the spectrum counting from the absorption maximum, red, yellow, and yellow-green are reflected much more powerfully than the corresponding rays on the violet side.

"The reverse is true if the magenta film is not in contact with air but with a highly refractive colorless substance such as diamond and if the light falls first on the latter. The relative importance of the two colors in question will then be reversed, since the indices of refraction of the two substances for red are the same while the values for violet are quite different. In contact with air the surface color of magenta was yellowish green instead of blue-green and in contact with diamond it is pure blue instead of blue-green. Magenta was the color required by Haidinger's law if it is in contact with a colorless substance having an average value for the indices of refraction, crown glass for instance.... As a matter of fact, magenta on ordinary glass shimmers under vertical illumination a green-blue which is very nearly complementary to the pink color transmitted by a very thin film of the dye. With grazing illumination the color changes very nearly to a pure sky blue, which shows how the shimmer colors vary with the angle of incidence.

"The colors which might be confused with the shimmer colors are:

1. Body colors.
2. Colors of turbid media.
3. Prismatic dispersion colors.
4. Grating colors.
5. Colors of thin films.

1. *Body Colors* (*Absorption Colors*).—This is the simplest and most common form of color. It occurs when a certain portion of the constituents of white light are absorbed by a given medium while the balance is not. Substances having this property are called pigments. There are two different ways in which body color may be brought out. The pig-

ment particles may lie close together, as in an oil painting, and form an opaque, colored cover over the background, the oil acting merely as a binder; or the pigment may be dissolved in a solid or liquid and this solution forms a transparent, colored coat over the background. In the first case we have an opaque color and in the second a glazing color. This lets the details of the underlying substance be seen while the first does not. With an opaque color the pigment particles absorb light relatively weakly, for if one were to use a strongly absorbing substance like magenta as an opaque color, one would not get the red body color but a surface color varying with the nature of the surrounding medium.[1] Magenta is therefore always used as a glazing color, by dipping a piece of white cloth into a dilute solution or by coating a piece of wood or metal with a varnish colored by it. The substance to be colored should be as nearly white as possible; otherwise one does not get the pure color of the colored coating but a subtraction color due to this and to the color of the ground.[2] If the latter is black, so that no light is reflected back from it, one will not see the color of the overlying coat, which therefore serves no purpose. If one dips a piece of black paper into a dilute magenta solution, the paper remains black. If one dips it into a concentrated solution of the dye and lets it dry, the red body color does not show; but we get the green surface color and showing up much better than on a piece of white paper because when the color layer is not very thick, one gets a mixture of the body color and the surface color. Since these two are approximately complementary, one gets merely the impression of a faded color approximately white.[3]

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[1] [The scale is distorted. Opaque colors absorb light strongly and substances like magenta absorb intensely.—W. D. B.]

[2] We speak of a subtraction color when we have the joint action of two different absorbing media. Since each absorbs its own portion of the spectral colors, the second takes out more or less of the rays which have passed the first.

[3] This is really an addition color because the rays which constitute the surface color do not penetrate at all and consequently nothing is removed from them. On the other hand there are added to them the rays reflected from the deeper layers, which give rise to the body color. To guard against this dis-

"It is easy to distinguish body colors from the surface colors because the first have the same color irrespective of the angle of incidence, the surrounding medium and the polarization of the light, which is not the case with the other colors. Further the substances with body color have not that lustre which is always associated with surface color and with some other forms of color. The body colors always show a matt effect which is like that of white paper except for the color. This is due to the fact that no regular reflection can occur at the surface of such a substance on account of the innumerable unevennesses which are invisible to the naked eye and consequently the colored light is scattered in all directions.

2. *The Colors of Turbid Media.*—These, usually faint, colors occur when there are many very small opaque particles suspended in an otherwise very transparent solid, liquid, or gaseous medium.[1] These particles scatter the transmitted light, sending out new wave-fronts. They act more strongly on the shorter wave-lengths than on the longer ones, so that in turbid media the transmitted light is always reddish and the scattered light is bluish. The most familiar example of this is in the sky where dust particles cause the sun near the horizon or the white clouds illuminated by it to appear a beautiful red, while the light scattered by these same particles form the blue of the sky. Similar turbid media can be obtained with liquids, for instance by pouring a dilute solution of rosin drop by drop into a large amount of water. Among solids the phenomenon occurs with the opalescent substances.

"These colors are readily distinguished from the surface colors because the changes they undergo with varying angle of incidence or varying polarization are relatively small. They

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turbing effect of the body color, the scales of those butterflies, which shimmer, very often have under them other scales which are almost completely black. This is especially likely to be the case if the shimmering scales are not very deeply colored.

[1] [The colors may be very rich and the suspended particles do not have to be opaque.—W. D. B.]

are usually still more matt than the body colors. They can be distinguished from these latter because the layers showing them must be fairly thick and are then always transparent with a turbid reddish color or are translucent, while substances with body color are always clear if they are transparent at all. The color of the light scattered by turbid media is always blue, which can only change into a dark green in case the particles are faintly yellow or in case there is a yellow colored film in front of the turbid medium. For instance, if one looks at the sky through a yellow glass, the sky appears dark green. This is due to the fact that if one removes from the scattered light the predominant color, blue, one perceives the next most important color, green.

3. *Prismatic Dispersion Colors.*—When two plane surfaces of any transparent substance meet at an acute angle, a ray of white light passing through the two surfaces is not only refracted but drawn out into a color spectrum. It was first suggested by Gadow that the shimmer colors of animals are formed in this way. Against this is to be urged that to get such a prismatic spectrum it is not enough to have a prism; one must also have at least two round or slit-shaped openings to form the well-defined beam of light which is absolutely necessary to the formation of a spectrum. One of the two openings is usually formed by the prism and this may be assumed to be the case with the shimmer colors; but if there is to be a beam of light, there must be a second opening at a considerable distance which is of course impossible in the animal organisms under consideration. The essentialness of these conditions for the production of a spectrum can be recognized very simply if one looks through a prism at the unclouded, uniformly lighted sky. One will search in vain for any color and it is only when the eye falls upon a dark object which separates the beams of light to some extent or, still better, when one looks at a small source of light, the luminous flame of a Bunsen burner in an otherwise dark room, that one sees the spectrum colors.

"Apart from this fundamental objection to this point of view, there are a number of insurmountable difficulties of which only the more important will be mentioned. First the shimmer colors should change with the distance of the eye from the shimmering surface, which is not the case. Further, it is not enough to assume one or several refracting prisms on every shimmering scale; the number must be infinite, or to be very accurate, double infinity. With the known transparent substances the dispersion of the whole visible spectrum under the most favorable circumstances subtends an angle of only a few degrees, so that if we are to account for the gradual and continuous change of the tints of the surface colors when the angle of incidence varies between 0° and 90°, we must postulate an almost infinitely large number of prisms arranged in a very peculiar way with the refracting edges all parallel. Even then one would have accounted for the play of colors only in one plane, for light falling perpendicular to the refracting edges. In order to have the same effect in all other directions, there must be an infinite number more of these prisms or twice infinity all told. All of this must be present not only on each single butterfly scale—but on the smallest portion of it which can be perceived under the microscope.

4. *Grating Colors.*—A beam of white light can be drawn out into a spectrum by means of a grating. This instrument consists essentially of a large number of very fine, equidistant, and accurately parallel lines, which occur in a plane or regularly curved surface of a substance which is either opaque to light or does not permit regular transmission. The slits can be replaced, as is the case with the metallic gratings, by regularly reflecting surfaces. In this case the interference spectra appear only on one side of the grating, whereas with the glass gratings they can be seen from in front or from the back. The number of spectra which can be produced in each of the four quadrants between the grating and the perpendicular, depends, as does the intensity of the color dispersion, on the distance between the lines, the number becoming smaller and the dispersion greater, as the distance between the lines decreases. If the distance is 0.002 mm for distance and if we

consider only vertically incident light, the first spectrum measured from the perpendicular extends from 11° to 21°, the second from 23° to 45° and the third from 37° to 90°; but in this last the red rays do not appear.

"Since very many butterflies' scales have lines like a grating and since the distance between them is apt to be about 0.002-0.005 mm, it has often been assumed that the shimmer was due to these lines; but this presents almost the same difficulties as in the case of the prismatic dispersion colors. To produce such a grating spectrum there must also be in addition to the grating a circular or slit-shaped source of light quite a distance from it, which forms a definite beam of light with reference to the grating. Under an open, uniformly lighted sky the finest Rowland grating shows no trace of dispersion color even though the distance between the lines is much less than in the case of most butterflies' scales. It is only when one gets in a room so far away from the window that the window may be considered a slit, that one begins to see the spectra and these become purer the narrower the source of light. Also one sees the colors of the gratings when the direction of the lines, like the refracting edge of the prism is perpendicular to the plane of incidence of the light, whereas the shimmering scales show their color from all angles.[1] This requires us to assume an infinite number of gratings turned in all possible directions, each one of which must consist of a large series of over-lapping grating systems. A single-line system in the range between 0° and 90° always gives several partly separated, partly over-lapping spectra and consequently when illuminated by a well-defined beam of light, the color of the dispersed light would vary with the angle of incidence very much more rapidly than is the case with the shimmer colors. It is worth mentioning that the shimmering portions of birds and beetles, for instance, rarely show such

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[1] In the case of many butterflies' wings and birds' feathers, there is an apparent exception in that the shimmer is not to be seen in certain directions. This is due to the shingled-roof arrangement of the scales and the barbs giving rise to the shimmer.

regular lines as do the scales of butterflies' that the lines on the butterflies scales and the surface of the scales are by no means regular enough, and that the scales are too small to give rise to perceptible dispersion colors.

5. *The Colors of Thin Films.*—These occur when white light is reflected from the front and the back side of a very thin colorless film. The two rays coming to the eye at the same time from the same direction differ in phase, by an amount which depends essentially on the ratio between the wave-length and the thickness of the film, and which therefore is different for different colors of the spectrum. If the thickness of the film is such that only one color of the spectrum is out of step half a wave-length, only that color will be extinguished. If only one other color is out of step a whole wave-length, that will be the only one brought up to maximum intensity while the other colors are in intermediate stages. In this case one color will predominate distinctly; but this will be true only for films of a very definite thickness. With thicker or thinner films the interference colors will be less pure. All this can be seen in Newton's rings which are of great importance, because they permit one to see at a glance all the possible colors of thin films which can occur with colorless substances. It is a simple matter theoretically. Though the interference colors of thin films vary with the thickness of the film, with the refractive index of the film and with the angle of incidence, all these changes produce merely a displacement of the color and never give rise to a new tint, except in regard to the changes due to the differences in dispersion of different colorless substances and these are not marked enough to change the tint of the color markedly. It is quite a different matter if the thin film has a body color or if there is a colored film in front of it for then only those colors which pass through can interfere, so that, in a sense, the interference color is then only a part of the body color.

"The colors of thin films are most nearly akin to the surface colors and therefore the differences between them should be brought out as clearly as possible. Both are reflection colors and both therefore show that peculiar lustre which one gets only with regularly reflected light. Further no slit is necessary as was the case with the prismatic and grating colors. The beauty of the colors of thin plates is often equal to that which we are accustomed to with the shimmer colors, though the more familiar instances of the soap-bubbles and of Newton's rings are not the highest manifestation. In their greatest perfection these colors are to be seen on thin films of mica which we can obtain with a little practice by pulling apart thicker sheets of this mineral. The beauty is due to the mathematical parallelism between the two reflecting surfaces of these films.

"As regards the difference between the colors of thin films and the shimmer colors, one is that the first change in intensity but not in color with changing polarization of the incident light, while both change in the case of the surface colors. With vertically polarized light at the definite angle of incidence corresponding to the polarization angle of the outer layer of the thin film, the color must disappear completely in the case of the thin films, to appear again more distinctly at large angles of incidence, whereas with such light the surface colors usually show greatest saturation in the region of the polarization angle and become pale very rapidly at larger angles of incidence. These two simple methods of differentiation are usually sufficient to distinguish between the two kinds of colors; but some other differences will also be discussed in detail. These differences show themselves chiefly in the changes which the two types of colors undergo with a change in the surrounding medium and with a change in the angle of incidence. The first is only to be used under definite limitations, of which the first is that the strongly absorbing substance which gives rise to the shimmer color is exposed so that the different liquids which one uses as surrounding media come in actual contact with it. The second limitation is that the thin film giving rise to the interference color consists of an equally accessible air film. With a thin film of a solid substance of course only the intensity and not the color changes when the film is placed in a liquid having a different index of refraction. Whether such thin air films occur in nature is a question that need not be answered. Dichroic substances lying exposed to the air do occur and therefore this point warrants examination. As more strongly refracting media the most suitable liquids are those which are completely colorless, which are easily volatilized so that one can observe the air color quickly after evaporation, and with markedly different indices of refraction, changing in as regular steps as possible. Ether, benzene and carbon bisulphide meet these requirements and have therefore been employed. Their refractive indices are about 1.36, 1.51, and 1.64 respectively. The displacement of color when these liquids are substituted for air on an exposed dichroic substance are quite perceptible but usually extend over one or at most two of the neighboring colors in the spectrum, from blue to green or the reverse, so that one may almost speak of a continuous color change in contradistinction to the interference colors of thin air films which change discontinuously on substitution of the air by alcohol, both the original and the new color being however one of the regular colors in Newton's rings, which is not necessarily the case with substances having surface colors.

"Just as one can deduce the thickness of the film from the color in air, so one can calculate the change of color from the index of refraction of the liquid used. To make this calculation of the most value for our purpose, we point out that the color displacement at thin films is more marked the thicker the air film, so that if any confusion between this type of color with the surface colors were possible, it would be when one has the thinnest air film which can give a distinct interference color. As one can see from Newton's rings this is the film which shows the blue of the second ring and we therefore select this as an illustration. The thickness is approximately 0.33 μ. If one fills the air space with ether, for which $n = 1.36$ in round numbers, and in which the wave-lengths for those colors are $1/1.36$ of what they are in air, this would be the same as having an air film 1.36 times as thick as air, in other words an air film with a thickness of 0.45 μ. This however corresponds to an almost pure yellow interference color, so that the interference color changes from blue to yellow just for this relatively small change in the index of refraction. This change is the smallest that could occur in any really marked interference color for with the blue of the next order for instance the change is to red. This thoroughly characteristic method of distinguishing between the two types of colors is unfortunately not always applicable, because in many cases the shimmering film is not in direct contact with the air but is enclosed in a colorless sheath of chitin or horn, which makes the introduction of the liquids very difficult or even impossible. For this reason the most generally applicable method of distinguishing between the two types of colors depends on the different way they change with varying angle of incidence.

"The displacements of color of the surface colors with increasing values of the angle of incidence is always from longer to shorter wave-lengths and extends over one or at most two adjacent colors, except for the rare and very characteristic cases in large portions of the spectrum are totally reflected. If the color at vertical incidence is blue or violet, this changes for larger angles of incidence to purple and occasionally also into red, a displacement precisely analogous to the others. In order to follow the way in which the color of thin films change with angle of incidence, it is necessary to distinguish the two cases in which the thin film consists of a thin layer of air between two solids as in the case of Newton's rings and in which an actual thin film occurs made of a solid or liquid with a higher index of refraction as with plates of mica or with soap-bubbles. In the first case the color of the thin film varies very much more strongly with the angle of incidence than in the second case, a difference which may be quite important in zoology....[1] The interference color of a thin film of air changes more rapidly with the angle of incidence

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[1] Brücke has often assumed that certain of the chameleon's colors are due to thin, parallel-walled air films.

the thicker the film. The color change is always in the same direction as with the surface colors, from red through yellow and green to blue; but no confusion is possible because the colors due to the thin film change so very much more rapidly than do the surface colors.

"A confusion is much more likely in the case where the film consists of a more highly refractive substance for which the internal angle of incidence can vary much less than with a thin air film. The sign of the color change is of course the same as for the first type of thin film and for the surface colors; but the displacement is nearly as small as that with the surface colors. The difference is least when the film is thinnest. By a simple calculation one finds that with a thin film of a substance having an index of refraction 1.6, and a thickness such that it just shows the blue of the second order with vertical incidence, an increase in the external angle of incidence from 0° to 90° changes the color only one step in the ring system, namely from blue to the immediately adjacent dark purple, a color change which often occurs with dichroic substances. In such a special case this method of differentiation would fail but only for these innermost ring colors. If the thickness of the film is assumed to be enough greater than, for instance, the blue of the next higher order shows on vertical incidence, the interference color would change under the same conditions through the four colors, blue, purple, red and yellow, an amount of change which the dichroic substances never show. If one were to rely solely on these tests, one would be in a ticklish position.

"Even though all the methods hitherto discussed should lead to no sure differentiation of the two types of colors, the general properties would be sufficient, the most important thing in the surface colors being the presence of a strongly absorbing pigment having a body color approximately complementary to its shimmer color, whereas a thin film which shows a marked interference color must be colorless.[1] Further

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[1] [This is begging the question. If we know we have a strongly absorbing pigment, there is no problem. If the thin film has a colored backing it will not appear colorless by transmitted light.—W. D. B.]

such a film must have an extraordinarily regular form. While one often finds this in nature in crystals, it is very rare in animal organisms. Even if this were the case in rare instances, it would still be inconceivable that the thickness of these thin films should be exactly the same not only in all parts of one and the same organ, for instance a butterfly's scale, but also the same in all these organs of the same animal, which is what one must assume if the same interference color is seen."

What Walter means is that it is very remarkable that different scales on a butterfly's wing should show the same color if the color is that of thin films. Since we do not know what determines the thickness of any given film, we have no way of knowing whether it is easier to make them all the same thickness or all different thicknesses.

"An examination under the microscope shows clearly that a shimmering butterfly scale is always more or less colored by transmitted light and the color is more or less complementary to that of the shimmer...A few illustrations will suffice. The scales of the Morpho butterflies are a beautiful lustrous blue by reflected light and yellow or yellow-brown by transmitted light. The greenish blue scales of Apatura Laurentia Godt have a dark reddish brown absorption color, while the pure green scales of Papilio Buddha Wesho. and oi Papilio Polyctor Bd. have a blood-red body color. Specially noticeable is the beautifully colored and beautifully marked Uranus Ripheus Drury, for the yellow-green lustrous scales on the upper wings are either red or bluish red by transmitted light while the red scales of the back wings have a pure green body color. In this one insect Nature has created as admirable a pair of dichroic colors as the laboratory colors of magenta and diamond green. Nature is even more bounteous, for this particular butterfly shows in addition other scales which give intermediate shimmer colors; and occasionally on Papilio Polyctor Br. one finds on the same scale two different shimmer colors, a blue shimmer color which is yellow by transmitted light and a lustrous green one with a red body color, so that there must be several dichroic substances of different chemical composition in the same insect and even in the same scale....

"A second proof for the identity of the shimmer colors of the butterflies with the surface colors of strongly absorbing media depends on the behavior of the butterfly colors in polarized light, for at grazing incidence not only the intensity but the color changes as one passes from parallel polarized to vertically polarized light. It is not possible to determine these changes very accurately because of irregularities in the reflecting surfaces; but it can be stated definitely that the color of the reflected vertically polarized light is not greater for very large incident angles than for medium ones, as is the case with the interference colors of thin films, the reverse being always true.

"On account of the previously mentioned irregularities in the surface of the scales, it is not possible to study carefully the change of the shimmer colors of butterflies with varying angle of incidence; but the general phenomenon is so marked that it is always the most important thing to the zoologists in their explanations. This change manifests itself by the shimmer color changing slowly with increasing incident angle, one, or at most two colors, in the direction from the red to the blue end of the spectrum, exactly as we have previously observed it to do with the surface colors. With gradual increase of the angle of incidence, the shimmer color of Papilio Buddha changes from a yellowish green to a beautiful deep blue. With Urania Ripheus under the same conditions the purple-red scales change to yellow, the yellow tones to green, and the green ones to blue. The lustrous blue or greenish blue scales of the Morpho family show first a pure blue color with increasing angle of incidence, followed by a reddish reflection color at grazing incidence. The jump from one end of the spectrum to the other is even more marked with the deep blue spots on the back wings of most specimens of Junonia Clelia Cram where increase of the angle of incidence gives a very strong reddish purple which goes over finally into a bright yellow. It should not pass unmentioned that in certain planes the shimmer color of certain scales, of Papilio Epiphorbas Bd. for instance, seems to change in exactly the opposite direction with increasing angle of incidence, from a dull blue-green through green to yellowish red. In these cases it always appears that the scales are only colored slightly and are so arranged that at grazing incidence the body colors are seen, whereby the displacement of color becomes quite abnormal.

"Another remarkable and instructive illustration of the identity of the shimmer colors of butterflies with the surface colors of strongly absorbing dyes comes from the changes in color caused by immersion in liquids of different indices of refraction. Except when the shimmer color is deep (blue or violet) increasing the index of refraction of the surrounding medium displaced the color one or two tones from the blue to the red end of the spectrum and makes it much weaker. In air the scales of Morpho Menelaus L. are a lustrous greenish blue; in ether ($n = 1.36$) they are green and fainter; while in chloroform ($n = 1.45$) they are yellowish green and fainter than in ether. In benzene ($n = 1.52$) or carbon bisulphide ($n = 1.64$) it is only by direct illumination with sunlight in a dark room that one can see a faint yellowish green. In like manner the scales of Urania Ripheus which are green in the air are golden yellow in ether, alcohol or water; the yellow ones become red, and the red ones blue; while in benzene and carbon bisulphide there is scarcely a sign of lustre. Now that we know that the color is due to a pigment, this last fact shows that in the lustrous butterfly scales we are dealing with solutions of the pigment in chitin, with solutions whose indices of refraction for most rays are very nearly equal to those for benzene and carbon bisulphide, so that these colors, so far as they are not absorbed by the dye, are practically not reflected from these two colorless liquids. The colors causing the lustre are therefore dissolved in the chitin skin of the insects and, as we shall soon see, also in the horny part of the birds' feathers in the same way as cobalt oxide in blue glass or any organic dye in a gelatin film. This is a natural point of view so soon as one looks at the scales by transmitted light and which is confirmed by the following facts.

"If we assume that the lustre is due to exposed pigment particles, the color must change with increase in the index of refraction of the surrounding medium in the direction from red to blue through the spectrum whereas the actual change is in the opposite direction. With solutions of these dyes the behavior is quite different from what it is with the dyes themselves, for if we assume that the index of refraction of the solvent, chitin, is about 1.6, which is not far from the truth, our experience with magenta and with diamond green solutions shows us that these constants are about 1.9 for those absorbed rays which are on the red side of the absorption maximum and are about 1.4–1.5 for the rays on the violet side. If one therefore brings the lustrous scale into alcohol or ether with indices of refraction about 1.36, the latter set of rays will practically not be reflected at all while the first set, though reflected less absolutely than in air, are reflected relatively much more than the rays at the violet end. Consequently when one substitutes such a liquid for air, there is a displacement of the color effect from blue to red. Only in case the air color of a lustrous substance is a deep-blue or even violet will those reasons fail to apply, so that in this way we account for the rule and for the exceptions to it very simply. A specially good instance which illustrates both cases is that of Prepona Euglenes Bates in which the scales having a greenish blue lustre in the air become yellow-green in ether while the immediately adjacent deep-blue, lustrous scales remain the same color in both media.

"In such highly refractive media it is easy to understand the marked change of the lustre with the angle of incidence. With increasing angle of incidence the color undergoes the same changes as with increasing refractive index of the medium and vertical incidence but in the reverse order. The tone of the lustre color undergoes a displacement with increasing angle of incidence from red to blue, a color displacement which we have already seen was characteristic of surface colors...

"It must not be denied however that there is one point which it is difficult to explain by this theory of the lustre colors of butterflies. The lustre disappears practically completely in benzene and carbon bisulphide, whereas we have emphasized many times that according to the theory of surface colors a strongly absorbed beam of light must always be reflected strongly under all circumstances. While it is true that a satisfactory explanation of this point must be left till some other time, we may mention that the body colors of these scales also disappear completely in these liquids, so that we are probably dealing with a peculiar action of the fine structure of these parts.

"Lustre is also very common in the insect world among the beetles and, in the animal kingdom, the birds furnish conspicuous illustrations of it. In birds the lustre occurs exclusively in the feathers, sometimes on the barbs and sometimes on the barbules. The latter case occurs with the humming-birds, the pheasants, the peacocks, and the Trogons (Guatemala birds), while the first case occurs with certain Parrots and Musophagides, also with Irena puella Lath., with Calliste tatao L., etc. In the case of the parrots the barbules often shows a brilliant body color which is different in different parts of the feather, so that a very gaudy effect is produced.

"A close examination of the lustrous parts by transmitted light shows that these are always colored and the color is approximately complementary to that of the lustre as required by Hardinger's law. Thus the deep sky-blue back and tail feathers of Irena puella are yellow brown by transmitted light; the beautiful green feathers of Pharmacrus auriceps Gld., one of the trogons is a deep red by transmitted light and finally the lustrous red neck feathers of the East Indian pheasant show a dirty green absorption color. Among the humming-birds Topaza L. there is something similar to that noticed with the butterfly Urania Ripheus, the apparent occurrence of two contrasting lustre colors like magenta and diamond green. The lustrous yellow-green neck-feathers are a red brown by transmitted light while the beautiful red belly feathers have a green body color. The humming-birds present the most brilliant of the lustre colors and the colors are purer, so that the corresponding absorption color is most marked among them. An especially striking example of this are the lustrous grass-green belly feathers of Aithurus polytarus L. where one can see the red body color with the unaided eye. This is of course to be seen much better under the microscope, since of course only those portions of the feather show the absorption color by transmitted light, which give the lustre by reflected light. With the humming-birds it is only the barbules that do this and not all of them. The skew position of the barbules to the whole plane of the feather has the effect that the lustre can be seen from very definite positions, a phenomenon which occurs also among the butterflies.

"As an especial proof that concentrated and very strongly colored solutions of a dye are essential to the production of a lustre color, I cite the case of the Bürzel feathers of Calliste tatao L. where the whole outer end of the barbs are a deep lemon-yellow by transmitted light, due to a colored solution which is not concentrated enough to give a perceptible surface color. On the under side of these barbs one can see under the microscope, even with slight magnification definitely marked groups of cells which are a lustrous blue-green by reflected light and by transmitted light are colored much more strongly than the other portions of the barb, the color being reddish yellow in accordance with Haidinger's law.

"When considering the change of the lustre colors of birds with the angle of incidence, one must remember that here, as throughout the animal kingdon, the reflecting surfaces are never so perfectly plane as one looks for in physical measurements, so that the phenomena are never so clear-cut as in the experiments on surface color with artificially prepared mirrors. The general characteristic of the gradual displacement of the lustre color from red towards blue is nevertheless always to be observed, although this is not well marked among birds for another reason. As very simple experiments have shown, the pigment producing the lustre is not exposed to the air as in the case of the butterflies; but is enclosed in a colorless horny sheath. At large angles of incidence, this latter reflects a large proportion of the incident light, so that the lustre tints corresponding to the angle of incidence are masked somewhat. If one eliminates the disturbing reflection by dipping the feather in benzene for instance, one sees that the lustre color for any angle of incidence is usually several tones richer than in air.

"In these experiments the tone of the color usually remains unchanged for small values of the incident angle,[1] and this is a proof for the presence of the colorless sheath which prevents the liquids from reaching the actual lustrous film and which can usually be seen under the microscope. If one damages the protecting film by cutting off the ends, for instance, of the lustrous blue barbules of a Musophagides feather, the liquid is sucked into the feather in time and one then sees exactly the same changes in tint that one gets with the butterfly scales the moment one dips them into the liquid. In water, ether, and alcohol the lustre color is displaced one to two tones from the blue end toward the red, in the case under discussion from blue to green, becoming weaker and disappearing almost entirely in benzene and carbon bisulphide. In the case of birds one is therefore also dealing with very concentrated solutions in the horny film of pigments from whose surface light is reflected with a colored lustre. The possibility of changing the tone of the lustre in this way proves further that the film in which it is produced lies free in the inner part of the barbs and is not in contact with the external colorless sheath, a conclusion which follows also from the fact that such a contact must destroy the lustre just as much as contact with benzene or carbon bisulphide. It is

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[1] The slight changes which occur sometimes are due probably to peculiarities of structure.

therefore probable that in those barbs the lustre is only on the upper side. A union of the colored film which produces the lustre has taken place with the colorless sheath, though one can also account for the facts by assuming that the presence of an opaque film prevents the lustre from being seen on that side.

"Those feathers which have one lustre on the upper side and a different one on the lower side, such as the belly and wing covert feathers of Calybtomena viridis Raffl. or the crest feathers of Calliste tatao L. must certainly contain two chemically different pigments on the two sides, of which perhaps one is formed from the other by long exposure to light.

"It is rather a striking fact that blue and green are predominant among the lustre colors, while red and yellow are found but rarely. The explanation for this is that among pigments also there are many more which absorb the violet end and are therefore yellow and red than there are of pigments with absorption exclusively in the red end of the spectrum and which therefore appear green and blue."

While Walter has made a number of excellent points, he has given a very one-sided presentation. It is practically certain that we do have metallic colors due to pigments having surface colors and this has been confirmed by the more recent work of Michelson.[1] It is also true that the possible occurrence of these surface colors has been overlooked. On the other hand, the colors of thin films are often metallic and the experiments of Pfund on mother-of-pearl show that there is nothing to prevent the production of extraordinarily uniform films in nature. While Walter probably limits his conclusions to the metallic colors, it would have been clearer if he had stated definitely that the non-metallic blues are structural colors. I have seen blue feathers which became white when wetted, which could not very well occur if the color was due to a pigment with a surface color. In presence of a solvent, it seems as though the surface color should disappear and

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[1] Phil. Mag. (6) 21, 554 (1911).

that one should get the body color, just as one gets magenta dyeing red and not green. There is still a great deal of work to be done in regard to the colors in individual cases and it apparently should be done by a chemist, preferably by one trained in microchemical analysis.

For the moment the only conclusions that we can draw are that, in birds at any rate, the non-metallic blues are structural colors and that most of the non-metallic greens are structural blues with a superposed pigmental yellow. Some of the metallic colors are due to pigments having surface colors and it is possible that this is true in all cases. With butterflies the evidence is very strong that most of the metallic colors are due to special pigments and are not structural colors.

Cornell University

SOME NEW HYPOTHESES AS TO DIFFERENT STATES OF MATTER

BY N. T. BACON

My mind has never been satisfied with the current reason given to explain why molecules condense from a vessel filled with saturated vapor when the temperature is reduced, for this same reduction should cause a reduction of pressure, even without condensation.

We have as a point of departure in considering this matter several assumptions which seem fairly enough based to be made the foundation for further reasoning. First among these is the consideration of matter in the solid state. Bragg's hypothesis seems to meet with general approval. This is practically that in the solid condition molecules are made up of atoms having their constituent electrons arranged according to a specific plan, so that they are virtually minute crystals continuously combined. This would preclude rotation of the molecules as such. From direct experiment it is evident that in the solid condition matter is generally almost incompressible. Moreover, in this state, these molecules cannot be displaced with reference to each other. We are, therefore, justified in assuming that they lie much as bricks in a wall, possibly not in absolute contact, though, if not, with almost absolutely constant spaces separating them, which would be represented by the mortar between the bricks in a wall; and that they are in three dimensional contact, that is to say, they touch each other up and down, north and south and east and west, so that their spheres of influence (which include the interstitial spaces), to use the word in a geographical sense as distinguished from a geometrical sense, are in contact on all sides.

In the liquid state much of this appears likewise to be true. There is generally no material difference in volume at the point of fusion, though, with the exception of ice, practically all solids are a little heavier than the liquid form of the same substance, so that practically in this state the molecules are again in three dimensional contact as in the solid condition, although the distance between the centers of their spheres of influence probably averages somewhat greater than in the solid condition. The distinction between these two states is sharp, however, in that the liquid molecules can be displaced readily from each other and probably the molecules are rotating around their axes or in orbits or both. The liquid state seems to be almost as incompressible as the solid, and this characteristic of incompressibility follows far up the temperature scale, although in the liquid condition expansion by heat averages greater than in the solid. It would, therefore, appear that in both of these states the expansion is probably due to increase in the diameter of the spheres of influence of the molecules. Bridgman's experiments on the fusion curve of ice VI show that the relative incompressibility of ice VI and water must remain very nearly the same, as from 8000 atmospheres up the curve is virtually a straight line.

Although the liquid condition expands materially as it approaches the critical point, nevertheless we have no reason to consider that there is any change from three dimensional contact of the molecules as they approach this point, although there comes into contemplation the possibility that the rapid increase in volume may be due to molecules in the vapor state dissolved as vapor by other molecules of the same kind in the liquid state. This is analogous to Richards' explanation of the action of water between 0° C and 4° C as due to solution of ice molecules as such, and like S_μ in S_λ.

The data with reference to critical points are insufficient, this point being extremely difficult to work over for most gases, on account of the combination necessary of immense pressure with high temperature. But from such data as we have, we assume that at this point the volume in the gaseous condition is the same as in the liquid condition.

We have seen that in the liquid condition, in spite of the rapidly advancing pressure necessary to maintain simultaneously the liquid and gaseous states, the volume of the liquid, and therefore, probably the volume of the molecule in the liquid condition, or at least the volume of the sphere of influence of the liquid molecule, was increasing rapidly. It appears, however, from the experiments of Andrews and others, that in spite of increasing temperature at least the sphere of influence of the gaseous molecule can be reduced by advancing pressure in spite of advancing temperature when above the critical point.

As we can have present there both liquid and gaseous phases, but beyond this only the gaseous phase, it is evident that the critical point marks the limit at which the substance can exist in the form of saturated vapor and, therefore, that at this point when both phases are in equilibrium the gaseous phase must be saturated. We find, therefore, that at this point the volume of the saturated vapor is the same as that of the liquid and also the specific gravities are the same, so that it seems almost certain that as the spheres of influence completely fill the space occupied by the liquid so that the liquid is immobilized, in like manner the spheres of action of the gaseous molecules must be in three dimensional contact so that for lack of a free path no translatory motion of the individual molecule is possible any more than in the liquid condition, though this motion is characteristic of gases and unsaturated vapors.

Summarizing, so far we seem to have demonstrated that in the solid and liquid conditions we have matter virtually incompressible, though under very high pressure, but constantly increasing in volume with increasing temperature, and for the liquid state with this condition continuing all the way to the critical point, except that near the critical point the apparent compressibility of the liquid phase may be increased by solution of molecules in their vapor condition, so that the inference seems justified that in these conditions the molecule is constantly increasing the diameter of its sphere of influence as temperature increases up to this same point. At this same point we find again the sphere of influence of the molecule in the gaseous condition to be of the same size as in the liquid condition since it occupies the same space and has the same specific gravity. We find also that at the critical point the volatile form is at the dividing line between a saturated vapor and a true gas, and moreover that at this dividing line the vapor cannot act as a true gas because the spheres of influence of its molecules are in three dimensional contact, precluding translatory motion. We find, however, that although the molecules in the liquid condition continue to increase the dimensions of their spheres of influence with advancing temperature in spite of advancing pressure, nevertheless gaseous molecules can be compressed materially so as to occupy a smaller volume than at the critical point even at temperatures well above the critical point. Is it not a fair inference, in view of these things, that in the condition of a true gas the spheres of influence of molecules decrease with advancing temperature so as to allow a free path and thus cause them to follow Boyle's Law?

Considering again the probability that in the gaseous condition the diameter of the sphere of influence of the molecule is an inverse function of the temperature, we should find a probability that in the vapor condition at temperatures below the critical the molecule would continue to expand. If this is true we should have a direct explanation of the separation of condensate whenever a saturated vapor is cooled under constant volume. There would no longer be room in their gaseous state for all the expanding molecules, so that some of them would be obliged to go into the less bulky liquid form. There is no latent heat at the critical point, so that the gradual increase in latent heat set free with descending temperature would be explained by the gradually increasing work of compressing the vapor molecules into the liquid form.

Of course in the condition of saturated vapor the spheres of influence of the molecules cannot represent a plenum, for we recognize that the quantity of water vapor to saturate any volume is nearly, if not absolutely, independent of whether any other gas is present of which the liquid phase at the temperature in question would not form a solution with water. I have seen statistics showing slightly greater amounts for saturation in the presence of air. If correct, these would indicate that air has a solvent power for aqueous vapor, but this difference falls within the margin of probable error, and may have been due to adsorption films on the walls or to infinitesimal liquid drops not observed or to errors in weighing. It seems unlikely that a greater amount could be present except chemically combined as a constituent of other molecules. Perhaps the delimitation of the spheres of influence is due to the shortening of the orbits of the outlying electrons, causing them to fall in towards the central nucleus and thus liquefy whenever they are checked in their flight by contact with, or even close approach to electrons charged with electricity of equal wave length, while immune to electrons of inharmonic charges.

Interesting information as to the size of the absolute spheres of influence should be obtainable by the study of the compressibility of vapors and gases near their critical points, and especially with mixtures where both are near this point. If the rapid increase in volume of the liquid approaching this point is due to solution as such of vapor molecules, we should find a different (and greater) specific volume for the liquid brought to this temperature in the presence of vapor than if carried up continuously under a pressure greater than the critical pressure; just as we find different densities for S_λ according to whether it has or has not S_μ dissolved in it.

A further development of this conception has grown out of consideration of saturated solutions of $BaSO_4$. We are so familiar with the idea of dilute solutions that until a few weeks ago it never occurred to me to ask how it could be that (according to Calvert's determination) one single ion of Ba, in the presence of a corresponding ion of SO_4, could so far affect simultaneously 10,000,000 molecules of water as to deprive everyone of them of the power to dissolve any more $BaSO_4$. It is bad enough to try to imagine how the conductivity is so much increased by any salt at such immense dilution, and all parts of such a solution must have like properties before passage of the current, as it will pass equally well up or down, East or West, or North or South. I cannot explain the increase in conductivity of water to many times its value in the pure state by addition of one molecule of $BaSO_4$ in 10,000,000 of water on the theory that the $BaSO_4$ breaks up into only two parts. I cannot see how in this case that the resulting ions should do more than act as at best metallic conductors bridging between the few water molecules with which they were in immediate contact, but leaving unaltered the conductivity through the vast mass of others, and thus changing the conductivity of the whole by an amount barely perceptible by the most delicate instruments. When it comes to showing why, after absorbing freely up to this point, the solution can thereafter take up no more, I find the easiest explanation in assuming a virtual expansion of the molecules of the solute so as practically to occupy all the inter-molecular space of the solvent, in much the same way in which I have supposed molecules in the volatile conditions to increase the diameter of the spheres of influence of their molecules as temperature falls.

It first struck me that $BaSO_4$ could not dissociate much, for we know from $CaSO_4$ that the solubility of the SO_4 ion is relatively high, and I thought that the solubility of $BaCl_2$ showed that of Ba to be high till it came over me that this alkaline ion was probably $BaCl+$. This led me to consider whether the Ba ion as such might not be totally insoluble (which now I do not think), but that led in turn to consideration of solubility of the metals at large.

It occurred to me that I had stumbled on a new characteristic of the metals as such. The metals are (except perhaps carbon, which is as insoluble) practically the only things which carry the electric current by what we call metallic conduction. I have, I believe, successfully refuted Findlay's argument for the solubility of mercury in bromonaphthalene, and Nernst's for the existence of theoretical vapor tensions of all substances at all temperatures above the absolute zero, postulating instead of this last, a critical point for each substance below which the expanding spheres of influence grow so great as to become wabbly and lose coherent structure, and cease to rebound on contacts, so that they adsorb or condense completely on limiting surfaces, making for the volatile phase a lower limit corresponding to the critical point at the upper limit for liquids.

Assuming that my explanation of the action of mercury is correct, I believe that we can postulate a general characteristic of the metals hitherto undescribed. Together with carbon they seem to be more or less soluble in each other, but otherwise totally insoluble except as they go into chemical combination. I know of no aqueous solution from which a metal can be separated as such by mere boiling or evaporation at lower temperature, or by change of temperature or pressure. In fact the only cases that I know of where metals separate as such from solutions are where the alkaline metals are left by evaporation of anhydrous ammonia, and there I believe that the remarkable changes of color point to the formation of chemical combinations in the solutions.

From my standpoint the so-called colloidal solutions are merely individual molecules held in suspension and carry a current only mechanically through a menstruum which does *not* dissolve them. They take a charge by metallic conduction and thus are repelled from one pole and attracted to the other so as to carry the current rather as a multitude of boats rather then as a bridge.

I find it hard to believe that the solvent power for $BaSO_4$ of a molecule of water can be destroyed by contact of whatever kind with $BaSO_4$ of a molecule of water separated from the former by sixty-five $(= {}^1/_2 \sqrt[3]{10,000,000})$ intervening molecules of water not in contact with $BaSO_4$ so that by way of explanation I find myself reduced to the conception of the $BaSO_4$ breaking up into an enormous number of electrons, or emanations of which electrons are built, each having the characteristic periodicity of $BaSO_4$ (and not solely of any constituent thereof) and that these so permeate the solvent that each molecule of this is in some way in contact, periodic at least, with such particles, so as to maintain an equilibrium relation.

It seems to me that hydrolysis represents a condition where the complicated periodicity of the salt becomes too extended, so that part of the solute loses coherence and the fractions revert to their simpler (though related) periodicity, each in its own condition, as if the other were not present. I believe these conditions to be quite different from those of electrolysis. In this I imagine the ions to exist as atoms combined with charges of electricity (instead of complementary atoms) to make virtual molecules suspended in the menstruum much as are the metallic molecules in colloidal solutions and very different from the clouds of diffused electrons or emanations filling intermolecular spaces which by my theory make a continuity of the particles of the solute roughly answering to that of Bragg for matter in crystalline form.

This involves recognizing inherent differences between solvent and solute. I have been led by other arguments to believe that while in many cases substances are mutually soluble, so that each acts both (or either) as solvent and (or) solute; in other cases one has a distinctly different type of action from the other. I have been able to prove false at least one of the arguments on which Findlay bases his assertion that solvent and solute are indistinguishable.

I appreciate that my idea is difficult to grasp, but it seems to me mechanically easier to imagine than the customary hypothesis that one Ba ion existing as a concentrated unit can simultaneously neutralize the capacity for Ba, in the presence of equivalent SO_4, of 10,000,000 molecules of water with which it is not in contact at all, and is only connected to by a chain of many other aqueous molecules, all equally out of contact with Ba.

Some of my friends have tried to explain this action by an effect radiating from the Ba ion, by adsorption, or by consecutive contacts with all the water molecules. Any radiant effect should diminish as the square of the distance increases, so that at say fifty times the diameter of an aqueous molecule the effect should be infinitesimal compared with that in contact with the Ba. If, therefore, another molecule of $BaSO_4$ should be mechanically introduced into the solution at this point, we should get there the relatively high effect near a nucleus, so that in a mud of precipitated $BaSO_4$ we should get a multiplicity of such local supersaturations, with reduction of the relatively great subsaturated volumes and thus a high average supersaturation under just the circumstances of contact with the solid phase, which we recognize as most destructive of supersaturation.

I cannot see how adsorption can act through a layer fifty molecules thick of homogeneous water, nor, especially in view of the very slow net progress of particles shifting by the Brownian movements, can I think it possible for the heavy Ba ion to strike consecutively each of 10,000,000 water molecules with sufficient frequency to prevent them from showing additional effect from additional $BaSO_4$ molecules in suspension.

It has been objected also that this involves an enormous amount of latent heat to overcome the centripetal forces of the atom. I am not at all sure that in cases of high dilution we do not have the latent heat of volatilization to add to the latent heat of fusion, which would signify that some of the dissolved molecules were dissolved in volatile form, as I supposed some to be in liquids approaching the critical temperature. This would perhaps indicate the existence of the vapor of the solute in the intermolecular spaces of the solvent.

We know almost nothing of the inter-molecular centripetal forces and why in the solid form they hold things together. Why might it not be the characteristic of solvents to cause these forces to attract the particles held in check by them toward molecules of the solvent instead of toward a common center?

Peace Dale, R. I.
Apr. 21, 1919

FLAME REACTIONS OF SELENIUM AND TELLURIUM

BY HARRY B. WEISER AND ALLEN GARRISON

In a recent communication, Papish[1] has extended the observations of Bancroft and Weiser[2] by showing that elementary selenium and tellurium can be precipitated on a cold object from flames charged with compounds of these elements The introduction of compounds of both selenium and tellurium into the hydrogen-air flame imparted characteristic flame colorations in distinct zones. Analogous to the conclusions reached by Bancroft and Weiser, Papish concluded that "processes of dissociation, reduction and oxidation are back of the luminescences in the different zones." The investigations were not carried to the point where it could be said with any degree of certainty what specific chemical reaction was responsible for a given luminescence. This seemed unfortunate, particularly in view of the fact that the colorations of the different zones in the flames of selenium and tellurium were apparently quite sharply defined. Accordingly, this investigation was undertaken to determine if possible the causes of the different luminescences. The experiments with selenium will first be considered.

Experiments with Selenium

The Hydrogen-in-air Flame.—Papish introduced elementary selenium and the oxide and hydride of the element into the hydrogen-air flame and obtained the results given in Table I.

For the purpose of familiarizing ourselves with the various colors as well as their location in the flame, the experiments of Papish were repeated and extended: Hydrogen from a cylinder was passed through a horizontal hard-glass tube, the end of which was bent upward and supplied with a platinum tip approximately 4 mm in diameter. The hydrogen was

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[1] Jour. Phys. Chem., 22, 430, 640 (1918).

[2] Ibid., 18, 213, 281 (1914).

TABLE I

Substance volatilized	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object
SeO_2	Deep blue	Se	Pale blue	Se	Greenish[1]	None
H_2Se	Very faint blue	None	Deep blue	Se	Greenish	None
Se	Blue	Se	Violet	Se	Greenish[2]	None

ignited at the tip and the flame was adjusted to a height of approximately 10 centimeters. By heating the metal or its salts in the hard glass tube, the vapors were carried into the flame in the stream of hydrogen and imparted to it three quite distinct colors in different regions: First, blue in the inner region surrounding the zone of unburned gas; and a deeper shade of blue in an outermost shell seeming to be not more than 4 mm in thickness. This shell extended from the base of the flame to two-thirds of the distance to the tip. Second, a reddish coloration in a mantle between the colorations of blue. Third, a greenish tip. Selenium may be precipitated as a red coating on a cold object such as a porcelain casserole held in certain portions of the flame. In this manner it was found that free selenium existed in the inner blue and the red portions of the flame but not in the greenish tip. From this tip white fumes of selenium dioxide were seen to rise. The pure oxide was condensed as a film on a cold sheet of mica held in the tip.

The flame luminescences were quite noticeably affected by varying the amount of substances introduced into the flame.[3] When only a very small amount of a substance was added, the blue color in the inner core appeared paler blue and the red luminescence was absent. The addition of an excess of the dioxide cooled down the flame and the white fumes modified the blue coloration. An excess of elementary selenium like-

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[1] Becomes red if much selenium dioxide is volatilized.

[2] Occasional red flashes.

[3] Bancroft and Weiser: Loc. cit.; cf. Mitscherlich: Pogg. Ann., 121, 487 (1864); Wüllner: Ibid., 120, 164 (1863); Wied. Ann., 8, 599 (1879).

wise modified the blue coloration and increased the amount of red luminescence.

The effect of cooling the flame was quite marked: When a coil of heavy copper wire, previously cleaned, was placed around the flame, thus conducting away part of the heat, the green and reddish colorations faded leaving the blue predominant. A somewhat similar effect was produced by compressing the flame longitudinally between two cold sheets of mica. Since the latter is transparent it was possible to view the flame as if a longitudinal section had been cut from the center. Because of the cooling effect the red and green disappeared entirely, leaving the section of the blue flame with a dark inner core of unburned gas. When the flame was compressed horizontally by a single sheet of mica, it could be viewed from above. The cooling caused the red and green light to disappear leaving a dark center of unburned gas surrounded by a ring of blue light that was deeper blue around the outer edge.

Selenium chloride and selenium bromide imparted to the flame the same colors as the metal and the oxide.

It will be noted that in the main our observations confirm those of Papish except that the latter did not call particular attention to the marked effect on the coloration of varying the amount of materials added to the flame. As pointed out this not only affects the flame temperature and hence causes a variation in the velocity of certain reactions; but it also modifies the flame colorations. When there is a possibility of more than one color of light being produced in a flame, each color has an apparent influence on the others so that what is actually seen is the resultant mixture of colors. In certain regions of the flame one reaction may predominate to such a degree that the modification is altogether inappreciable; while in other regions, the effect may be so marked as to indicate a distinct luminescence. The violet coloration observed by Papish in the flame charged with selenium was not a distinct luminescence but was a mixture of red and blue in the right proportion to make violet.

The effect of varying the amount of substance added to the flame was brought out quite clearly in an experiment with hydrogen selenide. A method similar to that used by Papish was employed in this experiment: Hydrogen from a cylinder was conducted through the side arm of a 500-cc. suction flask containing 200 cc of water. The flask was fitted with a two-hole rubber stopper supplied with a funnel tube that dipped below the surface of the water and with a platinum-tipped glass tube. After lighting the hydrogen at the tip, aluminum selenide was introduced into the flask through the funnel tube. The selenide reacted with water evolving hydrogen selenide which was burned with the hydrogen. In the presence of but little hydrogen selenide the inner zone appeared faintly blue as Papish observed. When the amount of hydrogen selenide was increased by opening the flask and adding to it a quantity of aluminum selenide, the entire flame was quite similar to those previously observed. The inner zone assumed the same blue color and from this region elementary selenium was precipitated as in flames charged with the metal or the oxide.

Particular attention should be called to the shell of deep blue around the outermost portion of the flames to which selenium or its compounds were added. This might easily be overlooked.

The Bunsen Flame.—Selenium and its salts were introduced into the Bunsen flame by volatilizing them in a stream of air which was led into one of the air ports at the base of the burner. The colorations produced were similar to those in the hydrogen-air flame. As before, the blue luminescence around the inner core seemed paler than that nearer the outside of the flame. In order to determine whether this was due to the colored zones through which the observations were made, the two cones of the flame were separated by means of the Smithells' separator. It was observed that the sheath of blue surrounding the inner core was distinctly paler blue than the luminescence in the outer zone where oxygen was in excess.

The Air-in-hydrogen Flame.—The experiments with the flame of air burning in hydrogen were carried out in an apparatus constructed and manipulated as follows: A hole one centimeter in diameter was blown in the bottom of a 1000-cc round bottom flask and was supplied with a platinum tip. The flask was inverted and held in place by a clamp. The one-hole stopper in the neck was supplied with a platinum-tipped inlet tube that could be moved up and down at will. Hydrogen was conducted into the flask through a side arm blown in the neck; and air through the tube in the stopper. After washing the flask free from air the hydrogen was ignited at the tip. The air-inlet tube was then forced through the flask into the flame and a gentle current of air turned on. A flame of air burning in an atmosphere of hydrogen was obtained simply by drawing the air-inlet tube down into the flask. When selenium or its salts were introduced into this flame by vaporizing them in the current of air, it was found that there was no green coloration and but very little red in the flame. There was, however, a narrow blue mantle which clung closely to the inner core where air was in excess. In an experiment to be described later on, it was found that the red luminescence resulted in part from the glowing of the vapors of elementary selenium. Since this reddish glow was not apparent in the outermost part of the flame where selenium was in excess, it was evident that the temperature in this region was not sufficiently high. An attempt was made to raise the temperature of the entire flame by substituting oxygen for air. This was found to be impracticable, however, since the glow from the highly-heated platinum tip masked the luminescence.

The Chlorine-in-hydrogen Flame.—In order to determine whether oxygen was necessary for securing the blue luminescence, telluric chloride was introduced into the chlorine-in-hydrogen flame obtained by substituting chlorine for air in the apparatus described in the preceding paragraph. Some metallic tellurium was placed in a hard glass tube through which the stream of chlorine passed. On heating, the element was converted into the chloride which was swept into the flame imparting to the outer mantle a distinct blue coloration unmixed with red or green. The coloration in the inner zone was masked by the greenish yellow hydrogen-chlorine flame.

The Luminescence of Selenium Vapors.—Since the vapors of selenium are colored one should expect them to glow when heated as do the vapors of iodine.[1] As a matter of fact, Evershed found this to be the case. To determine the intensity and color of this luminescence a few grams of selenium were placed in the bottom of a hard-glass test-tube 2 cm in diameter and 25 cm in length. The element and the tube above it were heated until the selenium boiled vigorously. The heated vapors coming in contact with the hot tube emitted a reddish glow which corresponds to the reddish luminescence observed in the hydrogen-air flame. These observations were made in the dark room and the flame which was used to heat the element was extinguished to make sure that the vapors were actually glowing instead of reflecting light.

Combustion of Selenium.—When selenium was heated in air or hydrogen it burned with a blue flame. The experiment was carried out as follows: Two grams of powdered selenium were placed near the center of a piece of hard-glass tubing 2 cm in diameter and 35 cm in length. Oxygen from a cylinder was passed slowly over the metal while it was being heated with a blast lamp. When the temperature was sufficiently high the selenium burst into a blue flame of a shade identical with that in the hydrogen flame charged with selenium compounds. When more strongly heated a reddish glow appeared just above the surface of the element. By heating the tube to a greater length it was found that the tip of the blue flame became greenish. White selenium dioxide was formed and deposited in the cooler portion of the tube.

In order to determine whether the reverse reaction of reduction emitted a characteristic glow, an intimate mixture of selenium dioxide and aluminum powder was heated. The speed of the reduction was varied by varying the relative

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[1] Evershed: Phil. Mag., 5, 39, 465 (1895); cf. Paterno and Mazzucchelli: Atti. accad. Lincei, [5] 17, II, 428 (1908); Bancroft and Weiser: Trans. Am. Electrochem. Soc., 25, 121 (1914).

amounts of oxide and aluminum; but in no case was a characteristic luminescence obtained.

The Color of Selenium Dioxide Vapors.—From the above experiments it was suspected that the greenish coloration appearing in the tip of the hydrogen flame must be connected in some way with the oxide after its formation which was complete in the blue flame. The fact that the oxide but not the element could be precipitated from the greenish tip also pointed to this idea. The color of the heated vapors of selenium dioxide were observed by sealing a few grams of the oxide in a hard-glass tube in an atmosphere of oxygen and heating in a blast. At a comparatively low temperature the oxide vaporized filling the tube with a greenish yellow color. On cooling the greenish color faded and the white crystals of the oxide redeposited on the walls of the tube.

Experiments with Cathode Rays.—In order to study further the luminescent reactions of selenium, the action of cathode rays on the element and its oxide were tried. Lewis[1] studied the effect of cathode rays on certain metals in a cathode tube constructed in such a manner as to isolate the effect of the cathode rays from the effect of the current. Under these conditions, with elementary sulphur, selenium and tellurium he obtained "an almost imperceptible blue glow."

The cathode tube used in these experiments consisted of a vertical portion into which was sealed the disk anode and the cathode; and a horizontal portion enlarged into a bulb below the cathode. One end of the horizontal portion was constricted and to it was sealed a stop-cock tube which connected with the pump. Substances were introduced into the apparatus from the opposite end of the tube which was closed with a cap making a ground-glass connection. The tube was evacuated with a mercury pump. With substances having a low vapor pressure at ordinary temperatures, no difficulty was found in getting and maintaining a cathode vacuum with this apparatus.

The bottom of the cathode tube was first covered with a layer of crystalline selenium, after which the entire apparatus

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[1] Astrophys. Jour., 16, 31 (1902).

including the pump was filled with hydrogen. This was done for the purpose of excluding oxygen. The surface of the metal apparently did not luminesce under the influence of the cathode rays; but the vapors throughout the bulb emitted a reddish glow very similar to that obtained by heating the vapors. Under the influence of the rays the metal volatilized and red amorphous selenium was deposited on the sides of the tube. In this experiment as carried out no attempt was made to isolate completely the effect of cathode rays from the effect. of the current and the latter unquestionably has some effect. It should be stated, however, that no reddish glow was obtained in a "blank" experiment in which the cathode tube contained nothing but hydrogen.

The effect of the presence of oxygen on the luminescence was next tried by introducing oxygen into the cathode tube before carrying it down to a cathode vacuum. The presence of oxygen introduced a blue luminescence along with the red which gave a violet effect similar to that obtained in the flame. The element was then removed and selenium dioxide put in its place. Under the influence of the rays a portion of the oxide dissociated and the recombination produced throughout the tube a blue luminescence[1] that was distinctly more marked than in the previous case where only a trace of oxygen was present. When the deep blue color was present, selenium dioxide collected as white crystals on the sides of the cathode tube. It was thought that a sudden lowering of the pressure while the discharge was passing might withdraw some oxygen leaving selenium in excess. To accomplish this the cathode tube was shut off by means of the stopcock and the space between the tube and the pump was evacuated as low as possible. When the stopcock was opened the pressure in the tube was suddenly diminished and immediately the blue color became a violet showing the presence of red luminescence; and amorphous selenium deposited on the tube instead of the oxide. If the bombarding was con-

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[1] Wiedemann and Schmidt: Wied. Ann., 56, 243 (1895); Wilkinson: Jour. Phys. Chem., 13, 691 (1909).

tinued more oxide was dissociated and the violet gradually gave place to blue.

In order to show that compounds other than the oxide would give a blue luminescence in the cathode tube, an attempt was made to use selenium tetrabromide and selenium tetraiodide. Owing to the volatility of these compounds it was found impossible to get a cathode vacuum at ordinary temperatures.

Discussion of Results

The three colorations in the flames of selenium will be considered separately:

The Blue Luminescence.—Blue luminescence is produced under the following conditions: (1) When elementary selenium burns in excess oxygen. (2) Pale blue in the region surrounding the inner cone of the hydrogen-air flame or the Bunsen flame charged with selenium, its oxide, hydride or halides. In this region air is present but not in excess. (3) A deeper blue in the outer portion of flames in air where there is excess oxygen. This is particularly marked in a sheath surrounding the outermost portion of the lower part of the flames. (4) A narrow mantle close tò the inner core of the air-hydrogen flame. (5) In the flame of chlorine burning in hydrogen. (6) When the oxide is acted on by cathode rays. From these results it is evident that the blue color is always produced when the element is oxidized rapidly enough. Air is unnecessary since the same coloration is obtained in an oxygen-free flame. The lowest oxide of selenium is the dioxide and this is formed when the element is burned in air or oxygen. When the oxide is acted on by cathode rays a blue luminescence is produced from which it seems probable[1] that the specific chemical action that produces the color is the reaction from selenic ion to selenic oxide or salt.

The depth of the blue color depends on the amount of selenium oxidized in a given space and the rapidity of the oxidation. This accounts for the blue luminescence appearing

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[1] Wiedemann and Schmidt: Loc. cit.; Wilkinson: Loc. cit.

paler in the inner portion of the hydrogen flame than in the outer portion where there is excess air. When selenium salts are introduced into the ordinary flame they are so readily acted on by the combined dissociating and reducing actions of the flame that some selenium is formed at once and can be precipitated on a cold object held but a short distance from the inner zone of unburned gas. This selenium coming in contact with a relatively small amount of oxygen a little further on, burns in part with a blue luminescence. Beyond this narrow zone in the hottest region of the flame the reverse reaction of dissociation predominates but this gives place to oxidation again in the cooler outermost portion of the flame. This last oxidation takes place in the presence of excess air and the luminescence appears deeper blue than it does in the inner zone.

If the amount of selenium added to the flame is very small, only a faint coloration appears in the inner zone. On the other hand, the presence of an excess of the element or compound cools the flame and masks the coloration in proportion to the amount present. The bluest color in the inner zone should result in the presence of the maximum amount of selenium that is capable of complete oxidation before reaching the zone of highest temperature where the reverse reaction predominates.

The Red Luminescence.—The red luminescence is produced under the following conditions: (1) In the hottest portion of flames charged with excess selenium or its compounds. This is most marked midway between the inner and outer cones. Elementary selenium is readily precipitated from this portion of the flame. (2) When the highly colored vapors of selenium are heated. (3) When selenium vapor is acted on by cathode rays in a hydrogen-filled cathode tube. Since the vapors of selenium are colored it is evident that at least a part of the luminescence on heating the vapors is a thermal luminescence; but in view of the fact that a similar glow was obtained in the cathode tube, it is probable that a part of the glow is due to chemiluminescence. A similar conclusion was reached concerning the luminescence of heated sodium vapor. In all probability this is due in part to thermal luminescence[1] and in part to chemiluminescence.[2] In connection with the flame reactions of sodium, the evidence indicated[3] that the familiar yellow luminescence was produced at least in part by some stage in the reaction from electrically neutral sodium vapor to sodium ion. It was impossible to specify the reaction more closely since it was not possible to account for all the sodium spectra observed by Lenard[4] and by Wood and Galt.[5] Similarly, we conclude that the red luminescence in the flames containing selenium is due in part to the color of the vapors, in part to a purely thermal luminescence and in part to some stage in the reaction from electrically neutral selenium vapor to selenic ion. It is as yet unsafe to specify the reaction more closely particularly since no quantitative study of the glow spectrum of selenium vapor under various conditions has been made as in the case of sodium vapor. In this connection Lenard[6] has shown the existence of selenium ions in the hottest portion of flames but not in the outermost regions. As previously pointed out, the amount of the red luminescence is determined by the amount of selenium added to the flame. The coloration may be eliminated almost completely by encircling the flame with a spiral of large copper wire. The part which each of the above mentioned factors contribute to the red luminescence can be decided only by a quantitative study of the flames under various conditions.

The Greenish Coloration.—The greenish coloration occurs: (1) In the outer tips of the hydrogen-air and the Bunsen flames. (2) When selenium is vaporized in a sealed tube. Although solid selenium dioxide is white, the vapors are greenish from which we conclude that the green color in the tip of certain flames is not a luminescence at all but is merely the

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[1] Evershed: Loc. cit.

[2] Wood: "Physical Optics," 537, 579 (1911).

[3] Bancroft and Weiser: Jour. Phys. Chem., 19, 310 (1915).

[4] Drude's Ann., 11, 636 (1903).

[5] Astrophys. Jour., 33, 72 (1911).

[6] Drude's Ann., 9, 632 (1902).

color of the dioxide vapors that appear more green because of the reflection of the blue luminescence just below. On cooling the flame the green coloration disappears, since the vapors are converted to a white smoke. A similar phenomenon was observed in the hydrogen-chlorine flame charged with copper salts and in the Bunsen flame charged with a large excess of copper chloride[1] The vapors of the chloride are colored and impart a coloration to the tip of the flame.

Experiments with Tellurium

By introducing tellurium compounds into the flame of hydrogen burning in air Papish[2] obtained the results given in Table 2.

TABLE II

Substance volatilized	Inner zone		Middle zone		Outer zone	
	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object	Luminescence	Deposit on cold object
TeO_2	Green	Te	Lilac[3]	Te	Green	None
H_2Te	Blue	Te	Lilac	Te	Green	None
Te	Green	Te	Lilac[4]	Te	Green	None

The Hydrogen-in-air Flame.—The experiments with the hydrogen flame were carried out in the same manner as previously described for selenium. The flame charged with the element and its compounds consisted of three distinct colors with sometimes a fourth: First, green in the inner cone surrounding the zone of unburned gases; second, an outer mantle of blue that could be modified considerably by the addition of varying amounts of material to the flame; third, a greenish tip; and fourth, in some instances a shade of red between the outer blue and the inner green in the hottest portion of the flame. Tellurium was precipitated as a metallic mirror when

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[1] Bancroft and Weiser: Loc. cit.

[2] Loc. cit.

[3] Accompanied by red flashes.

[4] Also red surrounded by blue when much tellurium is volatilized.

a cold object such as a porcelain casserole was held in the inner green or the reddish portions of the flame. It will be seen by referring to the above table that in most respects our observations agree with those of Papish. The so-called lilac color observed by the latter was not a distinct luminescence but was a mixture of blue and reddish orange in the right proportions. As was true with selenium flames, the respective colors can be modified considerably by varying the amounts of materials added to the flames. Thus Papish ordinarily obtained a lilac coloration but with excess of selenium he got the reddish luminescence surrounded by blue as we observed. A particular instance of the effect of the quantity of material introduced into the flame was again brought out in the experiments with the hydride. The experiment was carried out as previously described for hydrogen selenide substituting aluminum telluride for aluminum selenide. A considerable quantity of aluminum telluride was added to the flask and no difficulty whatsoever was experienced in getting a flame with the inner green region similar to the flames to which the metal was added. It was only after the telluride was almost gone that the inner zone took on more of the bluish color noted by Papish. This same effect was produced by adding a trace of the element to the flame. As will be pointed out in the subsequent discussion of these experiments, these results are in accord with what one might expect.

The effect of cooling the flame was quite as marked as in the case of selenium. When a spiral of large copper wire was lowered around the flame thus conducting away some heat, the greenish tip faded and all reddish coloration disappeared leaving only the green inner core surrounded by a mantle of very deep blue. When compressed longitudinally between two sheets of mica, the orange reddish luminescence and the green tip again disappeared. The section, appearing as though it had been cut from the center of the flame, consisted of a dark core of unburned gas along the sides of which was a narrow strip of green, followed by one of blue. By compressing the flame horizontally with a single sheet of mica and observing from above, the section was seen to consist of a dark center of unburned gas surrounded by a circle of green and a narrower rim of blue. Tellurium dioxide was deposited as a white ring outside the circle of flame. From this it seemed likely that tellurium dioxide could be precipitated on a piece of mica held in the greenish tip of the flame. This conclusion was confirmed as the oxide is much less volatile than the corresponding oxide of selenium and was readily condensed. The molten oxide as well as the vapors were found to be greenish yellow in color.

The Bunsen Flame.—The Bunsen flame contained the same colorations as the hydrogen flame. When the two cones were separated in the Smithells' separator, the inner flame, where air was not in excess, formed a sheath of vivid green unmixed with blue, surrounding the cone. The outer flame where air was in excess was blue with a greenish tip. The latter was less marked than in the ordinary hydrogen flame probably on account of the lower temperature. For the same reason there was but little reddish in the flame. A more brilliant coloration in both zones was obtained by using volatile salts of tellurium such as telluric bromide and telluric iodide. With these salts were produced an inner flame of very vivid green and an outer deep blue with a faint greenish tip.

The Air-in-hydrogen Flame.—When tellurium was introduced into the flame of air burning in hydrogen, the inner core surrounding the zone of unburned gas was blue and around it was a mantle of deep green like that observed in the inner zone of the Smithells' separator. Metal deposited on the walls of the bulb.

The Chlorine-in-hydrogen Flame.—Chlorine was passed over heated tellurium and the telluric chloride formed was swept into the flame of chlorine burning in hydrogen. An outer mantle of green was obtained identical with that in the same region of the air-hydrogen flame. The inner blue core was indistinct as it was masked by the yellowish chlorine flame.

Combustion of Tellurium.—A few grams of tellurium were placed near the center of a hard-glass tube through which was passed a slow current of oxygen. The tellurium was heated until it burst into a flame the color of which was greenish blue. The line of separation between the two colors was much less distinct than in the hydrogen flame. However, the flame was more green near the tellurium where the metal was in excess and more blue where oxygen was in excess. By heating to a high temperature it was possible to obtain the golden yellow vapors of tellurium just above the surface of the element. White tellurium dioxide was deposited on the tube beyond the flame.

Since in all cases the green luminescence was formed in the more reducing portions of flames and the blue in the more oxidizing regions, it should be possible to decrease the green luminescence to a minimum and to increase the blue luminescence to a maximum by increasing the concentration of oxygen in the region of the hydrogen flame charged with tellurium. To obtain this condition, the platinum-tipped hydrogen tube was jacketed by a tube 3 cm in diameter and 10 cm in length. A stopper in the bottom of this jacket-tube served the double purpose of closing the bottom and of holding it concentric with the hydrogen tube. The top of this jacket was about 2 cm above the hydrogen tip. After lighting the hydrogen and introducing tellurium into the flame, oxygen was run into the jacket from a side arm near the bottom. The oxygen arose and encircled the lower portion of the flame supplying it with an excess of the gas. Under these conditions the flame became almost entirely blue with only a small reddish orange inner core and the usual greenish tip.

No characteristic luminescence was obtained by the rapid reduction of tellurium dioxide with aluminium powder.

Cathode Rays on Tellurium and its Salts.—The experiments with the cathode rays were carried out in the same apparatus as previously described. Metallic tellurium was first introduced into the hydrogen-filled tube which was then evacuated. The glow in the bulb was reddish under the influence of the rays but the coloration was not so marked as with selenium on account of the greater volatility of the latter metal. When the metal was replaced by the oxide a faint bluish glow was obtained. Telluric bromide was next used with more marked results. When the salt was first bombarded a reddish glow was produced over the surface which soon disappeared, and did not return. The vapors throughout the bulb glowed with a bright blue color but the luminescence was green near the surface of the bromide. Since the cathode rays decompose the compound into its elements and since tellurium is much less volatile than bromine it seemed plausible, in line with previous experiments, to attribute the blue luminescence throughout the bulb to a relatively higher concentration of bromine and the green luminescence near the surface of the salt to a relatively higher concentration of tellurium. If this were true it should be possible to exhaust further during the passage of the discharge thereby decreasing the concentration of bromine. This was done as in the experiment with selenium dioxide and it was found under suitable conditions that the luminescence throughout the bulb changed from blue to green. The discharge was continued and after a time the green disappeared giving place to the usual blue as more telluric bromide was decomposed by the cathode rays. It was hoped to confirm these experiments with telluric iodide; but the salt was so volatile that a cathode vacuum could not be obtained at ordinary temperatures.

Discussion of Results

There are four colorations in the flames of tellurium to be accounted for. These will be considered in turn:

The Green Luminescence.—The green luminescence is produced under the following conditions: (1) In the inner zone of the hydrogen-air flame and the Bunsen flame charged with tellurium compounds. With volatile salts of tellurium such as the bromide and iodide, this coloration is particularly marked in the zone surrounding the inner core of the Smithells' separator. (2) Deep green outer zone in the flame of air burning in hydrogen. (3) Deep green outer mantle in the flame of chlorine burning in hydrogen. (4) Near the surface of the tellurium when the element is burned in oxygen. (5) Under the influence of cathode rays telluric bromide shows a green luminescence near the surface of the salt where tellurium is in excess. By suddenly lowering the pressure in the tube while continuing the bombarding, bromine is withdrawn and green luminescence fills the tube.

Tellurium differs from selenium in that it forms two oxides TeO and TeO_2 and series of salts corresponding to both oxides. When the element is burned in air or oxygen it goes to the dioxide; but it is altogether probable that the oxidation is stepwise although it does not stop at the monoxide stage. A stepwise oxidation is readily carried out with the halogens. By reference to the data above summarized it will be seen that the green luminescence occurs in the more reducing portions of flames which favor the reaction to tellurous compounds. This is true in every case whether the oxidation is in the presence or the absence of oxygen. Since the green luminescence is obtained in the cathode tube under the conditions which favor the formation of tellurous salt we conclude that the green luminescence in tellurium flames is due to the reaction from tellurous ion to tellurous salt.

The Blue Luminescence.—The blue luminescence is produced under the following conditions: (1) In the outer zone of the hydrogen-air flame and the Bunsen flame charged with tellurium and its compounds. (2) In the inner zone of the flame of air burning in hydrogen. (3) The flame of tellurium in oxygen. (4) Throughout the greater portion of the hydrogen flame charged with selenium compounds when the lower portion of the flame is encircled with an atmosphere of oxygen. (5) Throughout the cathode tube containing telluric bromide when bromine is in excess. From the above data it is evident that the blue luminescence occurs in the oxidizing portion of all flames which favor the formation of telluric compounds. Since the cathode rays on telluric compounds give a blue luminescence under suitable conditions, we conclude that this luminescence is due chiefly to the reaction from telluric ion to telluric salt.

As in the case of selenium flames the coloration is influenced by the amount of material present in the flame. If but a trace of the element is added to the hydrogen flame complete oxidation may take place in the inner zone which may then appear more blue than green in color. In the presence of excess selenium the blue luminescence is modified by reddish giving it a lilac appearance. If the flame is cooled by surrounding it with a coil of wire the reddish color disappears leaving a decided blue.

The Reddish Luminescence.—The vapors of elementary tellurium are golden yellow in color and when heated in a quartz tube Paternò and Mazzuchelli[1] found that an emission spectrum is produced which they considered was a temperature radiation. A reddish glow is obtained with the element in a cathode tube filled with hydrogen before evacuating. Analogous to the reddish luminescence in selenium flames, it is probable that the orange red color in the hottest portion of flames from which tellurium can be precipitated, is due in part to the color of tellurium vapors, in part to thermal luminescence and in part to chemiluminescence resulting from some stage in the reaction from electrically neutral tellurium vapor to telluric ion. A quantitative study is necessary to determine the part contributed by each of these factors under widely varying conditions.

The Green Coloration.—Tellurium dioxide melts to a greenish yellow liquid. The oxide is much less volatile than the corresponding oxide of selenium and the color of the vapors is not so marked. However, the greenish coloration in the tip of the flame is unquestionably due to these vapors reflecting the blue luminescence just below them. When the tip of the flame is cooled, the vapors are readily condensed and the green coloration disappears forthwith.

Summary

The results of this paper may be summarized briefly as follows:

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[1] Loc. cit.

(1) A study has been made of the flame reactions of selenium and tellurium and of the salts of selenium and tellurium.

(2) The reaction from selenium to selenic salt produces a blue luminescence which is the most characteristic in flames containing selenium. It is probable that this luminescence is due chiefly to the reaction from selenic ion to undissociated selenic salt.

(3) The reaction from tellurium to tellurous salt produces a green luminescence; and from tellurous salt to telluric salt a blue luminescence. It is probable that the green luminescence is due chiefly to the reaction from tellurous ion to the undissociated tellurous salt; and the blue luminescence from telluric ion to the undissociated telluric salt.

(4) Under certain conditions a reddish luminescence occurs in flames containing selenium that is as a rule less intense than the blue luminescence; and a reddish orange luminescence in the flames containing tellurium that is less intense than either the green or the blue liminescence. Since the vapors of both elements are colored, it is probable that the reddish coloration in both cases is due in part to the color of the vapors, in part to a purely thermal luminescence and in part to some stage of the chemical reaction from the vapors of the element to the tetravalent ion. It is unsafe to specify the reaction more closely until more is known of the glow spectra of the vapors of the respective elements.

(5) No characteristic luminescence has as yet been detected for the reverse reactions.

(6) A combination of the red and blue luminescence frequently gives a violet or lilac appearance to certain portions of the flames. This must not be mistaken for a distinct luminescence.

(7) A greenish tip in the flames in air charged with selenium and tellurium compounds is not a luminescence but is due to the greenish color of the vapors of the dioxide which appear more green by reflecting the blue luminescence just below.

(8) Particular attention has been called to the modifying influence on flame colorations by varying the amount of materials added to the flame.

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SUPERPALITE[1]

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Trichlormethylchlorformate, $ClCO_2CCl_3$, is called diphosgene by the British, surpalite by the French, and superpalite by the Americans. It is a colorless, mobile liquid, with a fairly pleasant sweet odor, boiling at 127.5°–128° (corr.). It has a vapor pressure of 2–4 mm at 0° and of about 10.3 mm at 20°. Hentschel gives the specific gravity of the pure liquid at 1.6525 at 14°; but our samples rarely went above 1.64. The refractive index at 26° was found by us to be 1.456 for the D line. Owing to the low volatility, superpalite is used only in shell and not in cylinder attacks. It has been used by the Germans only, who mark these shell with a green cross. The shell usually contain varying mixtures of superpalite and phosgene, though some duds have been found containing superpalite and chlorpicrin; diphenylchlorarsine has also been found in some of the Green Cross shell. The lethal concentration for dogs is 0.25 mg per liter (40 p. p. m.) for exposures of 30 minutes; but the concentration necessary to kill is very much less if the exposure is prolonged. Superpalite owes its importance to its high vapor density, its persistency because of its high boiling point, and to the increased toxicity on long exposure.

Superpalite is probably made as a war gas in Germany by chlorinating methyl formate to chlormethylformate and then chlorinating this to superpalite,

$$HCO_2CH_3 + Cl_2 = ClCO_2CH_3 + HCl$$
$$ClCO_2CH_3 + 3Cl_2 = ClCO_2CCl_3 + 3HCl$$

While superpalite has not been used by the Allies as a war gas, it has been prepared in this country for testing purposes by the action of phosgene on methyl alcohol, giving methyl chlorformate, which is then chlorinated to superpalite,

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[1] Published by permission of the Director of the Chemical Warfare Service.

$$COCl_2 + CH_3OH = ClCO_2CH_3 + HCl$$
$$ClCO_2CH_3 + 3Cl_2 = ClCO_2CCl_3 + 3HCl$$

In the first stage, a possible side-reaction is

$$COCl_2 + 2CH_3OH = (CH_3)_2CO_3 + 2HCl$$

after which the dimethyl carbonate is chlorinated to perchlormethyl carbonate, or triphosgene as the English call it,

$$(CH_3)_2CO_3 + 3Cl_2 = (CCl_3)_2CO_3 + 3HCl,$$

which has no toxic value and which has been thrown away in the past although it can be decomposed by prolonged heating into superpalite and phosgene

$$C(Cl_3)_2CO_3 = ClCO_2CCl_3 + COCl_2.$$

The chlorination of methyl chlorformate to superpalite takes place when the heated liquid is exposed to intense light while the chlorine is passed in.

Trichlormethylchlorformate was prepared by Hentschel,[1] who proved that it was the final product in the chlorination of methyl formate. The process of chlorination takes place in steps, methyl chlorformate being formed first and then, successively, the monochlor-, dichlor-, and trichlormethyl chloroformates. Methyl formate reacts readily with chlorine in the dark, giving methyl chlorformate. Further chlorination in the dark without the aid of an accelerating agent gives some chlormethyl chlorformate, but the reaction velocity is low and the yield poor. Complete chlorination can only be obtained with light as catalytic agent and near the boiling point of the liquid.

When the United States went into the war, Professor Neher of Princeton for a while made all the superpalite that was needed for testing purposes. He prepared the methyl chloroformate by the action of phosgene on methyl alcohol and chlorinated this compound in light raising the temperature as the chlorination proceeded. He used a "White Flame" cored arc as the source of light. Professor Neher will doubtless publish the details of his work. When the demand for

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[1] Jour. prakt. Chem., [2] 36, 99, 209, 305, 468 (1887).

superpalite for testing purposes increased, the production was taken over by Captain Uhlinger, of the Small Scale Manufacturing Section of the Research Division, who substituted nitrogen-filled lamps for the "White Flame" cored arc. Although it did not seem probable that the United States would use superpalite as a war gas, the Catalytic Section was asked to study the problem as a precautionary measure. It was hoped that perhaps some much better method of manufacture might be worked out.

The properties and preparation of superpalite were therefore studied with some care. Superpalite was supplied to us by the Small Scale Manufacturing Section, labelled B. Pt. 125°–130°, sp. g. 1.64. On redistillation it was found that approximately nine percent of this product was perchlormethyl carbonate. Even after a third distillation of the 125°–130° fraction, a three percent residue of crystals was left, showing that this impurity is not easy to remove. The fraction between 125°–130° in the third distillation was used by us as superpalite. The methyl chloroformate was also obtained from the Small Scale Manufacturing Section. Besides a large amount of hydrochloric acid and phosgene, it contained a fair amount of dimethyl carbonate. A typical fractionation of this product made in a long Hempel column is as follows:

58°–62°	8 cc
62°–69°	50 cc
69°–75°	305 cc
75°–85°	40 cc
85°–92°	8 cc

The last fraction consisted mainly of dimethyl carbonate. For our experiments in chlorination, the fraction coming over 71°–75° was taken as the starting point.

When heated to 300°–350° superpalite decomposes into phosgene in the ratio of one mole to two; but this may be the result of a catalytic action. Hentschel[1] states that when

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[1] Jour. prakt. Chem., [2] 36, 102 (1887).

perchlormethyl chlorformate is boiled with a reflux condenser, it breaks down to some extent into phosgene which can be detected in alcohol owing to the formation of methylchloroformate. We have found practically no loss of weight when superpalite itself is refluxed at the boiling point for fifteen hours. Since superpalite itself reacts with alcohol, it is possible that Hentschel's results were due to uncondensed superpalite vapor passing through the condenser.

Superpalite is hydrolyzed slowly by water at ordinary temperature and fairly rapidly at 100°, the products being hydrochloric acid and carbon dioxide, presumably according to the equation:

$$ClCO_2CCl_3 + 2H_2O = 4HCl + 2CO_2.$$

Boiling with an aqueous solution of sodium hydroxide for half an hour decomposes it completely. It reacts with methyl alcohol in the cold to give trichlormethyl methoxyformate,

$$ClCO_2CCl_3 + CH_3OH = CH_3OCO_2CCl_3 + HCl.$$

This reaction evolves heat and at higher temperature we get the further reaction,

$$CH_3OCO_2CCl_3 = CH_3OCOCl + COCl_2.$$

If there is an excess of methyl alcohol, the methyl chlorformate is formed,

$$CH_3OCO_2CCl_3 + CH_3OH = 2ClCO_2CH_3 + HCl.$$

Ammonia reacts rapidly with superpalite vapor, forming ammonium chloride and urea,

$$ClCO_2CCl_3 + 8NH_3 = 2CO(NH_2)_2 + 4NH_4Cl.$$

Aniline reacts to form carbanilid, which is insoluble in water,

$$ClCO_2CCl_3 + 4C_6H_5NH_2 = 2CO(NHC_6H_5)_2 + 4HCl,$$

and the carbanilid may react with more superpalite according to the equation,

$$2CO(NHC_6H_5)_2 + ClCO_2CCl_3 = 2(CONC_6H_5)_2 + 4HCl.$$

This compound breaks down into carbanil, C_6H_5NCO.

Superpalite does not react directly with benzene but forms triphenyl carbinol chloride in presence of aluminum chloride,

$$ClCO_2CCl_3 + 3C_6H_6 = (C_6H_5)_3CCl + 3HCl + CO_2.$$

When silver or sodium nitrite is treated with superpalite, phosgene, NO_2, NO, CO_2 and the chlorides of the metal are obtained.

The catalytic decompositions of superpalite are extremely interesting (Hentschel, Neher). Alumina decomposes it to carbon dioxide and carbon tetrachloride while iron oxide splits it into phosgene. The corresponding chlorides have the same effect but to a lesser degree. Iron oxide appears to decompose the superpalite more rapidly than does alumina. We have found that purified charcoal behaves like iron but is even more active. Vanadium oxide causes a slow decomposition, while uranium oxide causes a more rapid decomposition than does ferric oxide. The decomposition products have not been determined in the case of the vanadium and uranium oxides.

Due to the action of superpalite on most of the common materials used in the laboratory, it has been found difficult to construct apparatus which will withstand its action and that of the intermediate products. Rubber is strongly attacked and the filler used in manufacturing the common rubber articles is believed to decompose the superpalite. Cork will not stand up against chlorine and the intermediates; it becomes swollen and weak but has no decomposing action on the product, so far as we know.

Marshall and Satler recommended analyzing a mixture of air and superpalite vapor by absorbing the superpalite in a three percent alcoholic potash solution. It is reported from France that alcoholic sodium hydroxide may cause some loss of chlorine as carbon tetrachloride. Apmann and Wilson have absorbed the superpalite-air mixture in a N/10 $AgNO_3$ solution diluted to twice its volume with alcohol. Winkelmann decomposes superpalite with sodium peroxide. When working with the liquid and not with an air mixture, heating with aqueous caustic soda on a steam bath for thirty minutes is satisfactory.

In the canister superpalite is decomposed to phosgene by the charcoal and the phosgene is then converted into hydrochloric acid and carbon dioxide. The soda-lime also decomposes superpalite.

It was hoped that it might be possible to reverse the decompositions and to synthesize superpalite either from phosgene or from carbon dioxide and carbon tetrachloride by means of alumina or iron oxide; but we were not successful in this. Although it is possible to oxidize carbon tetrachloride to phosgene by means of carbon dioxide, there is no experimental evidence that superpalite is an intermediate stage in this reaction. Curiously enough, it is quite a simple matter to convert thiophosgene into the corresponding thiosuperpalite and we do not know why a similar reaction does not take place with phosgene. The only two obvious differences are that thiosuperpalite is a yellow liquid at ordinary temperature and phosgene is a practically colorless gas. By using ultra-violet light instead of sunlight, it was hoped to work with rays which are absorbed by phosgene, and by cooling to zero, to cause the ultra-violet rays to act on the liquid. It seems certain that this reaction must take place under some conditions; but we had not found them at the time of the armistice.

Certain preliminary results were obtained with iron oxide which are very interesting scientifically if they are confirmed. There is no evidence that iron oxide causes any measurable conversion of phosgene into superpalite. On the other hand, when liquid superpalite and iron oxide were placed in a sealed tube, the decomposition of the superpalite apparently did not run to a finish at constant temperature. There was a marked decomposition at first, which soon came to an apparent stop. This did not represent a true equilibrium for the decomposition went further if the temperature were raised a few degrees and did not go back again when the temperature was lowered. This experiment extended over quite a period of time and has not been checked. If it can be repeated, the only possible explanation that one can see is that the decomposition product, phosgene, is adsorbed strongly by the iron oxide and poisons the latter. Raising the temperature displaces some of the phosgene and lets some of the superpalite come in contact with the catalyzer.

This experiment is interesting because of its possible bearing on the Green Cross shell. The ratio of phosgene to superpalite in these shell varies rather remarkably. While, it is possible that the Germans were trying all sorts of fillings this does not seem very probable. It is quite conceivable that they added no phosgene at all or that they added some definite percentage, and that the variations are due to catalytic decomposition of the superpalite by the steel shell under temperature conditions. If this guess should prove to be true, there comes up the other interesting question whether chlorpicrin and diphenylchlorarsine poison the catalytic action of iron oxide on superpalite.

Since charcoal accelerates the chlorination of carbon monoxide to phosgene, it was thought that it might be a good chlorine carrier with methyl chlorformate While chlorination takes place, no appreciable amount of superpalite can be obtained because this substance is decomposed into phosgene by charcoal. When redistilled superpalite is added to Dorsey charcoal which had been purified by treatment with phosgene, there was a marked evolution of phosgene, and superpalite was lost. To make certain that this was not due to phosgene adsorbed in the pores of the carbon carrying off superpalite when the latter displaced the former, a sample of treated charcoal was heated to redness, allowed to cool in the absence of phosgene, and finally added to a flask containing superpalite. Decomposition took place immediately and phosgene was evolved until the flask was dry. A very rapid decomposition takes place also when superpalite is in contact with ordinary Dorsey charcoal which has not had the phosgene treatment.

In order to determine whether the decomposition of the superpalite was due to the charcoal or to some impurity in the charcoal, two samples of pure sugar charcoal were prepared by different methods. One sample was made by direct heating and charring, precautions being taken to prevent the introduction of foreign substances. This charcoal was found to decompose superpalite, though much more slowly than the Dorsey charcoal. The second sample of charcoal was made by treating white granulated sugar with a small amount of water and then adding concentrated sulphuric acid. The resulting mass was broken up and washed twelve times by decantation with distilled water. The water was then filtered off and the charcoal dried at 110° for a day. This charcoal also decomposed superpalite slowly. It is believed that the decomposition is due to the charcoal and that the power to adsorb phosgene plays an important part in determining the rate at which the liquid is decomposed. Sugar charcoal does not adsorb phosgene well and decomposes superpalite slowly, while Dorsey charcoal is a good adsorbent of phosgene and causes a very rapid decomposition of superpalite.

When methyl chlorformate was chlorinated in presence of powdered charcoal, the volume of the liquid decreased very much. It is believed that superpalite was formed but was decomposed to phosgene by the charcoal and passed off with the hydrochloric acid. The following data were obtained, using redistilled methyl chlorformate and completely dried and fresh Dorsey charcoal. The temperature was kept at 65° for 18 hours and then held at 100° for 6 hours more.

Initial volume, 650 cc
Final volume, 315 cc

B. Pt. of fraction	Vol.	Refractive index	Density
72°-105°	85 cc	1.4030	1.324
105°-112°	45 cc	1.4172	1.393
112°-122°	40 cc	1.4185	1.392
122°-135°	55 cc	1.4178	1.378
135°-175°	70 cc	1.4272	1.404
175°-180°	20 cc	1.4400	1.468
	(Superpalite	1.4533	1.6525)

When carbon tetrachloride is added to superpalite, the rate of decomposition by charcoal is decreased very much. A quantitative set of experiments was made to determine the relative rates of decomposition with different concentrations of carbon tetrachloride and superpalite. Up to 15 percent superpalite there is practically no decomposition; but from this point the rate of decomposition increases practically linearly with the percentage concentration, reaching a value of three grams per minute for the first ten minutes when 50 cc of pure superpalite was added to 9.5 grams of purified Dorsey charcoal. This experiment should be repeated in a sealed tube to see whether the charcoal is posioned in case phosgene is not allowed to escape.

Experiments were also made to see whether ultra-violet light decomposes superpalite. A quartz flask containing about 200 grams of superpalite was placed as close to the ultra-violet light of a R. U. V. lamp as was practicable. At the end of three days, where was a loss in the weight of 2.7 grams, which might very easily be accounted for by evaporation due to the heating action. The liquid, however, became somewhat yellow, probably due to a small amount of phosgene being formed which was then decomposed by the ultra-violet light into carbon monoxide and chlorine, this latter causing the yellow color. It is evident that ultra-violet light produces but a slight decomposition of superpalite, if any.

Sulphur chloride, phosphorus pentachloride, and selenium tetrachloride were tried as catalytic agents for the chlorination of methyl chlorformate, but without success. A special form of porous silica has been made by Prof. Patrick, of Johns Hopkins University; but it contains traces of iron and alumina, and consequently could not be used.

It is necessary to use a chlorinating agent which will not decompose the superpalite when formed or which will not decompose it rapidly. So far, light is the only catalyst available. Several chlorinations of the methyl chlorformate were made, using ultra-violet light. The chlorine was absorbed as fast as it could be added, the reaction evolving enough heat to keep the liquid at about 70°. It was found that if one added chlorine at a good fast rate until the liquid—fourteen inches from the lamp—absorbed no more chlorine, a yield of about 60 percent monochlormethyl chlorformate was obtained. To increase the chlorine content required a higher temperature and was a much slower process. It was proposed to make a quantitative run in order to find out the rates at which chlorine was taken up as the process was continued to superpalite. A preliminary run was made to determine the length of time required to produce superpalite. A quartz flask of about 200 cc capacity containing 100 cc of methyl chloroformate was clamped as close to the ultra-violet lamp as possible. Chlorine was bubbled through the formate at a rate of a liter a minute and the liquid was chlorinated completely in about three hours, a much shorter time than had been expected. This showed that variations in condition affected the rate of chlorination very much. It therefore seemed useless to make careful quantitative runs to determine the rates of chlorination because the results would hold good only for the particular conditions of each run and would tell nothing of general value. It was thought that the time could be used to better advantage by developing the best possible conditions.

An attempt was made to utilize all the available light from the lamp. Three concentric pyrex glass coils were made which surrounded the quartz ultra-violet lamp. A mixture of chlorine gas and methyl chlorformate vapor was passed through the outer coil, into the middle one, and lastly into the innermost coil and out through a condenser. The first part of the chlorination is very easy and requires but little light. The outer coil being in the shade of the other two, receives only a small amount of light. As the chlorination proceeds, the gases are carried in nearer the lamp, the intensity of light and the temperature both rising. The gases and vapors coming from the coils were cooled in a special condensing apparatus. Under usual running conditions the lamp gave off entirely too much heat, causing a rapid decomposition of superpalite. It was found that the temperature could be controlled very well by blowing air over the coil; but this decreased the efficiency of the lamp very much. The degree of chlorination could be controlled by varying the rate at which the gases were passed through the coil. From several runs a product was obtained containing approximately 90 percent of the dichlormethyl chlorformate. By decreasing the rate of flow, superpalite was readily obtained. It was planned to determine the best conditions of rate of flow, temperature, and concentrations; but the work was brought to a close before this could be carried out. It was found that the chlorination was more rapid in the liquid than in the vapor phase and an apparatus was therefore designed, based on the principle of the Vanier absorption bottle. The device was a success so far as the physics of it was concerned and there was every indication that it would make a rapid chlorination; but work was stopped before this could be tried out thoroughly.

Before discussing the stages in the chlorination it will be desirable to consider the behavior of the side-product, dimethyl carbonate. The carbonate was prepared by refluxing methylchlorformate and methyl alcohol for two days. When chlorine was bubbled through a mixture of dimethyl carbonate and charcoal at 60°, a product was formed boiling at 138°. There is reason to believe that this is monochlordimethyl carbonate. On chlorinating the carbonate in the presence of phosphorus pentachloride and charcoal, a product was formed, 60 percent of which boiled at 173°-178°. This is believed to be dichlordimethyl carbonate. When steel turnings were used in an attempt to chlorinate the dichlordimethyl carbonate, a decomposition took place into phosgene and formaldehyde. It is believed that the anhydrous ferric chloride is the catalytic agent, because steel does not cause this decomposition nor does crystalline ferric chloride. This particular decomposition is not exceptional, because the product called palite, boiling 105°-112°, which is chiefly monochlormethyl chlorformate decomposes on long standing into phosgene and formaldehyde. Under the influence of light dimethyl carbonate can be chlorinated to perchlordimethyl carbonate. If this hexachlordimethyl carbonate is distilled in an apparatus using a long distilling column, there is a marked decomposition into superpalite and phosgene, according to the equation,

$$(CCl_3)_2CO_3 = ClCO_2CCl_3 + COCl_2.$$

If perchlordimethyl carbonate is refluxed, the same decomposition to superpalite and phosgene takes place; but the rate of decomposition decreases rapidly as the concentration of superpalite increases. No experiments were carried out to determine whether it would be possible to free superpalite completely from the hexachlordimethyl carbonate by sufficiently prolonged boiling. A mixture of powdered charcoal and powdered perchlordimethyl carbonate showed no signs of decomposition at ordinary temperatures. When heated to the melting point of the carbonate, decomposition to phosgene took place rapidly; but it is hard to say whether the charcoal was decomposing the carbonate or whether under these conditions the carbonate was breaking down into phosgene and superpalite, which latter was decomposing in contact with the charcoal.

The available evidence is that methyl chlorformate is first chlorinated to the monochlormethyl chlorformate or so-called palite, boiling at 107°. The next substitution gives dichlormethyl chlorformate, sometimes called dipalite. This product boils at 114°. The last step gives the trichlor compound or superpalite, boiling at 128°. Since the crude methylchlorformate always contains dimethyl carbonate, we get small amounts of what is believed to be monochlordimethyl carbonate boiling at 138°, and appreciable amounts both of the dichlordimethyl carbonate, boiling at 180°, and of the perchlordimethyl carbonate, a volatile solid melting at 78°.

A series of vapor densities were made with some of these products so as to determine the approximate molecular weights. Runs were first made with a couple of known compounds. The following results were obtained:

Substance	Temp. of jacket	Molecular weight	
		Found	Calculated
Toluene	142°	94.0	92.0
Methylchlorformate	142	93.9	94.5
Superpalite	142	198.3	198.0
H-107	142	135.0	129.0
H-114	142	166.0	163.5
H-180 (boiling at 175°)	210	177.0	159.0
H-180 (boiling at 178°)	210	173-183	159.0
R-178	210	170-176	159.0

H-107 is the so-called palite and is believed to be monochlormethyl chlorformate. Efforts were made to get a sample boiling accurately at 107°; but it is apparently very difficult to eliminate completely the product boiling at 114°. H-114 is apparently the dichlormethyl chlorformate. H-180 is a product boiling at about 178° and which Hentschel believed to have the formula $C_8H_9O_8Cl_7$. It is our belief that this is dichlordimethyl carbonate. It is never made in large quantities, but seems to be more plentiful when one chlorinates a less pure methyl chlorformate. When dimethyl carbonate is chlorinated in presence of PCl_5 and charcoal a product is obtained which has identical properties, the densities and refractive indices checking as well as the vapor densities. This product is entered in the table as R-178 and was first made by Private Rosenblatt. The value for the molecular weight is too high and a chlorine analysis showed 46.8 percent chlorine instead of the theoretical 44.6 percent. It seems probable therefore that the product is dichlordimethyl carbonate containing about 9 percent of the hexachlorcarbonate as impurity. No molecular weight determinations were made on the product boiling about 138°; but it is a chlorinated compound obtained from dimethyl carbonate and must apparently be the monochlor substitution product.

Hentschel[1] considers that the chlorination product of

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[1] Jour. prakt. Chem., [2] 36, 99, 209, 305, 468 (1887).

methyl chlorformate is a liquid boiling at 180°, having the composition $C_8H_9Cl_7O_8$, which is formed by the reaction

$$4ClCO_2CH_3 + 3Cl_2 = C_8H_9Cl_7O_8 - 3HCl.$$

Our work has shown that this is the dichlordimethyl carbonate and that it is not a substitution product of methyl chlorformate at all. He found a molecular weight of 183.5 for his compound, which corresponds fairly well with the highest figure observed by us and does not correspond at all with Hentschel's formula; but Hentschel assumes decomposition in the vapor.

According to Hentschel the second stage in the chlorination is a liquid boiling at 108°–109°, having the composition $C_4H_3Cl_5O_4$, and formed according to the equation,

$$2ClCO_2CH_3 + 3Cl_2 = 2C_4H_3Cl_5O_4 + HCl.$$

This is really the first stage in the chlorination and is impure monochlormethyl chlorformate, $ClCO_2CH_2Cl$, boiling at about 107°. Hentschel obtained a molecular weight of 137 instead of the 302.5 required by his formula and the 129 required for pure monochlormethyl chlorformate.

The general conclusions of this paper are:

1. Superpalite is decomposed by charcoal and by iron oxide into phosgene. When working in a sealed tube at constant temperature, the reaction apparently comes to a standstill at almost any desired point in presence of iron oxide.

2. Superpalite is decomposed by alumina into carbon tetrachloride and carbon dioxide.

3. Perchlordimethyl carbonate breaks up, when heated, into superpalite and phosgene.

4. When methyl chlorformate is chlorinated in light at suitable temperatures, the products are monochlormethyl chlorformate, boiling at 107°; dichlormethyl chlorformate, boiling at 114°; and trichlormethyl chlorformate, boiling at 128°.

5. When dimethyl carbonate is chlorinated, the successive products appear to be monochlordimethyl carbonate, boiling at 138°; dichlordimethyl carbonate, boiling at 178°; and hexachlordimethyl carbonate, melting at 78°.

6. It has not been possible to synthesize superpalite directly from phosgene or from carbon dioxide and carbon tetrachloride.

7. An ultra-violet lamp was used in the experiments described in this paper. Professor Neher obtained good results at Princeton with a "White Flame" cored arc, and Captain Uhlinger used a nitrogen-filled incandescent lamp with success. There are no data as to the relative efficiencies of the three forms of light. Since chlorine has an absorption band in the blue and also bands in the ultra-violet, chlorination may be accelerated both by blue light and by ultraviolet light.

This work was begun when the Catalytic Laboratory was under the Bureau of Mines and was continued after the transfer to the War Department. It has been carried on under the general supervision of W. D. Bancroft, W. L. Argo and H. B. Weiser.

NEW BOOKS

Colloids in Biology and Medicine. *By H. Bechhold. Translated by J. G. M. Bullowa. 24 × 16 cm; pp. xiv + 464. New York: D. Van Nostrand Co., 1919. Price: $5.00.*—It is a great pleasure to welcome an English translation of this excellent book. This volume will increase the interest in colloid chemistry and help develop this important and much-neglected subdivision of chemistry.

The German edition has already been reviewed, but it will do no harm to call attention again to some of the interesting features of the book. The translator has added a number of comments here and there and thus has got in a reference, p. 36, to the incompatible views of Fischer and of Clowes on the subject of emulsions. There are a number of references throughout the book to the fact that gelatine is peptized more readily in aqueous alcohol than in water. This surprising observation should be checked carefully and an explanation for the phenomenon should be found.

Any discussion of swelling should take the following paragraph into account, p. 137: "If agar has been allowed to swell in cold water for a long time, it immediately becomes a homogeneous solution on warming. If solid agar is heated in water, we get a lumpy suspension of agar in water, which only very gradually becomes a homogeneous sol. It is evidently necessary for each particle of agar to have the amount of water necessary for solution in close proximity before it is warmed; otherwise the swelling will occur but slowly from the outside, where there is an excess of water, and proceed inward, since the peripheral particles of agar hold the water until they are dissolved. Indeed the phenomenon is one which depends on the size of the surface; the large mass with relatively small surface dissolves more slowly than the same mass divided so as to have a relatively increased surface."

On p. 174 it is stated that raw milk gives an ultrafiltrate much richer in lime than does boiled milk. When milk is boiled the calcium is bound to the milk colloid and remains with the latter on the ultrafilter. Thus a simple means is furnished for distinguishing raw from cooked milk.

While colloidal iron, albumin, silicic acid and humic acid have no effect on alcoholic fermentation, this is greatly accelerated by the presence of peat, filter paper, blood charcoal, and garden earth, p. 181. Söhngen showed that the carbonic acid which is developed during alcoholic fermentation impedes fermentation. All substances which favor the disappearance of the carbonic acid favor fermentation. The substances mentioned are believed to act purely mechanically. In the fermentation industry it is known that brewers grains and spun glass increase alcoholic fermentation.

If a rennet solution be shaken violently, p. 189, most of the rennet goes into the foam and coagulates there, the solution thereby suffering a great decrease in its power to coagulate milk. The hemolytic complement of guinea-pig serum is also inactivated by shaking at 37°. Reactivation, in other words the reversibility of the process, depends on the duration of the shaking.

Bechhold considers, p. 197, that there are two stages in the reactions between toxins and antitoxins. The two colloids, toxin and antitoxin, or bacterium and agglutinin, unite in accordance with the laws governing other colloids, and the specific substances react on one another. In the second stage the colloidal product of the reaction shows physical properties which distinguish it from the reacting substance. This does not seem to be a good point. There are plenty of cases where two colloids behave differently from either alone. While toxins and antitoxins may belong in a special class, there is no proof of this. The specificity of adsorption is very marked even when dealing with other substances. Thus boneblack adsorbs both diphtheria toxin and antitoxin strongly while wood charcoal, diatomaceous earth, talc, kaolin, and clay adsorb neither, though kaolin and clay adsorb tetanolysin and boneblack does not adsorb the antitoxin of tetanolysin. Serum albumin may prevent the adsorption of diphtheria toxin and antitoxin by boneblack. It is interesting to note, p. 238, that the loss of water by transpiration from large trees may vary from over 400 kilos on a very hot day to only a few on rainy days. Bechhold believes that the "living cells of plants assist in the elevation of the sap by their respiration. With respiration not only does CO_2 develop but also great quantities of organic acids. Both cause a swelling or attraction of water, which is liberated to the extent that CO_2 disappears, and the other acids are removed in any one of the many possible ways. This would fit in with the fact that the breathing in fully developed leaves and branches, in which the need for water is diminished, is less than in the developing shoots. The dead leaf, whose breathing has ceased, withers." This is interesting, but it raises more questions than it answers because we now need a definition of a living cell and we need to know what has happened to a leaf when it dies.

A possible suggestion is given on p. 246, where it is stated that the change into the colloidal condition is usually associated with a metamorphosis into a substance native to the body from which the cells and tissues of the organism are built up. It may be concluded from the investigations of Alexis Carrel and Burrows that the circulating nutritive fluid already contains all the elements required for the most varied organs. These investigators suspended pieces of tissue from freshly killed mammals in drops of plasma from the same kind of animal. The tissues continued to grow, cartilage produced cartilage, a spleen produced cells which resembled spleen pulp, and pieces of kidney grew tubes of cells which resembled the kidney tubules.

One of the most interesting of colloid-chemical problems according to Bechhold is the formation of bone, p. 268. "From an aqueous solution containing blood salts, calcium carbonate and calcium phosphate precipitate. The precipitation is hindered by the presence of the blood colloids, though two-thirds of the Ca salts, at least in the serum of the higher animals, occur in the crystalloid state. This interference must stop during the formation of bone. To account for this there are several theoretical possibilities: it may be assumed that changes in the serum colloids are brought about at or from the bone cells, which remove their protective action and result in the precipitation of the calcium salts. This agrees with the views of Pauli and Samec. It was shown in their researches that the increase in the solubility of calcium carbonate by serum albumin was 475 percent, and of calcium phosphate 90 percent. We would consequently expect to find a very much more extensive precipitation of calcium carbonate than of calcium phosphate when the protective action was removed.

But in the case of bones, the proportions are just the reverse. The bone ash of man contains about 850 parts $Ca_3(PO_4)_2$ and 90 parts $CaCO_3$ per 1000.

"But in the case of a cleavage product of albumin, Pauli and Samec found that the solvent action upon calcium salts was the reverse. Witt's peptone, consisting almost entirely of albumoses, holds in solution only the calcium carbonate, whereas the calcium phosphate exhibits a diminution in solubility. Based on these results, ossification might occur in the following way: In the bone or cartilage cells, there occurs a concentration of colloids in which a large quantity of calcium salts are piled up. When these tissue colloids are broken down a precipitation occurs, the precipitate consisting chiefly of calcium phosphate with smaller amounts of calcium carbonate. This corresponds with the histological evidence, by means of which a tissue destruction may be seen to accompany ossification.

"A further possibility, which does not in the least contradict the above explanation but possibly coincides with it, is that phosphates are set free and come into contact with the carbonates always present when the tissues, especially the cell nuclei, break down. In accordance with well-known physico-chemical laws, an increase in the concentration of an ion (in this case the phosphate ion) results in an increase in the calcium phosphate molecules, and this changed albumin must, accordingly, favor the precipitation of calcium phosphate."

On p. 363 there is an interesting paragraph on the effect of adsorbents in protecting against poisons. "In 1830 the apothecary Thouery, experimenting on himself, took without harm one gram of strychnine (ten times the fatal dose) with fifteen grams of charcoal. The use of charcoal as an antidote against poisoning, though neglected in practice, has been mentioned in several textbooks. Only freshly precipitated iron hydroxide is in general use as an antidote for arsenic poisoning, thanks to the authority of Bunsen. From the earliest times, greater usefulness has been accorded to such hydrophile colloids as gruel (against aloes, cantharides, colchicum, croton oil), milk or white of eggs against mercury weed, glue solution against alum. Scientifically exact study of the adsorptive action of suspensions on poisons was undertaken only in recent years. Mechowski, Adler, Zunz, and Lichtwitz have contributed valuable researches on the adsorption of poisons (phenol, strychnine and various poisons, arachnolysin) by animal charcoal which proved to be in some ways equivalent to kaolin (*bolus alba*), silicic acid, chalk, diatomaceous earth and bismuth subnitrate. In practical toxicology the results did not meet expectations. Consequently, as a matter of course, colloidal carbon was tested. Sabbatani actually inhibited the toxic action of strychnine intravenously, by injecting simultaneously six times the quantity of colloidal carbon."

Somebody ought to do some experiments with "synthetic active hemoglobin," negative ferric oxide mixed with serum, p. 385, because the present state of our knowledge in regard to the ordinary oxyhemoglobin is far from satisfactory.

The author points out, p. 314, that incomplete oxidation of the tissues resulting from insufficient oxygen leads to circulatory disturbance; that in obesity the oxidizing forces of the tissues are reduced so that the fat is no longer attacked; that it is in the obese especially that circulatory disturbances regularly appear.

Wilder D. Bancroft

Lectures on the Principles of Symmetry. *By F. M. Jaeger. 27 × 16 cm; pp. xii + 333. Amsterdam: Publishing Company Elsevier, 1917.*—The object of this book is to draw the attention of students of mathematics and natural philosophy in general to a principle of which the significance in the morphological description of objects, as well as in the definition of chemical and physical phenomena is gradually becoming more and more evident in every domain of research. After testing seriously the methods of argumentation hitherto elaborated, the writer has in many places finally adopted that of Schoenflies, chiefly because in his opinion it offers from a teaching standpoint, undeniable advantages over the often not less happy and concise ways of treating the problem employed by such authors as von Fedorow, Wulff, Viola, Barlow, Boldyiew, and others.

In the first chapter the author says: "In the mathematical outlining of nature, human science makes use of a number of fundamental notions and priciples which, commonly after a long period of error or opposition, have been generally accepted in the end. The method of mathematical physics with its classical mechanics, as well as its recent views on electromagnetics, are well-known illustrations of this. Such fundamental notions are at last adopted generally if they prove to be extremely effective in the further theoretical development and schematizing of natural phenomena. Among ideas of this kind playing an important rôle in modern science, the principle of symmetry may certainly be considered as one of the most remarkable and interesting.

The author of course discusses the principles involved in the different types of crystals, the results of the Braggs on X-ray spectra, and Pasteur's work on the optically active modifications. He goes much farther afield than this, discussing cubical and hexagonal piling, the symmetry of the pineapple and the sunflower, etc.

The symmetry of objects in animate and of non-living nature, p. 195, seems to be quite different. We have the occurence in living nature of axes of symmetry which are characterized by irrational values of the cosines of their periods α; and we have the much higher symmetry of the older species of animals in comparison with that of the living beings of later periods of evolution. In non-living nature there seems to be rather an oppositely directed tendency, a drift towards the highest degree of symmetry possible. The cases of apparent and mimetic symmetry serve to sustain this view: and also the fact that polymorphic substances generally change into higher symmetrical forms when temperature increases. Evolution in living nature seems to proceed in exactly the opposite direction, the lower animals showing in many cases a much higher symmetry than the mere bilateral one of the animals which have appeared in the later periods of the earth's history. A certain preference for pentagonal symmetry seems to exist in the case of animals and plants, a symmetry unknown in the world of inanimate matter.

While not easy reading, the book is an instructive one and contains a great deal that is of interest. It is quite different in conception and treatment from "Growth and Form" by D'Arcy W. Thompson.

Wilder D. Bancroft

THE ELECTROCHEMISTRY OF URANIUM AND THE SINGLE POTENTIALS OF SOME OXIDES[1] OF URANIUM

BY CHESTER A. PIERLÉ

I. INTRODUCTION

The element uranium although classed with chromium, molybdenum and tungsten in the periodic system is peculiar in that it resembles members of other groups of elements as well. Beyond the electrolytic analysis,[2] the conductivity of the aqueous solutions of its salts,[3] the effect of light on the potential of uranous uranyl solutions using platinum electrodes,[4] and[5] a similar investigation by Luther and Michie,[6] very little is found in the literature concerning the electrochemistry of uranium. McCoy and Bunzel[7] have used potential measurements for determining the rate of oxidation of uranous solutions.

In the paper here presented are contained accounts of experiments on the electrolysis of various uranium compounds. These experiments were made in order to ascertain the electrolytic behavior of different uranium compounds in aqueous solutions, non-aqueous solutions and in fusions. The hope at first was that a method of preparing uranium electrolytically might be found. While metallic uranium was not thus prepared in the pure state, quite a number of compounds of uranium were formed electrolytically. The conditions of the formation of these compounds have been detailed and their single potentials have been ascertained whenever a sufficient amount of pure material was formed in the experiment.

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[1] A portion of the thesis submitted to the graduate school of the University of Wisconsin in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

[2] Smith: Am. Chem. Jour., 1, 329 (1879).

[3] Dittrich: Zeit. phys. Chem., 29, 449 (1899).

[4] Baur: Zeit. phys. Chem., 63, 683 (1908)

[5] Titlestad: Zeit. phys. Chem., 72, 257 (1910).

[6] Zeit. Elektrochemie, 14, 826 (1908).

[7] Jour. Am. Chem. Soc., 31, 367 (1909).

The difficulties involved in the electrolysis of uranium compounds are many. The metal does not deposit as such from aqueous solutions of either uranyl or uranous salts but it is deposited as a poorly adhering oxide of variable composition, most probably in the form of the uranyl radicle UO_2 or its hydrates. Prepared in other ways, such as the reduction with metallic potassium[1] or metallic sodium,[2] by electrolysis of fused double sodium uranous chloride,[3] reduction in the electric furnace with carbon[4] and the reduction with aluminum,[5] the metal has never been obtained absolutely pure. It is a metal that burns at a low temperature (170°), reacts with cold water and combines with nitrogen, carbon, and oxygen so readily that its preparation in absolutely pure form is well-nigh impossible.

The uranous salt solutions are easily oxidized and for this reason an attempt to electrolyze a uranous solution always results in the formation of uranyl salts around the anode and a deposition of oxide on the cathode. It may also be possible that the reaction of the metal with water is the explanation of the deposit of the oxide at the cathode. Whatever the explanation may be, it has thus far been experimentally impossible to plate pure metallic uranium, especially from aqueous solutions.

Muthmann and Fraunberger[6] measured the single potential of metallic uranium against a normal solution of potassium chloride and reported a value of 0.19 volt. No analyses indicating the purity of the metal used are given. My own measurements with a sample containing 91.49 percent metallic uranium in normal potassium chloride solution gave a single potential of —0.099 volt which is substantially the same as that developed by the same sample of metal immersed in uranyl nitrate solutions containing 14.3 grams per liter.

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[1] Peligot: Ann. Chim. Phys., (3) 5, 1 (1842).

[2] Zimmermann: Liebig's Ann., 216, 14 (1882).

[3] Moissan: Comptes rendus, 122, 1088 (1896).

[4] Moissan: Comptes rendus, 116, 369 (1893).

[5] Aloy: Bull. Soc. chim. Paris, (3) 25, 153 (1901).

[6] Akad. Wiss. München, 34, 201 (1904).

It is possible that Muthmann and Fraunberger attach a different meaning to the ± sign before the figure which they give. On the other hand the uranium they had was undoubtedly of a different state of purity as my own which was contaminated with ferric oxide. Neither result can of course be considered as final since the metal used was not pure.

II. EXPERIMENTAL

Note—In all the electrolytic experiments the potential impressed is given in volts and the current density is stated in amperes per square decimeter.

1. Pyridine as a Solvent for Uranyl Salts

Tests upon the solubility of uranyl nitrate, chloride, acetate, sulphate and oxalate were made by treating small portions of the different salts with pyridine. Uranyl nitrate was found to be the most easily dissolved though uranyl chloride and acetate are also appreciably soluble. They are more soluble in cold pyridine than in hot. When heated in a water bath at the boiling temperature, a flocculent yellow precipitate was thrown down in each case. Uranyl sulphate and uranyl oxalate were only slightly soluble in pyridine. The yellow precipitates thrown down on heating the solutions were not dissolved when the solution cooled and could not be brought into solution again in the pyridine.

2. Electrolysis of Uranyl Salts in Pyridine Solution

Many electrolytes are known to yield conducting solutions when dissolved in pyridine and metals have been deposited electrolytically from such solutions,[1] which could not be deposited from aqueous solutions. A saturated solution of uranyl nitrate in pyridine was tried in hopes that metallic uranium might be deposited from this solution electrolytically. The uranyl nitrate used was Merck's "highest purity," while the pyridine used was Baker's pure pyridine. In the preliminary trials the pyridine was not anhydrous. The solution was not a very good conductor. A pressure of 14 volts was

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[1] Jour. Phys. Chem., 3, 602 (1899).

required to give any perceptible reading on the milliammeter used. When the voltage was increased to 30 a current density of 0.31 amp. was obtained. The solution became very dark due to the carbonization of the pyridine. After allowing the current to run for three hours the cathode was covered unevenly with a black deposit. The side facing the anode naturally was covered thicker than the other. The excess of pyridine was washed from the deposit with petroleum ether and after drying in the air examined for uranium. The deposit resembled carbon but on dissolving the black material in nitric acid it gave a straw colored solution which when tested qualitatively, showed that uranium was present in considerable quantity.

A fresh solution of uranyl nitrate in pyridine was prepared and electrolyzed with a voltage of 30 and current density of 0.311 amp. In this trial the anode was surrounded by a muslin bag acting as a diaphragm. This arrangement did not prevent the blackening of the pyridine. After three hours the cathode was removed and examined. A black deposit was spread unevenly over the cathode and had a striated appearance. It was washed with gasoline and then allowed to dry in the air. When dry it had a reddish color like partially oxidized copper and was loosely adherent. An attempt was made to measure the single potential of the plated material against a uranyl nitrate solution but as soon as the electrode was dipped into the electrolyte a portion of the coat fell off exposing platinum so that a reliable measurement was not obtained. Diaphragms of other materials were tried including a Schleicher and Schull extraction thimble, a bag made of filter paper and also a bag made of bolting cloth but nothing was found that would prevent the spread of the carbon formed around the anode so that the product on the cathode would not be contaminated. A smoother adhering deposit was obtained by revolving the beaker during electrolyzing but no clear metallic deposit could be obtained nor was the deposit large enough to analyze. The pyridine also charred when uranyl acetate and uranyl chlorides were used as electrolytes, a positive proof that the nitrate radicle UO_3 was not responsible for the charring of the pyridine. Although uranyl sulphate and uranyl oxalate were both slightly soluble in pyridine neither prevented the charring of the solution when electrolyzed. The anode in both cases became very dark brown but no uranium deposit could be found on the cathode. The voltage used was 100 in each case. The current was not recorded in this case because of a faulty ammeter.

No satisfactory deposit of uranium can be obtained from the solutions of the uranyl salts in pyridine because of (1) the charring of the solvent, (2) the failure of the uranyl radicle to reduce, and (3) the contamination of the deposit by the charred pyridine.

3. Electrolysis of an Ether Solution of Uranyl Nitrate

One gram of uranyl nitrate containing its water of crystallization was dissolved in fifty cubic centimeters of anhydrous ether and placed in a closed cell connected with a reflux condenser. It was electrolyzed under a pressure of 100 volts and gave a current density of 0.12 amp. at the beginning. The side of the cathode facing the anode became covered with a silvery white deposit. After electrolyzing for 6 hours the cathode was removed and the deposit washed with fresh ether. It dried quickly in the air leaving a deposit, white in appearance but slightly tinged with yellow. This deposit did not adhere well to the electrode and was easily brushed off with the finger. It could not be washed off with water but was readily removed with nitric acid. The nitric acid solution gave a qualitative test for uranium.

Further tests made in the same solution under similar conditions and also made with a rotating cathode gave in each case deposits silvery white in appearance at first but when allowed to stand in a calcium chloride desiccator for a while they became yellow. Freshly dissolved uranyl nitrate containing its water of crystallization always conducted better at first. After running for a short time the current gradually fell off finally becoming practically zero. The conductivity of the ether solution, therefore, appears to be a function of the amount of water present. After the electrolysis has decomposed the water present, the conductivity practically ceases. Solutions made with ether that was not anhydrous were better conducting media than when anhydrous ether was used but eventually they behaved in the same way. Because of the poor conductivity of ether solutions the use of ether as a solvent was abandoned. The nature of the deposit formed was not ascertained. It could only be obtained in small quantities insufficient for analysis.

4. Electrolysis of Ethyl Acetate Solution of Uranyl Nitrate

A solution of uranyl nitrate in ethyl acetate was prepared. No attempt was made to get perfectly anhydrous material for the uranyl nitrate carried water of crystallization. The solution contained 1 gram of uranyl nitrate in 50 cc. It was electrolyzed with a voltage of 95 and at this pressure gave a poorly conducting solution. The current density was 0.2 amp. A deposit began to form on the side of the cathode facing the anode immediately but the opposite side remained clear. The beaker was rotated throughout the run but an even deposit was not obtained. The cathode was removed after two hours, washed with fresh ethyl acetate and dried in a desiccator over calcium chloride. The deposit was dark when first dried but became yellow while standing over night in the desiccator. The weight of the deposit was only 30 milligrams. It was removed from the electrode by 1 drop of concentrated nitric acid and washed back into the solution with ethyl acetate. The addition of the 1 drop of nitric acid increased the conductivity of the solution. The latter was electrolyzed with a voltage of 50, and a current density of 0.21 amp. A flocculent yellow deposit collected around the cathode but did not adhere. It sloughed off at once and piled up under the cathode when stationary. This deposit was not analyzed but to all appearances was the yellow oxide of uranium UO_3. No trace of uranium could be found on the cathode when removed and washed with fresh ethyl acetate.

Another trial with a freshly prepared solution of uranyl nitrate in ethyl acetate containing no free nitric acid was made. The voltage used was 40 and the current density 0.100 amp. The electrolysis was made without rotation of the solution and was allowed to continue for 12 hours. A yellow deposit was formed on the side of the cathode facing the anode but the other side remained clear. The deposit was spongy and poorly adherent, a part falling off during the electrolysis. The deposit was washed with fresh ethyl acetate and allowed to stand in a calcium chloride desiccator over night. When dry, the deposit weighed only 4.7 milligrams and was easily brushed off. It appeared to be principally the yellow oxide of uranium mixed with a small bit of a black oxide.

Because of the poor conductivity of the solution and the small amount of deposit obtained no analysis of the product was made and no potential reading could be taken because the electrode was not covered entirely with deposit. The use of the ethyl acetate solution for electrolysis had to be abandoned.

5. Electrolysis of an Amyl Alcohol Solution of Uranyl Nitrate

A solution of uranyl nitrate in amyl alcohol was prepared. The solution contained 1 gram of crystallized uranyl nitrate in 50 cc of the alcohol. No attempt was made to prepare anhydrous alcohol because of the water contained in the uranyl nitrate. The solution was poorly conducting, giving a current density of 0.19 amp. under a pressure of 130 volts. A bronze-like deposit, very smooth, was formed on both sides of the cathode. The deposit was quite thin and iridescent. The potential of this deposit was taken with a solution of uranyl nitrate containing 12.3190 grams of anhydrous uranyl nitrate per liter. The single potential was found to be —0.2691 volt. Attempts to get a sufficient quantity of this bronze-like deposit for analysis were futile. In each case only a few milligrams were deposited after electrolyzing under the conditions mentioned above for periods of 12 hours and longer.

On adding 5 cc of water to the amyl alcohol solution, the conductivity increased. The solution became warm and a heavier deposit was obtained. The maximum current density reached under a pressure of 130 volts was 0.65 amp. The deposit formed under these conditions was black and poorly adherent. It was washed with ether and dried over calcium chloride to constant weight and analyzed for its uranium content. It contained 73.72 percent or uranium and gave a single potential against the uranyl nitrate solution of —0.483 volt.

Sample No. 2, deposited under conditions exactly as the above, gave on analysis 71.36 percent of uranium.

It is evident, that the electrolysis of uranyl nitrate in amyl alcohol solution does not give metallic uranium, and when water is present the composition of the deposit approaches that obtained from aqueous solutions.

6. Electrolysis of Double Potassium Uranyl Cyanide

Moissan[1] states that the cyanides of uranium have not been prepared. When a potassium cyanide solution is added to an aqueous solution of uranium tetrachloride, hydrated uranium oxide is precipitated with evolution of hydrocyanic acid gas. Aloy[2] prepared uranyl potassium cyanide by precipitating the uranium from uranyl nitrate with potassium cyanide and dissolving the precipitate first formed in an excess of potassium cyanide and then concentrating the solution.

To a solution of Merck's pure uranyl nitrate, potassium cyanide solution was added slowly. A canary-yellow, gelatinous precipitate formed at once and an odor of hydrocyanic acid was noticed. The precipitate was filtered off and washed with cold water to remove the potassium nitrate. The precipitate was removed from the filter and treated with an excess of potassium cyanide. Some of the precipitate would not dissolve in the potassium cyanide solution but was soluble in a solution of hydrocyanic acid.

The hydrocyanic acid was prepared by treating silver nitrate solution with potassium cyanide solution in the molecu-

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[1] Traité de Chimie Minerale, 4, 885.

[2] Ann. Chim. Phys., (7) 24, 412 (1901).

lar ratio required to just precipitate all the silver as silver cyanide. This was filtered off and washed with water until free from any slight excess of silver nitrate and then stirred up thoroughly, while kept ice cold, with hydrochloric acid keeping the hydrochloric acid just short of the amount needed to convert all of the silver cyanide to silver chloride. The filtered solution was free from silver and left no residue when evaporated. This solution was used to dissolve the precipitate that remained insoluble in the excess of potassium cyanide. It dissolved completely in the hydrocyanic acid solution. This portion insoluble in potassium cyanide but soluble in hydrocyanic acid was in all probability potassium uranate.

Electrolysis of the double potassium uranyl cyanide solution under a pressure of 4 volts and a current density of 0.62 amp. gave deposits of yellow uranic hydroxide in neutral solution and evolved cyanogen. The deposit sloughed off and settled to the bottom of the cell. The solution became alkaline toward phenolphthalein during the action due to the loss of the volatile acid.

Solutions made acid with hydrocyanic acid likewise evolved cyanogen and deposited yellow uranic oxide on the cathode. This deposit immediately sloughed off but dissolved again as long as there was free acid in the solution.

By the use of a roughened platinum electrode and a higher current density a better adhering product was obtained which was black and uniformly deposited on the cathode.

The weight of the deposit was 67 milligrams and was obtained by electrolyzing the acid solution for three hours under a pressure of 8 volts and a current density of 0.2 amp. The deposit when washed with alcohol and ether gave a single potential of —0.461 volt against the standard uranyl nitrate solution.

The deposition of metallic uranium does not take place in aqueous potassium uranyl cyanide solution either neutral or acid with hydrocyanic acid. With low current density the deposit is uranic oxide. Higher current density changes this to a black hydrated oxide. The composition of the deposit was not ascertained since it was only obtained in quantities too small for analysis.

7. Electrolysis of a Solution of Double Sodium Uranyl Oxalate.

The electrolysis was made with an aqueous solution of double sodium uranyl oxalate prepared by dissolving 5 grams of uranium oxalate (E. de Haen, labelled "chemically pure") in 75 cc of water and adding sodium oxalate (Squibb's "C. P. reagent") to the solution in the molecular proportion required to form the double salt. It was electrolyzed with a pressure of 5 volts and a current density of 1.55 amp. There was formed immediately a black deposit, poorly adherent, which sloughed off leaving the cathode exposed in spots. The usual yellow deposit that first forms on electrolyzing aqueous solutions of uranyl salts did not appear. The weight of the deposit after electrolyzing for three hours was 40 milligrams. The greater portion of the uranium had been precipitated during the electrolysis and remained undissolved in the solution.

From this almost depleted solution with a pressure of 7 volts and current density of 0.77 amp. a deposit was obtained which adhered well, was smooth in appearance and showed no trace of the yellow oxide. It weighed 30 milligrams and gave a single potential of —0.381 volt, against the standard solution of uranyl nitrate.

The same solution was made acid with oxalic acid and electrolyzed with a pressure of 10 volts and a current denisty of 7.75 amp. The solution became warm during the electrolysis. The evolution of gas from the cathode prevented the formation of a smooth deposit. After three hours the deposit formed weighed only 13 mg. No trustworthy single potential could be obtained of this material since the platinum was exposed in spots.

Plating from an aqueous solution of double uranyl sodium oxalate does not deposit metallic uranium. The deposit was not obtained in sufficient quantity for analysis, but its single potential was ascertained.

8. The Electrolysis of an Aqueous Solution of Double Potassium Uranyl Fluoride

Double potassium uranyl fluoride has been prepared by Baker[1] and also by Smithells[2] by precipitating the uranium from uranyl nitrate with potassium fluoride and also by the action of hydrofluoric acid on potassium uranate or by mixing potassium fluoride and uranyl fluoride in molecular proportions required for the formula $2KF.UO_2F_2$. The double salt of uranium tetrafluoride with potassium fluoride has not been prepared.

Attempts to prepare the latter salt were made by fusing uranium tetrafluoride with the required amount of potassium fluoride to give the salt $2KF.UF_4$ corresponding to the analogous double potassium uranium chloride. This was unsuccessful because uranium tetrafluoride is converted into an oxide with loss of fluoride on heating. The residue left was only partly soluble in water but completely dissolved in hydrofluoric acid. The yellow solution thus prepared was used for the electrolysis after evaporating to dryness to remove the excess hydrofluoric acid and redissolving in water.

It was electrolyzed in a hard rubber beaker under a pressure of 6 volts and a current density of 2.32 amp. for one hour. On removing the cathode and washing with water no deposit could be seen. The cathode was treated with concentrated nitric acid and the washings were tested for uranium with negative results. On heating the electrode the platinum first turned a yellow color and on stronger heating became green. The coat now dissolved in nitric acid and gave a splendid test for uranium.

A second experiment made with the same solution gave a deposit silvery white with just a tinge of blue-green. Its weight was uncertain because the glass stem of the electrode had been attached by hydrofluoric acid. The deposit was obtained by electrolyzing the solution for two and one-half hours with a voltage of 7 and a current density of 3.9 amp.

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[1] Jour. Chem. Soc., 35, 760 (1879).

[2] Ibid., 43, 125 (1883).

The single potential of the plated material was measured against the standard uranyl nitrate solution and gave —0.389 volt. Under the same conditions, the same general deposit could always be obtained and the deposits gave nearly the same potential as recorded.

The conditions were varied slightly and a different deposit was found. In this experiment under a voltage of 4 and a current density of 2.54 amp. a white deposit seems to form first but is covered with a black oxide. The deposition was carried on in the same solution as before, except that it had been acidified with hydrofluoric acid. With a higher voltage 8 volts, and a current density of 14 amp. a heavier deposit of the black oxide is formed. The deposit appeared silver white beneath a coat of black. A potential reading of this deposit against the standard solution of uranyl nitrate gave a single potential of —0.470 volt.

The results obtained by plating on the same electrode after running a potential are given in tabular form.

TABLE I

Volts	ND_{100} in amp.	Time	Weight of Deposit Gram	Color	Single potential
4	3.64	3 hrs.	0.0040	white under black	—0.472 volt
5	2.16	1.5 hrs.	0.0050	white	—0.471 volt
6	2.16	1 hr.	0.0058	black	—0.478 volt
7	2.16	1 hr.	0.0064	black	—0.479 volt
8–9	2.16	2 hr.	0.0080	black	—0.475 volt

The single potential shows that the same material was being deposited throughout. During the successive experiments a portion of the uranium oxyfluoride was reduced to uranous fluoride and this salt separated out during the electrolysis. By thus depleting the solution of its electrolyte it became necessary to increase the voltage to keep up approximately the same current density throughout. From the potential of the clear white and that of the blackened deposit it is evident that the two deposits are not the same. The potential of the blackened deposits agrees with those obtained from the nitrate solution in amyl alcohol and also the deposits from the double cyanide and oxalate, in aqueous solution.

Analysis of the Deposit from the Double Fluoride

A deposit, silver white in appearance, was obtained by electrolysis, of a solution of the double potassium uranyl fluoride solution with a pressure of 4 volts and a normal density of 0.485 amp. This was analyzed for its uranium content by heating the electrode until the white deposit had changed to a golden yellow oxide, after which the deposit was dissolved in nitric acid. The uranium was determined by precipitation from the uranyl nitrate solution with ammonia.

TABLE II

	Weight of deposit Gram	U_3O_8 found Gram	Wt. of uranium Gram	% U
Sample 1	0.0522	0.0374	0.0313	57.50
Sample 2	0.0494	0.0362	0.0303	61.45
Sample 3	0.1457	0.1014	0.0818	56.20

Sample 2 was not the clear, white deposit obtained before but showed contamination with the black oxide above mentioned. Sample 3, obtained from a fresh solution of the double salt was white. It was obtained with a voltage of 4 and a current density of 1.63 amp.

The similarity of the behavior of the white deposit, when heated, to the behavior of uranium tetrafluoride when it was heated, suggested that the deposit might be a fluoride of uranium. This was proven to be correct as the following analysis shows: Tests for fluorine were made by placing one of the electrodes in a large platinum dish, adding concentrated sulphuric acid and covering the dish with a glass plate coated with paraffin. The design drawn in the paraffine was not etched in any case though several tests were made in this way.

After failing to find fluorine in this manner an analysis for fluorine was made on a newly prepared deposit.

Method of Analysis

A mixture of sodium and potassium carbonates in such proportion as to give the lowest fusing mixture possible were brought to a quiet fusion in a platinum dish. The electrode with its deposit was then dipped into the fused mass and rotated until the electrode was coated with the fusion material. The temperature was then raised, and the heating continued until the electrode showed a smooth coat of the fused carbonates. The melt was taken up with water and carefully acidified with dilute nitric acid until just neutral or slightly basic. A large portion of the carbon dioxide was removed in this way. The slightly basic solution was then heated to boiling for a short time and allowed to cool. A slight excess of nitric acid was then added and the solution was again made alkaline with a slight excess of ammoia. On boiling the solution several minutes, the remaining carbon dioxide was driven off as ammonium carbonate. At the same time the uranium was precipitated as ammonium uranate. This was filtered off and the fluorine in the filtrate was then determined by precipitation from a neutral solution as calcium fluoride.

TABLE III

Data	Voltage	$N.D._{100}$	Wt. of deposit Gram	Wt. of U_3O_8 Gram	% U	Wt. of GaF_2 Gram	% F
Sample 1	3	1.63	0.2444	0.0880	57.70	0.0404	16.05
Sample 2	3	1.63	0.1076	0.0736	53.40	—	—

The varying results in the uranium content given in Tables II and III would indicate that the deposit was not always uniform. The fluorine result in Sample 2 was lost through breakage. The amount of fluorine found in Sample 1 is very close to the theoretical amount required to form UF_4 with the uranium present. Taking the difference between

100 and the percent of uranium and fluorine as water, the empirical formula for the deposit would be $UF_4.6H_2O$. The water was not determined quantitatively directly but its presence was proven qualitatively. The fluorine was proven to be present by testing the precipitate formed with calcium for fluorine.

The white deposit formed when an aqueous solution of potassium uranyl fluoride is electrolyzed, whether in neutral or acid solution, is insoluble uranous fluoride. The uranium is evidently deposited upon the cathode as UO_2 and immediately converted to the fluoride by the hydrofluoric acid present. No metallic uranium is obtained by the electrolysis of the double potassium uranyl fluoride.

The potential of the uranium fluoride deposit is —0.389 volt. Whenever the deposit was blackened, the potential found was the same as that of the black deposit obtained from aqueous solutions of uranyl nitrate and uranyl oxalate.

9. Electrolysis of Potassium Uranyl Fluoride in Ammoniacal Solution

It was found that ammonium hydroxide would not precipitate uranium from aqueous uranyl solutions in the presence of hydroxylamine. The deposition of uranium from alkaline solution was tried with no results. The deposits formed were the color of bronze with a fringe of green. A larger deposit could be obtained in a shorter time than was possible in acid solution and this deposit contained a larger percent of uranium. The composition of the deposit was not constant as shown by analysis.

TABLE IV

	Weight of deposit Gram	Weight of U_3O_8	Weight of uranium	% of uranium
Sample 1	0.3046	0.2237	0.1878	61.55
Sample 2	0.1975	0.1508	0.1264	64.50
Sample 3	0.1386	0.1142	0.0958	69.20

The deposits were obtained by electrolyzing the solution with a pressure of 4 volts and an average current density of 1.8 amp. Stationary electrodes were used and the container rotated. The single potentials of these deposits were not measured.

10. Electrolysis of Fused Potassium Sodium Uranate

A fused bath of potassium sodium uranate was prepared by fusing a mixture of potassium and sodium carbonate in a nickel crucible and adding the green uranium oxide to the melt. This dissolved in the carbonates with evolution of carbon dioxide and formed a molten mass. The first attempt was made with platinum electrodes. The fused material was electrolyzed under a pressure of 3 volts and a current density approximately 33 amp. The alkali metals, which separated out along with the uranium at the cathode, burned near the surface of the melt. The platinum was attacked by the burning alkalies and almost eaten through at the surface of the melt. The portion below the melt was not injured quite so much but became brittle and broke up when the electrode was removed. The electrode was washed first with cold water and finally with dilute acetic acid. The platinum that was below the surface of the melt was gray and would not clear up in treating with concentrated nitric acid. When heated on the lid of a platinum crucible the gray coat became green and could then be dissolved off with nitric acid. Qualitative test indicated that metallic uranium had actually been deposited on the platinum. The black powder that had washed off the electrode with water was uranium oxide.

Electrolysis of a similar bath with nickel electrodes gave a black powder around the cathode. This was insoluble in water and in acetic acid and was difficultly soluble in dilute nitric acid. From its behavior toward nitric acid, it appears to be powdered metallic uranium mixed with some black uranium oxide. The nickel electrode contained no deposit of uranium with which a potential reading could be taken nor was it possible to make an analysis of the small amount of the black powder obtained.

11. The Electrolysis of Uranyl Sulphate Solution

Bunsen[1] and also Carveth and Mott[2] were able to obtain metallic chromium by electrolyzing a chromous chloride or chromous sulphate solution with high current density. They used an unglazed porous cup as a diaphragm. Because of the strong analogy between chromium and uranium their method of procedure was tried.

Experiments were carried out in various ways. Different current densities were used in different temperatures varying from 0° to boiling. Strong acid solutions, weak acid solutions, neutral solutions, and solutions made alkaline with ammonia after adding hydroxylamine to hold the uranium in solution were tried. Many of the deposits obtained had a metallic appearance, but they were always contaminated with the black oxide or with a sulphate. The electrodes were also varied. The material tried as electrodes were platinum smooth and roughened, copper, carbon, graphite, and nickel. The deposits formed with the different electrodes were always the same in general properties varying with the kind of solution used, the current density, temperature, and length of run. In strongly acid solutions the amount of deposit obtained was always small. The solutions showed by their color a reduction to uranous sulphate and all the solutions remained clear. The solutions neutral at the beginning, soon precipitated a voluminous yellow deposit that settled to the bottom of the container thus depleting the solution of the electrolyte. When this occurred the solution showed an acid reaction, but the acid content was not sufficient to hold the deposit in solution while the current was running. Where a porous cup was used as a diaphragm, the cathode compartment contained reduced uranium sulphate and the solution in the anode compartment remained that of the uranyl salt.

Table V contains the summarized data of the electrolytic experiments.

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[1] Pogg. Ann., 91, 619; Jour. prakt. Chem., 62, 178.

[2] Jour. Phys. Chem., 9, 231 (1905).

TABLE V

Summarized Data of the Electrolytic Experiments

Experiment	Cathode	Character of electrolyte	Volts	N.D.$_{100}$ in amp	Character of deposit	Time of run	Wt. of deposit Gram	Uranium content Percent	Potential	Remarks
1	Platinum	Acid H_2SO_3	7	14.55	No deposit	2 hrs.	....	...	..	....
2	Platinum	Slightly acid H_2SO_4	7	10.00	Metallic mixed with black oxide	1 hr.	Too small to weigh	...	..	A green hydroxide precipitated
3	Platinum	Slightly acid H_2SO_4	7	17.5	Metallic mixed with oxide	1 hr.	0.0195	...	..	Diaphragm used, anolyte 1.12 sp. gr. H_2SO_4
4	Platinum	Slightly acid H_2SO_4	4	2.58	Black oxide with green tinge	3 hrs.	0.1098	62.25	..	Greenish yellow precipitate in cathode compartment
5	Platinum	Strongly acid H_2SO_4	3.5	3.50	No deposit	2 hrs.	..	...	..	
5	Platinum	Reduced acidity with Na_2CO_3	3.5	2.50	Greenish white with black oxide	2 hrs.	0.0356	...	..	Yellow oxide precipitated in cathode compartment
6	Platinum	10% solution UO_2SO_4 in water neutral or slightly acid by hydrolysis	5	2.15	Brownish tinged with green poorly adherent	3 hrs.	0.1569	68.20	..	Reddish brown precipitate in cathode compartment
7	Platinum	10% solution UO_2SO_4 neutral	8.75	3.88	Dense black coat covered with yellow oxide	1 hr.	Small	...	..	Cathode compartment contained a precipitate of yellow oxide
8	Platinum	10% solution UO_2SO_4 strongly acid	3	11.6	No deposit	2 hrs.	....	...	..	Solution in cathode compartment reduced
9	Platinum	10% solution slightly acid H_2SO_4	8.5	2.2	Brown-black deposit with tinge of green	20 min.	0.1854	60.50	..	Solution in cathode compartment completely reduced and dissolved
10	Platinum	10% solution slightly acid H_2SO_4	11	12	Brown-black with yellow adhering	20 min.	....	...	—0.6295	Cathode compartment filled with yellow precipitate

TABLE V—(*Continued*)

11	Platinum	10% solution UO_2SO_4 acid and treated with formaldehyde	5.5	2.48	Greenish crystals with dark metallic deposit beneath	1 hr.	0.0940	64.60	..	Green crystals when dried were gray-yellow mixed with black beneath diaphragm used
12	Platinum Rotating	10% solution UO_2SO_4 acid and treated with formaldehyde	11	10.82	Black with green crystals stuck to electrode	20 min.	0.0200	...	..	Solution boiled deposit poorly adherent. Diaphragm used
13	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	7	15.28	Metallic beneath crystals which washed off	25 min.	0.026	...	..	Deposit very hard to remove HNO_3
14	Platinum Rotating	10% solution UO_2SO_4 1 cc conc. H_2SO_4	10	12.50	Metallic beneath green powder that washed off	25 min.	0.0120	...	..	Solution kept cool by ice water bath
15	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	10	13.00	Bronze beneath solution. Crystals near surface that broke off	1 hr.	0.0620	...	—0.3259	Brown precipitate in bottom of cathode compartment
16	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	20	27.8	Deposit brown changed to yellow on standing	20 min.	0.050	...	..	Solution boiled
17	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. H_2SO_4	18	5.00	Small amount of white, slimy material that washed off	1 hr.	..	...	..	Cathode compartment full of black precipitate
18	Platinum Rotating	10% solution UO_2SO_4 1 cc. conc. $\%_2SO_4$	18.5	10.6	Yellowish in spots slightly green in others. Poorly adherent	1 hr.	0.1487	42.00	..	Deposit also had sulphate present. Temp. of bath 40°

As shown in the table the electrolysis of a sulphate solution of uranium has been tried under varying conditions. Wherever sufficient deposit has been obtained for analysis, the analysis has been made. Potential readings could not be obtained on all, because when dried the platinum was exposed. Some of the deposits had a decidedly metallic appearance, were difficultly soluble in nitric acid, and in many respects resembled metallic uranium, but the product was so contaminated with oxide and sulphate that no analysis of the metallic looking portion could be obtained. It is impossible to get a deposit of pure metallic uranium under any of the conditions tried, though some metal seems to be deposited at higher current densities. This, however, is always contaminated with the oxide.

12. Electrolysis of Uranyl Acetate Solution

The electrolysis of a neutral solution of uranyl acetate containing 10 grams of metallic uranium per liter was carried on for 1 hour at 20° with a pressure of 34 volts and a current density of 1.95 amp. The cathode was rotated and a porous cup was used as a diaphragm. The cathode was covered with a thin, iridescent film that appeared metallic. The porous cup in the meantime had become partially filled with the yellow oxide of uranium.

The catholyte was made acid with acetic acid and again electrolyzed with 30 volts and a current density of 3.76 amp. for 1 hour at a temp. of 60°. The electrode became covered with a slight deposit of the yellow oxide mixed with a thin film quite metallic in appearance. The catholyte remained acid throughout and no precipitate of the yellow oxide appeared under these conditions.

A larger voltage, 85, and a current density of 18.2 amp. gave a deposit quite metallic in appearance but contaminated with a small portion of the oxide. Only a little deposit adhered to the cathode, in quantity insufficient for analysis. The solution soon became heated to boiling and the larger portion of the uranium precipitated as a mixture of yellow and black oxides. Attempts to keep the solution cool were not successful when high current densities were employed. The temperature was kept below 60° by surrounding the cathode with a glass coil through which cold water could be circulated, and by keeping the electrolytic bath surrounded with a mixture of salt and ice.

Pure metallic uranium could not be plated from an aqueous solution of uranyl acetate even with high current densities. The electrolysis under these conditions, always produced a mixture of what seemed metallic uranium mixed with the black oxide. No analysis of the deposit could be obtained.

13. Electrolysis of Uranyl Salts in Acetone

A saturated solution of uranyl nitrate in acetone, when electrolyzed with a voltage of 14 and a current density of 0.77 amp. gave a deposit at the cathode of the yellow oxide. The saturated solution of uranyl chloride under the same voltage and current density gave likewise a deposit of the yellow oxide which sloughed off and piled up below the electrode. When made acid with hydrochloric acid the deposit was the same in appearance, but it dissolved as soon as it fell off. Formaldehyde added to the solution lowered the conductivity but caused the deposit to adhere to the cathode. The deposit was smooth and bronze-like in appearance. On analysis the deposit yielded 46.50 percent uranium. The bronze color was due to some organic matter from the formaldehyde and acetone and the solution had a distinctly caramel odor. No pure metallic uranium was deposited.

14. Electrolysis of an Alkaline Solution of Uranyl Sulphate

A uranyl sulphate solution made alkaline with sodium carbonate was electrolyzed with a rotating cathode using a voltage of 6 and a current density of 6.68 amp. at 58° C. The greater portion of the deposit dropped off the cathode but there was left a small amount, very metallic in appearance, which did not dissolve readily in nitric acid. A portion of the deposit showed it to be the black oxide as usual. The deposit was washed with cold dilute nitric acid and the insoluble portion dried and weighed. Its weight was very small. It was dissolved in hot nitric acid and the procedure repeated until the accumulated deposits were large enough for an analysis; The error introduced in this way is great but this deposit was found to be richer in uranium than previous deposits analyzed; 72 percent of uranium was found.

15. Electrolysis of Double Potassium Uranyl Tartrate

An acid solution of potassium uranyl tartrate containing 5 percent uranium was made by dissolving potassium uranate in tartaric acid. It gave a poorly conducting solution and deposited a smooth black coat on the cathode. This like other deposits was poorly adherent and the greater portion fell off the electrode. The temperature at the time of electrolysis was 70° and the voltage 19.5 which gave a current density of 5.45 amp. The portion that adhered was dried and analyzed. It contained 73.8 percent uranium.

A tartrate solution made alkaline with potassium carbonate was electrolyzed with a potential of 15 volts and a current density of 19.4 amp. at boiling temperature. Under these conditions a more adherent deposit was formed which on analysis showed 73.5 percent uranium.

Another sample prepared under similar circumstance gave a uranium content of 76.4 percent. In this run the electrolyte was prepared by dissolving sodium uranate in sodium acid tartrate. The solution was slightly acid during the run.

This same solution when made just alkaline with sodium hydroxide and electrolyzed with a potential of 12 volts and current density of 14 amp. at 76° gave a fairly adherent deposit. It was black with the exception of a few grains that were yellow. The deposit contained 81.5 percent uranium.

With a rotating cathode and a temperature of 80°, a voltage of 9.5, and a current density of 7.5 amp. the deposit formed from this same solution was smooth and well adhering while wet. Its color was black with a slight tinge of brown. When dried with alcohol and ether the brown portion scaled off easily. Analysis showed it to contain 70.8 percent of uranium.

The same solution electrolyzed with a potential of 35 volts and a current density of 35 amp. at a boiling temperature gave a strongly adherent black deposit. This deposit contained 75.8 percent uranium.

The uranium content of deposits obtained from alkaline tartrate solutions approaches and some times exceeds the amount found in the later work with acetate solutions. The products are doubtless the same in general but vary in their uranium content, in the oxygen present and in the amount of hydration. Pure uranium was not obtained.

16. Electrolysis of Double Sodium Uranyl Citrate

A solution containing 5 percent uranium was prepared by dissolving sodium uranate in citric acid in the molecular quantity for producing the double salt. It was electrolyzed at 80° with a potential of 40 volts and a current density of 12.4 amp. The solution was slightly acid at the beginning but soon became basic. A dense, poorly adhering, black deposit formed at the cathode but dropped off rapidly. At the same time there was a precipitate of uranic oxide formed. No deposit was obtained uniform enough in appearance to justify analysis. The black deposit was always contaminated with the yellow oxide.

During the electrolysis the anode became bronze in color. On examination this proved to be carbon contaminated with some uranium salts.

According to Smith[1] a deposit does not form when a double alkali tartrate or citrate is electrolyzed, but this is contrary to my experience.

17. Electrolysis of Uranium Tetrachloride Dissolved in Pyridine

Since the oxides of uranium are deposited from aqueous solutions of either uranyl or uranous salts it would seem possible to obtain metallic uranium from a solution which contains no oxygen. A solution of uranium tetrachloride in anhydrous

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[1] Smith: Am. Chem. Jour., 1, 336 (1879).

pyridine might give the conditions necessary for such an experiment.

Preparation of Materials

Uranium tetrachloride was prepared by passing dry chlorine over an intimate mixture of the green oxide of uranium and carbon heated in a combustion tube to about 600°. The uranium oxide was prepared from Merck's pure uranyl nitrate by ignition. The oxide was mixed with starch paste, and then the starch was carbonized in closed porcelain crucibles. There are formed in the reaction between chlorine, uranium oxide and carbon at least two products and possibly three. The first product comes off at a low temperature and crystallizes in colorless needles on the cooler portion of the combustion tube. At a slightly higher temperature a yellowish green product sublimes. This has all the appearance of anhydrous uranyl chloride. The tetrachloride melts around 400° but does not sublime until heated to 600° and above. It can be slowly driven along the combustion tube and eventually sealed up in small portions of the tube. It is brown when melted and produces brown vapors when sublimed. On cooling the melted product, it crystallizes somewhat, leaving an apple-green mass. In contact with air it fumes and gives off hydrochloric acid and is converted into the more stable salt UO_2Cl_2. Because of this behavior it had to be kept sealed until used, and then handled rapidly when required.

Anhydrous pyridine was prepared by distilling pyridine that had been standing for two years over potassium hydroxide and barium hydroxide. It was distilled under atmospheric pressure of 726 mm. and only the fraction that came over between 112.7° and 115° was used.

The anhydrous pyridine was placed in a closed cell, and pure, dry hydrogen bubbled through the solution to replace all air from the pyridine and cell. The cell and the sealed tube of uranium tetrachloride were opened quickly, and the uranium salt was dropped into the pyridine. The reaction was not extremely violent but was accompanied with evolution of heat, considerable hissing, and the formation of dense, white fumes. At the same time the pyridine darkened as though charred and a greenish black, flocculent precipitate was formed.

The closed cell was immediately connected with the battery and the contents electrolyzed, while being stirred with a slow current of pure dry hydrogen. The conductivity was poor, 40 volts across the electrodes were necessary to give a current density of 0.14 amp. Within twenty minutes the potential had to be increased to 64 volts in order to maintain the current density and by the end of two hours the conductivity was practically nil.

The deposit was white, tinged with brown, and did not wash off with gasoline. It was placed over calcium chloride in an atmosphere of hydrogen until dry. Its potential against uranyl nitrate solution was —0.695 volt.

The weight of deposit obtained in consecutive runs was small and analysis of two samples for the uranium content showed 10.65 percent and 10.76 percent of uranium. Another deposit was dried to constant weight and then heated to 120° in a dry test tube by immersing the tube in a bath of paraffin. Pyridine distilled from the solid and condensed in drops on the colder portions of the tube. The deposit formed was a compound containing uranium and pyridine.

No metallic uranium could be obtained in this way.

18. Electrolysis of a Solution of Uranyl Tetrachloride in Acetone

Renz[1] made use of acetone as a solvent for uranium tetrachloride in preparing derivatives of pyridine and quinoline. This reagent was tried as a solvent from which to plate metallic uranium.

The anhydrous acetone was prepared by allowing the commercial product of Mallinckrodt to stand over fused calcium chloride for several days with frequent shaking. The product was distilled and only the portion which came over at 56° used in the experiments.

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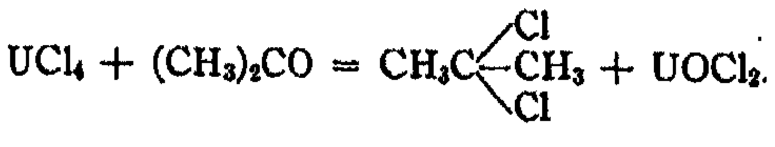
[1] Zeit. anorg. Chem., 36, 110.

The solution was prepared by adding anhydrous UCl_4 directly to the anhydrous acetone in the electrolyzing cell. There was considerable hissing and fuming, and the acetone became blackened. The air was removed from the electrolyzing cell with hydrogen as in the electrolysis of the pyridine solution.

The conductivity of the solution was good, but very little deposit of uranium could be obtained. Electrolysis of the solution for periods varying from one and one-half hours to six hours and longer gave only small amounts of deposit. Hydrogen is evolved copiously during the electrolysis and the solution boils. In all the experiments the solvent was returned to the electrolytic cell with a reflux condenser.

The deposits formed were very dark and gave potentials consecutively around the value —0.64 volt. This value for the potential is of the same order of magnitude as that commonly obtained when uranyl salts are electrolyzed in aqueous solution. No deposit could be obtained of sufficient weight to justify an analysis for the uranium content.

The solvent was subjected to fractional distillation. The first fraction collected between the temperatures 56° and 60° was pure acetone. The second fraction was principally acetone but contained a little methyl alcohol. This fraction was collected between 60–65°. The third fraction which came over between 65° and 74° had a different odor. Fraction 1 contained no chlorine, fraction 2 a slight amount, and fraction 3 contained a large amount of chlorine. This latter fraction comes over at the boiling point of 2, 2-dichlorpropane, and while there might have been present some chloroform, rests showed it to be absent. It seems quite probable that the uranium tetrachloride here plays the same role as phosphorous pentachloride, replacing the oxygen from acetone with chlorine and forming uranium oxychloride according to the equation



$$UCl_4 + (CH_3)_2CO = CH_3C\begin{array}{l}\diagup Cl\\ -CH_3\\ \diagdown Cl\end{array} + UOCl_2.$$

It is quite evident from the abundance of hydrogen obtained that this reaction does not explain all that is taking place. The production of hydrochloric acid would be possible only by the formation of substitution products. The boiling points of mono and dichlor acetone eliminate these as products and chloroform was not found. The only other possibility is the breaking up of the acetone and reduction to carbon by the chlorine present. This would seem to be the case from the deep black color of the solution.

No pure uranium could be plated from this solution, and all deposits obtained seemed to be nothing more than the oxide usually obtained with perhaps a small bit of uranium. The deposit formed replaced mercury from mercurous sulphate.

19. Electrolysis of Fused Nitrate Baths

Attempts to plate uranium from a fusion of potassium nitrate and uranyl nitrate were not successful. The uranyl nitrate was decomposed with evolution of oxides of nitrogen and formation of potassium uranate. As long as there was present any potassium nitrate the fused mass would conduct but as soon as the potassium uranate was formed the melt froze and conduction ceased. Examination of the mass around the cathode showed no uranium. There was plenty of the green oxide formed.

The same behavior was observed with a silver nitrate, uranyl nitrate fusion. There was some conductivity at first but the melt soon decomposed, leaving the oxides behind. These fused to form some silver uranate. No metal could be detected at the cathode.

20. Electrolysis of Uranyl Acetate with a Mercury Cathode

A 5 percent solution of neutral uranyl acetate was electrolyzed with a potential of 30 volts and a current density of 4.55 amp., using a mercury cathode to see if the metal could be amalgamated with the mercury. The deposit that first comes out of the solution is the yellow oxide. This settles on the mercury, but, of course, does not enter into it. On continued running of the current the yellow oxide changes to a darker greenish black and eventually quite black, in all respects similar to the black deposit formed on platinum from aqueous solutions. Portions of the mercury removed and evaporated left no uranium. The uranium is not deposited from aqueous uranyl solutions as metallic uranium but as the oxide.

21. Electrolysis of Fused Double Potassium Uranyl Fluoride

The electrolysis of a fused mixture of uranium tetrafluoride and potassium fluoride was not successful. The uranium fluoride first melted and at the beginning conducted the current, but the mass soon froze and could not be melted again. There was a loss of fluorine accompanied with the formation of potassium uranate with high melting point. No deposit could be found on the cathode that resembled metal.

22. The Character of the Oxide Formed when an Aqueous Solution of Uranyl Acetate is Electrolyzed

In the early work on the quantitative determination of uranium electrolytically Smith[1] determined the composition of the dark deposit to be $U_3O_4H_2O$. His results are calculated by using the atomic weight of uranium as 120. If his analysis are calculated using the present atomic weight (238.5) the composition of the deposit becomes $U_3O_8.2H_2O$.

Several grams of the black residue were prepared according to Smith's directions and subjected to careful analysis and the results obtained would indicate that the product is not the hydrated green oxide as given. The difference is easily explained on the basis of the analysis made.

The residue left after the determination of the water content was taken to be the green oxide of uranium and calculated accordingly. All analyses made have shown that when the water is driven off by passing a current of air or oxygen over the residue heated in a combustion tube, the residue left is richer in oxygen than the compound U_3O_8.

Results of analyses are given in the following table. In

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[1] Amer. Chem. Jour., 1, 329 (1879).

samples 1 and 2 the uranium content was found by dissolving the material in nitric acid and precipitating the uranium with ammonium hydroxide.

TABLE VI

Sample	Weight Grams	Weight of water Gram	Weight of residue	Weight U_3O_8	% H_2O	% U
1	0.2998	—	—	0.2783	—	78.74
2	0.3021	—	—	0.2800	—	78.62
3	1.0318	0.0385	0.9650	0.9578	3.73	78.73
4	1.0258	0.0403	—	—	3.92	—
5	0.5905	0.0209	0.5511	0.5490	3.54	78.86

The empirical formula as calculated from the results obtained becomes $U_3O_{10}.2H_2O$. Smith explained the discrepancy between the weight of his residue and the weight of water found as due to loss of oxygen, but it is highly probable that the product which he weighed as U_3O_8 was still richer in oxygen than U_3O_8 should be.

28. A New Method for Measuring the Single Potential of Metals and Oxides in Powder Form

The single potentials of metals against their salt solutions are usually measured by using either cast pieces of metal, where this is possible, or an electrode prepared by plating the metal in question on another metal. In case the metal cannot be plated or cast, the determination of the single potential is difficult.

The measurement can be made on metals and oxides in powder form by pasting the finely powdered metal on platinum or any other good conducting metal, with gelatin. In the experiments tabulated below the electrodes were prepared by first moistening a platinum electrode with a solution of gelatin and then spreading the finely divided metals or oxides over the platinum and pressing them firmly with a spatula. Each measurement was compared with results obtained by other investigators using electrolytes of the same strength as have been used in this investigation. The results are given in Table VII.

TABLE VII

Results of Potential Measurements of Some Metals and Oxides

Chain	Observer	Form	Value given	Value found by pasting with gelatin
$Zn/ZnCl_2N/1//KCl.Hg_2Cl_2N/1/Hg$	Neumann	Cast	0.5030 volt	0.5026 volt
$Cu/CuSO_4N/1//KCl.N/1Hg_2Cl_2/Hg$	Neumann	Plated	—0.515 volt	—0.516 volt
$Ag/AgNO_3N/10KNO_3N/1//KCl.N/1Hg_2Cl_2/Hg$	Kahlenberg	Plated	—1.018 volt	—1.0024 volt
	Egli	Plated	—0.993 volt	
$MnO_2/Mn(NO_3)_2N/5.HNO_3N/20//KCl.Hg_2Cl_2/Hg$	Tower	Plated	—1.5042 volt	—1.1156 volt (fresh pasted) —1.3621 volt (left in air) —1.5159 volt (plated)
$PbO_2/H_2SO_42N//KCl.N/1Hg_2Cl_2/Hg$	Dolezalek	Plated	—1.893 volt	—1.7145 volt (fresh pasted) —1.7794 volt (after 2 hrs.) —1.7475 volt (fresh pasted) —1.8203 volt (after 2 days)

NOTE—Values taken from Landolt-Börnstein.

The zinc used was Bakers "C. P." zinc dust. The copper was precipitated electrolytically from a copper sulphate solution by metallic zinc and the excess zinc removed by digesting with dilute sulphuric acid. The silver was prepared by reduction of the pure oxide in hydrogen. The gelatin was the commercial product labelled "Gold edge." The solution was prepared by dissolving 0.5 gram in 25 cc of water and applied while still liquid.

The measurements made with metals show that the method is reliable.

The manganese dioxide was Merck's "C. P." product and the lead peroxide Mallinckrodt's preparation, labelled "C. P." The potentials obtained by plating manganese dioxide give higher values than the pasted material. This is no doubt due to a different state of hydration. An electrode, when prepared by plating, always gave lower readings after it had dried in the air. The moist, pasted electrode gave higher readings when left exposed to the air. This was also true of the lead peroxide when pasted, but the potentials found are of the same order of magnitude and possess the same polarity. The potential measurements for manganese dioxide as made by Tower[1] were obtained immediately upon removal from the plating bath.

24. The Single Potential of Uranium and Its Oxides

With the exception of the green oxide of uranium, the oxides are difficult to prepare in absolutely pure form. The hydrated oxide UO_3H_2O is first deposited when an aqueous solution of any uranyl salt is electrolyzed but the product obtained is usually contaminated with a black oxide especially when the uranium is almost depleted. Uranous oxide UO_2 can be obtained in a fair state of purity by reducing ammonium uranate in a current of pure, dry hydrogen. This, however, is pyrophoric and absorbs oxygen from the air, becoming U_3O_8. This is especially true when prepared from the uranyl salts of organic acids such as the oxalate and acetate.

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[1] Zeit. phys. Chem., 32, 566 (1900).

Anhydrous UO_3 has been prepared by heating uranyl nitrate to 250° for several hours.[1] However, the purity of the product is questionable unless the work is done in an atmosphere of oxygen since the green oxide U_3O_8 tends to form.

Other oxides have been described in the literature, but their existence as definite compounds is more or less questionable.

The green oxide U_3O_8, being the high temperature oxide, is most easily prepared by igniting ammonium uranate in the air to constant weight. The pure oxide was prepared in this way and used for the potential measurements herein recorded. The finely ground powder was pasted on a platinum electrode with gelatin and the single potential was then measured against a solution of uranyl nitrate which contained 14.3 grams of anhydrous uranyl nitrate per liter. The half element was the usual form of a normal mercury calomel electrode. The results are given in volts and are fairly constant for the different electrodes prepared from different samples of the oxide.

TABLE VIII

Sample	Observed potential
1	—0.778 volt
2	—0.787 volt
3	—0.779 volt
4	—0.785 volt

A sample of pure uranium oxide U_3O_8 obtained from Dr. S. C. Lind of the Bureau of Mines, Boulder, Colorado, when pasted on platinum with gelatin, gave a single potential of —0.773 volt.

A sample of uranous oxide UO_2 prepared by heating ammonium uranate in a current of hydrogen was used for measuring the potential. It gave an analysis 87.65 percent uranium. By calculation pure UO_2 contains 88.17 percent uranium.

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[1] Jacquelain: Chem. Pharm. Centralblatt, 1845, 193.

The potential of this material gave a value for three different electrodes prepared with gelatin.

—0.778 volt
—0.773 volt
—0.776 volt

With UO_2 the value is the same as that found for U_3O_8. It is possible that there is a superficial oxidizing effect which causes the result to be the same.

The hydrated yellow oxide was prepared by electrolysis of a neutral solution of uranyl acetate. It was deposited in small quantities with a voltage of 6 and a current density of 0.108 amp. at room temperature. The first deposit formed is entirely yellow, but if allowed to remain until considerable free acetic acid is present, the yellow compound is contaminated with the lower black oxide. As soon as the cathode showed a slight blackening, the electrolysis was interrupted and the solution filtered from the yellow deposit. By proceeding in this way with other portions of fresh uranyl acetate, enough yellow hydrated oxide of a high grade of purity was obtained for analysis and for potential measurements. Ammonium hydroxide or fixed alkali hydroxde added during electrolysis of an acetate solution reduces the acidity and prevents the formation of the black deposit but the product obtained in this way is the alkali uranate and not the yellow oxide.

Analysis of the product showed:

U 76.53 percent, water 7.36 percent, oxygen by difference 16.11 percent. The formula of the product thus becomes UO_3H_2O.

The single potential of the product measured against the standard solution of uranyl nitrate gave a constant value of —0.860 volt. The value given was obtained on four different electrodes prepared by pasting the oxide on platinum with gelatin.

The black deposit formed when an aqueous solution of a uranyl salt is electrolyzed when pasted on platinum with gelatin gives a single potential of —0.6872 volt. This is conclusive evidence that the deposit is not U_3O_8 as formerly supposed, and both the potential and the analysis support this conclusion.

A sample of metallic uranium prepared by Schuchardt was analyzed and found to contain uranium 91.49 percent, ferric oxide 8.34 percent.

It was used for making a single potential measurement by pasting the finely powdered material upon platinum with gelatin. The maximum potential obtained in this way was —0.093 volt for the sample. The potential decreases rapidly in contact with the uranyl nitrate solution which indicates a rapid oxidation of the metal.

25. The Single Potential of the Black Oxide Plated on Platinum

By using an electrode covered with platinum black a smooth, adherent deposit of the black oxide can be obtained. Single potentials of this measured against the standard uranyl nitrate solution gave variable results depending upon the treatment given the deposit. The first deposit obtained with a pressure of 13.5 volts and a current density of 3.11 amp. gave the same potential formerly obtained from aqueous uranyl salt solutions, namely, —0.497 volt. With this sample, the small amount of the yellow oxide present was washed off with dilute acetic acid.

The electrode was used for obtaining a heavier deposit, and under similar treatment gave for the second reading a maximum of —0.361 volt. The value diminished rapidly.

Electrolyzed again for one hour with all factors identical the maximum potential reading was —0.302 volt.

When the electrolysis was allowed to continue until the uranium was depleted, the value for the potential was much greater. If the potential is measured immediately upon removal from the electrolytic bath higher values will be found. Voltages as high as —0.4999 volt have actually been measured. This product when allowed to stand in contact with the standard uranyl nitrate solution or in the air gives decreasing values. The voltages fall off gradually and change polarity due to slow oxidation of the deposit. When washed with dilute acetic acid before taking the potential, the initial value was repeatedly found to be about ± O potential, but here the value was dependent upon the time which elapsed between the removal from the electrolytic bath and the measurement of the potential.

These variable results are no doubt due to occluded hydrogen in the deposit. However, experiments showed that this deposit does not serve as a hydrogen electrode in the same manner as platinum black does. No constant value for hydrogen was obtained, and the potential readings decreased in the usual manner when the deposit was used as a hydrogen electrode. No constant values could be obtained upon which to base a conclusion.

26. Reaction of Uranium Tetrachloride with Paraffin

An attempt to prepare metallic uranium by allowing uranium tetrachloride to react with metallic sodium under molten paraffin was not successful. Instead of reacting with the sodium the uranium tetrachloride reacts with the paraffin, evolving hydrochloric acid. The exact nature of the reaction is as yet unknown. When the excess paraffin is removed by petroleum ether and washed free from all chlorides present there is left a brownish black material insoluble in ice water. The product gives a potential exactly the same value as U_3O_8. In this respect it behaves like UO_2 produced by reduction in hydrogen. From its polarity and potential, it is probably an oxide of uranium rather than metallic uranium.

The analysis of the substance dried to constant weight over sulphuric acid gave 52.67 percent metallic uranium and 46.54 percent carbon. A portion of the carbon was probably oxidized by the nitric acid used to separate the uranium from the mixture. Further examination of the reaction of uranium tetrachloride with organic material will be made.

III. SUMMARY OF RESULTS

The conclusions drawn from the experimental results, briefly stated, are:

1. In aqueous solutions with low current density uranyl salts deposit first the hydrated uranic oxide UO_3H_2O, which is later changed by the action of current to a black oxide of varying composition.

2. With higher current density uranyl sulphate is reduced to uranous sulphate, but in the presence of free acid the deposit obtained is small in amount and poorly adherent though metallic in appearance. In neutral or alkaline solution, the deposit formed is a mixture of the black and yellow oxides.

3. The use of a porous cup as a diaphragm does but little good. The deposit is the same in character as when no diaphragm is used.

4. The deposit obtained when alkaline uranyl tartrate and citrate solutions are electrolyzed is an oxide much richer in uranium than that deposited from solutions acidified with tartaric or citric acid.

5. The conductivity of non-aqueous solutions of uranyl salts is a function of the water present, and the deposits formed are oxides contaminated with organic matter.

6. Anhydrous pyridine treated with anhydrous uranium tetrachloride forms solutions conducting electricity. From these deposits a compound containing uranium and pyridine may be obtained on the cathode.

7. Anhydrous acetone, when used as a solvent for uranium tetrachloride, gives a solution which conducts well but deposits no pure metallic uranium. The deposit replaces mercury from mercurous sulphate. The uranium tetrachloride reacts with acetone forming 2,2-dichlorpropane and also further decomposes acetone. Hydrogen is evolved during electrolysis of the solution.

8. Solutions of potassium uranyl fluoride, whether neutral, acid or alkaline, form a deposit containing fluorine. In acid solution the deposit is $UF_4 6H_2O$. Neutral and alkaline solutions give a mixture of UF_4 and uranium oxide.

9. Deposits from double potassium uranyl cyanide solutions, when neutral, consist of potassium uranate. When

acid with hydrocyanic acid, the deposit is the yellow hydrated oxide contaminated with some of the black oxide.

10. The single potential of metals and oxides in powder form can be measured accurately by pasting the finely powdered material on a platinum electrode with gelatin.

11. The single potentials of the more stable oxides of uranium have been measured.

12. Uranous oxide UO_2 gives a single potential identical with that obtained for the green oxide U_3O_8.

13. The black deposit formed when uranium salts are electrolyzed is not $U_3O_8.2H_2O$ as claimed by Smith but it is a product having the composition $U_3O_{10}.2H_2O$. Further, it does not give the same potential as U_3O_8.

14. The position of uranium in the electrochemical series has not been definitely fixed because of inability to make pure uranium, but the potential of a sample of uranium containing 91.49 percent uranium and 8.34 percent ferric oxide has been measured.

This work was undertaken at the suggestion of Professor Kahlenberg and carried out under his direction.

University of Wisconsin
Madison, June 20, 1919

THE COLORS OF COLLOIDS. IX

BY WILDER D. BANCROFT

Colloidal Metals

In 1857, Faraday[1] made colloidal solutions of gold which were red, violet or blue by transmitted light. Nearly forty years later, Zsigmondy[2] worked out methods for preparing stable colloidal solutions of gold. In the red solutions the particles are green by reflected light, they are yellow to reddish brown in the blue solutions, while the violet solutions contain a mixture of the two.

By precipitating metallic silver under suitable conditions, Carey Lea[3] obtained colloidal silver which was yellow, red, or blue by transmitted light. Carey Lea of course assumed that these were allotropic forms of silver and this view was shared by Blake.[4] No evidence has been brought forward to show the existence of allotropic modifications and it is, therefore, necessary to account for the color phenomena solely on the basis of the size and the structure of the suspended particles.

Garnett[5] has given a theory of the phenomenon which has been summed up by Wood[6] as follows:

"We will now consider the effects of these small gold spheres upon the color of the transmitted light. The subject has been very fully discussed by Garnett, who has investigated it from the standpoint of the electro-magnetic theory. His treatment is much too long to give in full, but we can examine to advantage the general method of attack and some of the conclusions.

Let the light of wave-length λ fall on a metal sphere of

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[1] Phil. Trans., 147, 145 (1857).

[2] Liebig's Ann., 301, 30 (1898); Zeit. anal. Chem., 40, 711 (1901).

[3] Am. Jour. Sci., (3) 37, 476; 38, 47 (1889); Phil. Mag., (5) 31, 238, 320, 497; 32, 237 (1891).

[4] Zeit. anorg. Chem., 37, 243 (1903).

[5] Phil. Trans., 203A, 385 (1904); 205A, 241 (1906).

[6] "Physical Optics," 643 (1911).

radius a, refractive index n, and absorption coefficient k. Further let

$$N \equiv n(1-ik) = \sqrt{\epsilon'},$$

ϵ' being the complex dielectric constant. This case has been considered by Lord Rayleigh[1] who showed that the sphere excited by a periodic electric force E_0 emits the waves which would be emitted by a Hertzian doublet, which at time t was of moment equal to

$$\frac{N^2-1}{N^2+2}a^3E_0.$$

If there are a large number of spheres in close proximity, the electric force exciting each one will be E', *i. e.*, the force E_0, together with forces due to the neighboring doublets. This force E' causes the polarization

$$f(t) = a^3\frac{N^2-1}{N^2+2}E'.$$

If the average moment of a doublet be $f(t)$, and there are n doublets per unit volume, the polarization of the medium will be $f'(t) = nf(t)$. By means of analyses by Lorentz and by Larmor it can be proved that

$$E' = E_0 - \frac{4\pi f'}{3} = E_0 + \frac{4\pi}{3}na^3\frac{N^2-1}{N^2+2}E',$$

provided the doublets are distributed through a space large in comparison to the wave-length. This gives us

$$E' = \frac{E_0}{1-\frac{4\pi}{3}na^3\frac{N^2-1}{N^2+2}},$$

so that

$$f = \frac{E_0\frac{N^2-1}{N^2+2}}{1-\frac{4\pi}{3}na^3\frac{N^2-1}{N^2+2}}.$$

By substitution of these units in Maxwell's equation, the com-

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[1] Phil. Mag., 44, 28 (1897).

plex dielectric constant of the medium containing the spheres is found to be

$$\epsilon' = 1 + \frac{3D\dfrac{N^2-1}{N^2+2}}{1-D\dfrac{N^2-1}{N^2+2}}$$

in which D is written for $\frac{4\pi}{3}na^3$, denoting the volume of the metal per unit volume of the medium. This is for spheres *in vacuo:* in glass of refractive index μ the equation becomes

$$n'(1-ik')^2 = \epsilon' = \mu^2 + \frac{3\mu^2 D\dfrac{N^2-\mu^2}{N^2+2\mu^2}}{1-D\dfrac{N^2-\mu^2}{N^2+2\mu^2}}.$$

The optical constants of the medium n' and k' thus depend only on D, the relative volume of the metal, and not on the size of the spheres, restricting them, however, to sizes small in comparison to λ. By reducing the above equation, and substituting in it the values for N and μ, the absorption can be found for any given value of D.

"Now D varies with the nature of the glass. The gold glass as first prepared is colorless, becoming red on reheating, the process causing the metal spheres to form within the body of the glass—'excretion of the metal' Garnett calls it. Colorless gold glass turned red on exposure to the emanation of radium, and it is probable that the blue color of X-ray tubes, and tubes which have contained radium, is due to the excretion of metallic potassium or sodium by radiation. Sir William Ramsay exposed glass containing silver to radium rays and found that it turned yellow. Quartz glass is not colored, as no metal is present.

"Elster and Geitel[1] found that salts of alkaline metals, colored by the action of cathode rays, exhibited photo-electric properties which suggested the presence of free metal; this supports the view held regarding the coloration of glasses by X-rays and radium rays.

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[1] Wied. Ann., 59, 487 (1896).

"Garnett took the values of N calculated from Drude's tables of the optical constants of the metals, and the value of D calculated from the total gold content of the glass, and the observations of Siedentopf and Zsigmondy, and showed that the medium should be much more transparent for red than for yellow light. Values *n* and μ for green and blue light not being available, the best that could be done was to infer that, since yellow is less freely transmitted than red, the medium is still more opaque to green and blue.

"Garnett next develops an expression for the scattered light, and finds that the amplitude at any point of the light emitted from a sphere is proportional to

$$\left| \frac{N^2 - \mu^2}{N + 2\mu^2} \right| \frac{a^3}{\lambda^2}.$$

The λ^2 in the denominator indicates that the scattered intensity increases with the inverse fourth power of the wavelength, but that it is also dependent on N, *i. e.*, on the optical constants of the metal. Calculations showed that yellow light would be scattered more powerfully than red, from which it was inferred that green would be still more powerfully scattered, which is in agreement with the observations of Siedentopf and Zsigmondy. Certain types of gold glass scattered a muddy, red light however. In this case the particles are probably so large that they reflect light in the ordinary sense, and, as we know, gold reflects red light in greater excess than any of the other colors.

"In an appendix to the paper, the transmission of gold and silver glass has been calculated for red, yellow, green, and blue light, from values of *n* and *k* given by Rubens. The colors in the order of the degree in which they were transmitted were found to be: for gold glass—red, yellow, blue-green; for silver glass—yellow, red, green, blue. Certain gold glasses appear blue by transmitted light, and it appears probable that large particles (diameter >0.0001), by reflecting out the red and orange, give the glass a blue color.

"In the second part of the paper above referred to, Garnett examines the conditions which hold in cases where the metallic granules are deposited in thin films. The equations already given were developed on the assumption of a uniform polarization in the medium, which is only the case when the spheres are distributed in three dimensions. For a two-dimensional distribution, in the xy plane, it is shown that the complex dielectric constant in the direction of the xy axes is the same color as for the medium in bulk, whereas the constant in the direction of the z axis may be quite different. If this were the case the film would behave like a doubly refracting substance, the 'optic axis' being perpendicular to the film.

It is found that for films of thickness greater than $^2/_3$ of λ the absorption is governed by nk, while in the case of films less than $^1/_{25}$ λ it is governed by n^2k. Curves are given showing how the absorption depends on D, the volume of metal per unit volume of the medium. The values of nk, or n^2k, are plotted as ordinates, and the values of D as abscissae. In the case of a nongranular film of solid metal, it is evident that $D = 1$.

"Garnett was able to explain all of the effects observed by Wood in the case of the sodium and potassium films deposited in exhausted bulbs, at least all of the effects which fell within the scope of his equations. The curves for a potassium sodium amalgam show how the absorption depends on the value of D. For $D = 1$, *i. e.*, solid metal, the absorption is strongest for red and weakest for blue. For $D = 0.5$, that is, for a film with equal volumes of metal and empty spaces, the absorption is strongest for yellow, while for $D = 0.3$ the blue is practically the only color absorbed. For thin films we find that for $D = 0.5$ yellow is very powerfully absorbed, which agrees with Wood's observation that when the conditions were such as to cause an absorption band in the yellow, the band was much blacker and narrower than when it occurred in some other part of the spectrum.

"The graphs for gold indicated that for $D = 1$ the color in the case of very thin films of gold leaf should be blue. This was the color observed by Mr. Beilby in the case of the thinnest leaf which could be procured. For thick films the graphs showed that the color of the transmitted light should be green. Many very curious and interesting changes, observed by Mr. Beilby[1] in the colors of thin, gold films, produced by heating and annealing, are discussed and explained by Garnett, whose paper is by far the best on the optical properties of metallic films which has appeared up to the present time.

"It appears that the theory of optical resonance can be regarded as in a measure confirmed by these investigations, though the phenomenon is very much more complicated than in the case of large resonators and electro-magnetic waves. The optical constants of the metal enter as a factor, and for very small particles at least the absorption depends not on their size, but on the total bulk of metal in unit volume. It is probable that very definite and more easily interpreted results can be obtained by experimenting with very long heat-waves, either with cross-ruled films of metal or fine metal powders."

While Garnett's papers are very interesting, I do not find them as helpful as I should like. They are very mathematical in form, and yet it is difficult to find any clear-cut general statements. It has seemed to me that it might be of assistance to others if I were to put the matter as I see it, laying more stress on simplicity of treatment than on accuracy. No discussion will be attempted in regard to polarization. It does not seem to me that the theory to be outlined is the same as Garnett's; but it could perhaps be deduced from his equations.

In the case of selective reflection, some or all of the light which is absorbed very strongly by a given substance is reflected strongly from a polished surface of that substance. The surface color of magenta is green, while the body color or the color due to the transmitted light is red. With indigo the surface color is red and the body color blue. The surface color is believed to be due to resonance, the substance emitting the rays which it absorbs very strongly. If this is the case, it is easy to see that a very small granular particle might emit surface color by resonance on the opposite side from the source

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[1] Proc. Roy. Soc., 72, 226 (1903).

of light, in which case we should have the surprising phenomenon of a substance apparently transmitting the light which it absorbs most strongly. On the other hand, the amount of reflection from the back surface of a particle of the light ordinarily transmitted will be greater, the less the thickness of the particle. In the case of a colloidal solution of a substance showing selective reflection, we should expect that with decreasing size of particles, the apparently transmitted light will contain more and more of the light which is usually reflected, while the reflected light will contain more and more of the light which is usually transmitted. In other words, we should expect a more or less complete reversal of the usual colors as the suspended particles became smaller and smaller.

While this is theoretically sound, it might easily happen that one did not get apparent transmission of the strongly absorbed light at any size of particle which could be realized satisfactorily. Fortunately, this seems not to be true.[1] "Wien focussed sunlight upon the highly polished edges of thin plates of various metals, and observed that light was diffracted far into the region of the shadow, the edge of the plate appearing luminous. The color of the light varied in a remarkable manner with the nature of the metal, appearing red with copper and gold screens, orange with silver, yellow and yellow-green with platinum and tin-foil. The color only appeared when the edge was clean and quite free from dust; it was complementary[2] to the color most strongly absorbed by the metal, and polarized with the vibration perpendicular to the diffracting edge. If the incident light was polarized to start with, the color was only seen when the vibration was perpendicular to the edge. The phenomenon is evidently related in some way to resonance, vibrations being set up in the metal along the edge which emit energy into the region behind the screen. In addition to the colored light, Wien found that white light was also present, and that it could also be cut off by a Nicol

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[1] See Wood: "Physical Optics," 634 (1911).

[2] [This is wrong. It does not agree with the statement in regard to resonance two sentences further on.—W. D. B.]

prism, though its plane of polarization appeared to depend upon the azimuth in which the incident light was polarized, and also upon the angle of diffraction."

The thickness of the film at the edge of the plate is finite, and it, therefore, seemed probable that the desired effect could be realized experimentally with colloidal solutions. Since indigo in mass transmits blue and reflects red, a colloidal solution of indigo should be red by transmitted light. Professor H. N. Holmes of Oberlin was good enough to try this experiment for me and found that the prediction was verified. Apparently, the reason that this has not been formulated clearly before has been that people have worked chiefly with colloidal metals which are so very opaque that the reversal of colors has not been noticed. One should really study the problem using aniline dyes having a metallic surface color.

We can now apply this general principle to the case of gold. Under ordinary conditions gold reflects yellow; but the color is said to change to red with multiple reflections.[1] Pulverulent gold is black, and, consequently, gold will change from yellow through brown to black, as it becomes more and more porous. Brown gold is obtained in assaying.[2] This turns yellow again when subjected to pressure, or when heated so that it sinters. Very thin gold leaf is green.[3] Consequently, we should expect gold particles to reflect yellow, brown, or green light, depending on the conditions. Massive particles would reflect yellow and very fine particles green, while porous particles would reflect brown light, more or less irrespective of size. Zsigmondy[4] points out that colloidal gold solutions contain ultramicrons which reflect yellow, brown, or green. "Both green and brown ultramicrons may have all possible dimensions from the amicroscopic to 120 $\mu\mu$ and over. As a general thing, however, the large particles are yellow or brown while the very fine subdivisions are green. At present, there

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[1] Wood: "Physical Optics," 456 (1911).

[2] Hanriot: Jour. Soc. Chem. Ind., 30, 89, 216 (1911).

[3] Faraday: Phil. Trans., 147, 145 (1857).

[4] "The Chemistry of Colloids," 94 (1917).

is no explanation for the fact that very small particles are sometimes brown. Nevertheless, the following may be the key to the situation: According to Mie's theory, particles of gold having a diameter of 40 $\mu\mu$ and under must be green. The assumption is thereby made that the shape is spherical and the particle a compact mass of metallic gold. Any divergence from the theory may mean that the conditions are not fulfilled. In other words, when the very small particles are brown, either the shape is not spherical or the entire space occupied by ultramicrons is not filled with metallic gold. The first assumption does not seem to be entirely necessary. It may also be contended that the divergence from the theory is due to allotropic modifications of gold. The assumption is quite unnecessary for the explanation of the color and leads to contradictions in certain cases.

"With regard to the brown color of very small particles, a large number of experimental facts point to the assumption that the ultramicrons are not composed of massive gold. For instance, whenever the green particles become flocculent or approach very close to one another, the color changes to brown, even when the aggregate is still amicroscopic. It would seem, therefore, that small, brown particles are in reality conglomerates of the green. Green ultramicrons, on the other hand, are composed of compact gold, and are the result of the normal growth of amicroscopic particles, or, better, perhaps, they are tiny crystals."

This agrees admirably with the theory as outlined. Compact gold reflects yellow when it does not resonate, and green when it does. Porous gold is brown. Apparently the green particles cannot resonate after agglomeration. While the smallest particles must be green, there is no reason that some brown particles should not be smaller than the coarser green ones and this is the case. When green ultramicrons are pressed between the cover glass and the platform of the cardioid ultramicroscope, they become brown.

The color of colloidal gold solutions by transmitted light is red, violet or blue. The solutions containing green particles transmit blue light, those containing yellow to reddish brown particles transmit blue light, while solutions containing a mixture of green and yellow to reddish brown particles transmit violet light. Since in general, the green particles are the largest, it follows that coagulation of a colloidal gold solution should cause a change in the color by transmitted light from red to violet to blue, which is what actually occurs.[1]

"A characteristic property of all pure red gold solutions is the change to blue during coagulation. This change is occasioned by the union of two or more particles that diffract green. The complex thus formed diffracts only brown light waves. It is impossible to explain the color change on the grounds of an increase in the size because it occurs regardless of whether amicrons or submicrons unite. In the first of these cases the complex may still remain amicroscopic and have a mass several hundred times smaller than that of a large, red particle. Nevertheless these tiny complexes diffract brown and the liquid appears blue.

"It seems necessary to assume that the particles unite to form a somewhat loose, flocculent mass, and do not melt into one another as drops of liquids do. For if the latter were the case the color would be the same for all particles of the same substance having like dimensions. However, as already stated, there is no relation between size and color unless the growth has been normal; that is not caused by union of several ultramicrons larger than molecules.

"There is another important conclusion to be drawn from the considerations discussed in the foregoing, *viz.*, that a decrease in the surface is not a very prominent factor in the coagulation. Even if one assumes that the liquid films between the particles are broken, the decrease of surface must be confined to the edges or faces that touch.

"A reversible change of color may be brought about by evaporating a colloidal gold solution with a very small amount

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[1] Zsigmondy: "The Chemistry of Colloids," 101 (1917).

of gelatin.[1] The dried residue is blue while the color changes to red if moisture is added. The change of color has been explained by Kirchner[2] on the basis of Planck's[3] dispersion theory for isotropic dielectrics. He regards the particles as resonators that, on coming into close proximity with one another, displace the absorption maximum toward the red end of the spectrum, at the same time causing a widening and increased intensity of the maximum. This is borne out very well in practice. Mie[4] has raised objections to Kirchner's theory so that a satisfactory elucidation is not yet at hand. A complete optical theory of metal colloids must unquestionably explain the change of color that is so characteristic of gold and other metal colloids.

"Siedentopf[5] has observed an unmistakable dichroism of gold gelatin films when viewed at an oblique angle. He assumes that the change of color on drying is due to a change of form of the particles and not to the distance between them. It is difficult to conceive of a reversible change of form, however, and it seems much better to assume an orientation of the particles parallel to the distention surface of the film. But this cannot be the only factor involved in the change of color on dry desiccation, because the color of the residue seen through a Nicol's prism suitably placed is a turbid violet-red and differs greatly from the deep red obtained by the addition of moisture. The distance between the particles must play a part here just as it does in the coagulation of gold solutions.

"A word may be added with regard to blue-gold hydrosols. The blue obtained on the reduction of gold chloride solutions may be attributed to three causes: First, the reduction

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[1] F. Kirchner and R. Zsigmondy: Drude's Ann., 15, 573 (1904); R. Zsigmondy: Zur Erkenntnis der Kolloide, 114 (1905).

[2] F. Kirchner: Ber. Kgl. Sächs. Ges. Wiss. Leipzig, 54, Math. phys. Kl., 261 (1902).

[3] Planck: Drude's Ann., 1, 69 (1900); Sitzungsber. Akad. Wiss. Berlin, 1902, 470.

[4] Drude's Ann., 25, 429 (1908).

[5] Verh. deutsch. phys. Ges., 12, 36 (1910).

may be incomplete and colloidal gold oxide be formed instead of gold.[1] Further reduction, perhaps at higher temperatures, might cause the blue to change to red. This condition has not been taken cognizance of up to the present time. Secondly, the reduction may be complete and the blue color be attributed to the flocculent union of particles already spoken of; or perhaps to the irregular growth so that, instead of flakes or needles, husk-shaped bodies are called into being. These, of course, may be submicroscopic. Finally the liquid may contain large, massive, gold particles that, according to the theory of Mie, would account for the blue color."

The red color which is said to be obtained by multiple reflection from gold is undoubtedly the same as the red color transmitted by certain colloidal solutions, while the purple color which one gets with less effective multiple reflection, probably corresponds to the so-called violet solutions. Wood[2] has summarized the data obtained by Hagen and Rubens on the reflecting and absorbing power of gold with varying thickness of film. "We see from the data that the reflecting power increases with the thickness, reaching its maximum value at about 80 $\mu\mu$ or 0.00008 mm., which is about one-eighth of the wave-length of red light, after which it remains constant. For red light this maximum value is 90 percent; for green light it is less than 50 percent. This explains the yellow color of gold and the green color of gold leaf by transmitted light." From this it is clear that red light is reflected the most by gold, and, consequently, it should be the color transmitted most readily by the finest particles of colloidal gold, which is actually what happens.

It may be of interest to include here the table given by Helmholtz showing which spectrum colors are complementary, even though the surface color and the body color are not necessarily strictly complementary.[3]

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[1] R. Zsigmondy: Zur Erkenntnis der Kolloide, 114, 133 (1905).

[2] "Physical Optics," 467 (1911).

[3] Wood: "Physical Optics," 440 (1911).

Name	Wave-lengths in μμ	Name	Wave-lengths in μμ
Red	656.2	Blue-green	492.1
Orange	607.7	Clear blue	489.7
Yellow	585.3	Clear blue	485.4
Yellow	573.9	Clear blue	482.1
Yellow	567.1	Indigo	464.5
Yellow	564.4	Indigo	461.8
Greenish yellow	563.6	Violet	433.0

It may be asked why it should not be possible to make gold leaf thin enough so that it would transmit red light. The answer seems to be that a coherent film does not resonate so readily as a granular one. Beilby[1] found that a coherent green film becomes granular when heated and then transmits either purple or blue light, even though the diameters of the particles must be greater than the thickness of the film from which they were formed. We get a similar thing in the case of the dried gelatin films which were blue by transmitted light instead of red, showing that the contraction due to drying brings the particles of gold sufficiently near together to be equivalent to reversible agglomeration, thereby destroying the resonance. There is also some evidence that Beilby did actually get some continuous films which were thin enough to transmit purple light. Garnett[2] says: "A very thin leaf of gold should not show the green color distinctive of gold leaf, but the red color should predominate over the yellow. The arbitrary graph for n^2k for blue would, if correct, show that blue should predominate over either yellow or red. The color of a thin film of gold leaf would, therefore, be chiefly blue, less red, and least yellow, *i. e.*, blue-purple, and this is the color observed by Mr. Beilby in the thinnest piece of gold leaf he possessed. It should be noticed that it has not been proved that a very thin film will let through more red than yellow light and that it, therefore, will not exhibit the green color

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[1] Proc. Roy. Soc., 72, 226 (1903).

[2] Phil. Trans., 203A, 385 (1904).

of gold leaf. It has only been stated that it seems probable that it will let through more blue than either."

The case of silver is not so simple because the polished silver has no marked color of its own. The color obtained by repeated reflections from silver is said to be golden yellow, while the color of a thin film of silver is blue. We should, therefore, expect the colloidal solutions having the finest particles to transmit yellow and that actually happens. By reflected light, these particles should be blue, and they are. Müller[1] reports that "the very coarse particles of a colloidal silver solution are red in the ultramicroscope; but the color is not saturated because shorter wave-lengths are also present. The smaller the particles, the more the color changes to the blue end and the more saturated and intense it becomes. At 80 $\mu\mu$ diameter they are an intense blue." If no other factor came in, the color reflected from massive silver would be yellow and this is said to be true in the case of multiple reflections. The apparent reflection is gray. To account for the facts, one must assume that on repeated reflections from silver, the light becomes first red and then yellow; but I do not know whether this has actually been observed or not. With gold the apparent reflection changes from yellow to purple to red and silver might easily change from gray to red to yellow. The particles of silver which reflect red, transmit blue, while a mixture of the particles reflecting blue and those reflecting red give a reflection of blue-green and a transmission of red. Colloidal solutions of silver transmit yellow, red, and blue with increasing size of particles. The transmission of yellow follows from the application of the theory to known facts. The transmission of blue cannot be predicted from any qualitative facts now known to me. Starting with the experimental fact that the coarser silver particles reflect red light, it is possible to predict that one should get red light reflected from massive silver under suitable conditions and this will have to be tested experimentally at some time. Since

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[1] Drude's Ann., 35, 500 (1911).

a thin film of silver transmits blue to green light it is probable that it can easily be made to reflect red light.

It is to be noted that the blue which is transmitted cannot be at all pure because Gallagher[1] has shown that when a blue film is precipitated on glass, and then a second superposed on the first and so on, the color changes from blue to yellow to red, which could not happen if the coefficients of absorption were not very different for different wave-lengths.

The very small particles of gold reflect green and transmit red, while those of silver reflect blue and transmit yellow. This shows that the phenomenon is specific, which is not in accordance with the views of Wolfgang Ostwald.[2] "The order in which the colors change from one to the other as the degree of dispersion changes seems also to be definite. As a rule, the most highly dispersed colloidal metals are yellow or orange; in other words, they absorb violet and blue light. As the degree of dispersion decreases, the color passes from yellow through orange to red, violet, blue and finally green. The absorption maximum gradually moves toward the side of the greater wave-length as the degree of dispersion decreases. The same order is frequently observed in organic dyestuffs, when the colors of any homologous series are studied. Yellow is usually the color of the chemically simpler members, while the dyes of greater molecular complexity in the same series are often blue and violet."

Since copper has a red surface color, it is natural that colloidal copper solutions should be red by transmitted light when the particles are very fine, and blue when the particles are coarser. The conditions for the brown and the olive-green solutions are probably very simple; but I have not had time to look up the literature on this point carefully, so I shall omit a discussion of them.

With metallic fogs, Wood[3] has obtained results similar

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[1] Jour. Phys. Chem., 10, 701 (1906).

[2] "Introduction to Theoretical and Applied Colloid Chemistry," 62 (1917).

[3] "Physical Optics," 639 (1911).

in principle to those of colloidal solutions. A condensing cloud of sodium vapor scatters violet light and transmits yellow, which, of course, it apparently ought not to do, because sodium vapor absorbs the D-lines and lets through blue. What happens is that we get resonance and the sodium particles transmit the yellow light which they absorb and reflect the blue or violet light which they do not absorb. Wood says that "it was difficult to understand this at first, since the vapor is perfectly transparent to blue light, and somewhat less so to yellow-green light. The cause was finally found to be a scattering of the violet and blue rays by the fog of condensing vapor, which was so powerful that none of these rays was transmitted." A potassium fog behaved similarly but scattered longer waves than the sodium fog. By regulating the conditions, it was possible to get a potassium fog to scatter red, yellow, and green rays, the blue being transmitted. This is not in accord with the fact that metallic sodium in sodium chloride transmits blue and that a colloidal solution of sodium in ether is blue by transmitted light.[1] There may be a confusion between transmitted and reflected light.

The scattering of light which is ordinarily transmitted has been shown well by Wood[2] in the case of an iodine fog. "In the course of some experiments on the fluorescence of iodine, the precipitation of what appeared to be an iodine fog in one of the glass bulbs was observed. This fog scattered powerfully light of a deep red color, and on examining it with a Nicol prism it was found to be plane-polarized in a direction at right angles to that which is usually observed in the case of light scattered by small particles. When a powerful beam of light was sent through the bulb in a horizontal direction, the scattered light came off at right angles, with its direction of vibration (electric vector) horizontal instead of vertical. If the light was polarized before it entered the bulb, the light was scattered laterally in the directions of the vibration in the incident light...... The best method of producing the

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[1] Svedberg: Ber. deutsch. chem. Ges., 38, 3616 (1905).

[2] "Physical Optics," 628 (1911).

colored fog is to precipitate the iodine upon a smoke-cloud already existing in the bulb....... The red fog persists for some time, once it is formed. When at its best, its scattering power is so great that a reddish color is seen within the bulb at a distance of a meter from the arc without any concentration. Examined by transmitted light in a well-lighted room, no trace of color is to be seen, which proves that the red light is selectively scattered and not produced by the absorption of iodine vapor. With the concentrated beam from the arc, the scattered light is blood red and of great intensity. A Nicol placed with its long diagonal horizontal nearly, but not quite, extinguishes it."

Wood[1] has obtained some very interesting results while working with heat waves of very great wave-length (110 μ), though it seems to me that his interpretation is not entirely satisfactory. Polished marble reflects over 40 percent of the radiation in question. When reduced to an impalpable powder, and pressed into a flat cake with a smooth surface, it was found to reflect practically nothing, though the irregularities of the surface were much too small to account for the absence of specular reflection. "The particles were apparently so small that the resonance necessary for selective reflection could no longer take place. Similar results had previously been obtained with films of very finely divided aniline dyes which showed colors quite different from those exhibited by continuous films. Metal powders were found to behave in the same way. A film was obtained by shaking reduced copper in a jar and then allowing the finely divided dust to settle from the air upon a quartz plate. This film was absolutely opaque for visible light, yet it transmitted 90 percent of the long-wave radiation, and reflected practically nothing. A continuous film of copper of much less thickness would reflect nearly 100 percent and be absolutely opaque to the radiation."

Wood considers that the particles are not resonating; but it seems to me that this is another case in which a granular material transmits by resonance the wave-lengths which it

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[1] "Physical Optics," 632 (1911).

ordinarily reflects selectively. There is no necessary contradiction in the two points of view because Wood is assuming that the particles are too small to reflect selectively by resonance and he is not considering the possibility of transmission by resonance.

There are a great many points in regard to the colors of colloidal metals on which I have not touched; but it seems to me that this qualitative, non-mathematical theory is more likely to be helpful as a guide to research than the more elaborate mathematical theories on which this is based. The general results of this paper are:

1. With very fine particles the light which is ordinarily reflected selectively is transmitted by resonance, while the light which is ordinarily transmitted is scattered.
2. Massive gold is red by multiple reflection and thin films are green by transmitted light. Very small particles reflect green and transmit red.
3. Massive gold reflects yellow when compact and brown to black when porous. Particles which do not resonate are yellow or brown by reflected light and transmit blue light.
4. Silver is yellow by multiple reflection and thin films are blue to green by transmitted light. Very small particles reflect blue and transmit yellow. Particles which do not resonate transmit blue (probably blue-green) light and reflect red. It should be determined experimentally whether compact silver reflects red light under suitable conditions.
5. The effect of porosity has been discussed only for gold. The matter should be studied experimentally with silver, copper, etc.
6. Colloidal indigo solutions transmit red light and the surface color of indigo is red.
7. Sodium fog scatters blue light and transmits the yellow which the vapor absorbs. There is an apparent contradiction with Svedberg's experiments on colloidal solutions of sodium in ether.
8. Iodine fog scatters red light.

Cornell University

ACTION OF FLUORINE ON ORGANIC COMPOUNDS[1]

BY BURR HUMISTON

The action of fluorine on organic compounds is usually very violent resulting in the total disintegration of the compound in question. In the case of hydrocarbons, hydrofluoric acid and carbon fluorides are formed. Saturated hydrocarbons such as paraffin and "Nujol" when exposed to undiluted fluorine burn with incandescence, giving free carbon and carbon fluorides as the reaction products. Many experiments were tried in this laboratory on the preparation of organic fluorides, the first work being on carbon fluorides.

Carbon and graphite are attacked by fluorine if in a granular or powdered condition. Moissan[2] gives the action of fluorine on lamp-black, charcoal, graphite, and diamond. He found that lamp-black and charcoal are easily attacked; but pieces of graphite must be brought almost to redness before the reaction sets in; while diamond does not lose weight when heated to redness in a Bunsen burner and then exposed to fluorine. He obtained a mixture of carbon fluorides in every case.

Fluorine was passed over approximately twenty grams of "filtchar" in a copper tube and the gases led into a test tube cooled to —80° by solid carbon dioxide and ether. Although the tube containing the charcoal was at room temperature, the reaction started as soon as the fluorine was passed in; and the temperature rose quickly. After about six hours fluorine came through the system and it was supposed that the carbon was entirely converted to fluoride. On opening the reaction tube it was found that a large portion of the carbon was covered with a gray dust which appeared to be mineral matter. This materially slowed down the action of the fluorine. Only ten grams of carbon fluoride were condensed whereas if all the fluorine which acted on the charcoal had gone to carbon

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[1] Published by permission of the Director of Chemical Warfare Service.

[2] Comptes rendus, 110, 276 (1890).

tetrafluoride, approximately 35 grams would have been formed.

The product condensed was a mixture of CF_4 which boils at —15° and C_2F_4 which boils at —32°. No attempt was made to condense the compound that distills below —80°.

Since the fluorides of carbon boil at so low a temperature it was thought that more satisfactory results could be obtained with selenium. Lebeau[1] found that SeF_4 boils at 100°. Prideaux[2] found a low-boiling selenium fluoride to which he assigns the formula SeF_6. Forty grams of selenium in small granules were placed in a reaction tube and fluorine passed in. The receiver was kept cold with ice and a secondary condenser cooled with solid carbon dioxide and ether placed next to it, to remove the last traces of selenium tetrafluoride. Fluorine was passed into the tube until all the selenium had been acted on. This was ascertained by the presence of fluorine at the mouth of the last receiver. But six grams of product were found in the condenser cooled with ice while theory calls for 97 gm. SeF_6 or 78 gm. SeF_4. No appreciable quantity was found in the condenser cooled with CO_2 and ether. As was the case with carbon most of the product could not be condensed above —80°.

If acetone in an open platinum dish be exposed to fluorine, the liquid quickly takes fire. In the first experiment fluorine and air saturated with acetone were brought together in a small copper tube which led to a test tube cooled in solid CO_2 and ether. Fluorine was noticed at all times at the mouth of the test tube used as condenser and to reduce this excess a larger percentage of acetone was sent in. An explosion resulted which wrecked the apparatus.

In the next experiment fluorine diluted with carbon dioxide was bubbled through acetone at room temperature. The dilution of fluorine was such that small explosions and burning did not take place at the mouth of the fluorine delivery tube. Fluorine appeared to dissolve in the liquid

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[1] Comptes rendus, 144, 1042 (1907).

[2] Jour. Chem. Soc., 84, 316 (1906).

and as the reaction proceeded, the liquid went from a deep yellow to a brown or black. Some low-boiling carbon fluoride was always found in the condenser cooled to —80°. The final product was distilled under reduced pressure. After distilling off the excess acetone, only a charred residue remained.

Further experiments were carried out keeping the acetone cooled with ice and using nitrogen in place of CO_2 as a diluent. The same results were obtained as in the previous experiment.

An attempt was next made to bring the vapors of acetone and fluorine together in fluorspar sand at 100°. Charring again resulted. If fluorine was passed for a long time a viscous, tarry product was obtained. It was observed that the glass apparatus was attacked showing that some hydrofluoric acid had been formed. Since the results with acetone were so unsatisfactory, it was decided to use a chlorinated compound.

Twenty-five grams of chloroform were placed in the same apparatus and fluorine passed at a rate of 2 grams per hour for 3 hours. A yellow liquid collected in the first flask. This appeared to be a mixture of chloroform, chlorine and phosgene. The liquid which condensed in the condenser at —80° boiled at —65°. It was a mixture of phosgene, chloroform and probably carbon fluoride.

An experiment similar to the above was carried out at a lower temperature. The reaction tube was cooled with ice and the chloroform was brought in as a vapor by bubbling nitrogen through it at a temperature of 40°. On distilling the product found in the first receiver, a 2 cc fraction that smelled like chloroform came over below 50°. In the condenser cooled with CO_2 and ether, 3 cc distilled over between —3° and 25°. This was largely phosgene. One cc distilled from 25° to 50°; the residue was a burnt tarry mass similar to that obtained in the experiments with acetone.

If fluorine be bubbled through Nujol at ordinary temperatures the reaction takes place with a brilliant flame and carbon is deposited.

If fluorine is bubbled through phosgene at six degrees there appears to be no action on the liquid. The vapor above the liquid was tested for the presence of fluorine by bringing an inverted gas jet near the vessel. The gas ignited and a small explosion took place which we assumed to be due to the reaction between phosgene and fluorine in the gaseous phase. This is the first evidence we have had that fluorine and phosgene react, and experiments were begun to study the reaction. The first experiment tried was heating phosgene vapor with a coil of nichrome wire in the presence of fluorine.[1] As the wire was exposed to both chlorine and fluorine at a temperature of approximately 200° it was rapidly attacked and disintegrated before either a reaction was detected or products were collected.

Phosgene and fluorine were next passed over granulated CaF_2 heated to 200°, in a glass tube. A product was condensed that boiled at —42°. With an excess of fluorine the color of the product was red; with an excess of phosgene it was yellow. On three occasions an explosion took place in the reaction tube or in the condenser wrecking the apparatus. For this reason a copper apparatus was set up and fluorine and phosgene passed as in the glass apparatus.

As no provision was made to take care of the chlorine that resulted both from the decomposition of the phosgene and the reaction a mixture was collected which contained a great deal of chlorine. Attempts were made to fractionate the product but with little success. To obviate the difficulty a condenser was put in the line ahead of the condenser that was to receive the pure product; the former condenser being maintained at —40°. A product was then collected that boiled at approximately —42° and had a molecular weight of 66.26. The molecular weight of COF_2 is 66, and it was thought that this compound was formed. It was analyzed for fluorine and but 9.75% was found. More of the product was made and a fraction collected that distilled below —52°. This likewise contained a relatively small amount of fluorine. There is unquestionably a reaction between phosgene and fluorine and it is probable that some COF_2 is formed. The product analyzed contained a large amount of chlorine and it is thought that it was a mixture of COF_2 and chlorine.

Carbon monoxide prepared by heating oxalic acid and sulphuric acid was passed through caustic and dried with sulphuric acid. It was then led into a quartz tube along with fluorine and exposed to ultraviolet light. No reaction was noticed nor were any products condensed at —80°.

Fluorine and carbon monoxide were then passed over Dorsey charcoal at 35°. The charcoal was first heated to 250-300° and allowed to cool while carbon monoxide was passing. Then fluorine and carbon monoxide were passed in together and the product condensed in a test tube at —80°. The charcoal became hot in the end where fluorine entered and small explosions could be heard. After running in fluorine at the rate of 3 grams per hour for four hours the condensing tube was examined and a colorless liquid found that boiled at —20°. As much of the carbon was used up there is no question but that it was largely carbon fluorides.

Since phosgene is not acted on by fluorine at low temperatures it suggests itself as a good solvent for diluting other organic substances on which it was desired to test the action of fluorine. The boiling point is so low however that considerable experimental difficulty is involved in its use. It was found that carbon tetrachloride was attacked but slightly at ordinary temperatures and so could be used more simply than phosgene.

Fifty grams of C_2Cl_4 were mixed with 100 grams of CCl_4 and fluorine passed into the solution. The mixture which was cooled with an ice bath, was stirred continuously with a mechanical stirrer. The solution was clear for a time but gradually blackened. Charring was rapid in case the solution was allowed to heat up. On distilling the product a considerable quantity of C_2Cl_6 was found. The experiment was repeated and the action was watched closely. It was found that chlorine was liberated giving a yellowish tinge to the solution that would disappear on standing. It was further noted that little charring took place at the start but as the amount of C_2Cl_6 increased the charring was quite marked. The action of fluorine on C_2Cl_6 alone dissolved in CCl_4 should be tried.

The action of fluorine on C_2Cl_4 is probably as follows:

$$C_2Cl_4 + 4F = C_2F_4 + 2Cl_2$$

The liberated chlorine then attacks the C_2Cl_4 forming C_2Cl_6,

$$C_2Cl_4 + Cl_2 = C_2Cl_6$$

while the ethylene tetrafluoride breaks down to carbon tetrafluoride and carbon.

$$C_2F_4 = CF_4 + C$$

It is also possible that the intermediate, instable compound is C_2F_6 but this seems less probable. This point was not determined.

The work was done in the Catalytic Laboratory of the Research Division.

TETRACHLORDINITROETHANE[1]

BY W. L. ARGO, E. M. JAMES AND J. L. DONNELLY

Tetrachlordinitroethane is a white, crystalline solid, insoluble in water, soluble in alcohol, ether, and ligroin. In ether and ligroin it decomposes at 60° with evolution of brown fumes. It is also very soluble in liquid N_2O_4 and somewhat less so in carbon tetrachloride. When pure, decomposition does not begin until the compound is heated about to its melting point, 142-143°. It is probable, though not proved that the behavior in ligroin is due to a difference in reaction velocity rather than to a difference in equilibrium. Tetrachlordinitroethane is toxic to mice at one-sixth the concentration for chlorpicrin. It produces lachrymation in man at one-eighth the concentration that chlorpicrin does. It is not stable when exploded in a three-inch shell, but would probably stand up satisfactorily if dissolved in chlorpicrin.

The only method of preparation described in the literature is that of Kolbe[2] who heated a mixture of nitrogen peroxide and tetrachlorethylene in a sealed tube at 110°-120° for three hours. The tube was opened, the excess N_2O_4 allowed to boil away, and the crystals of $C_2Cl_4(NO_2)_2$ collected and analyzed. Biltz[3] obtained a larger yield by heating for the same length of time to 100°-110°. We have obtained the best results at about 80°; but, even at this lower temperature, the pressure developed in the tube is apt to cause a violent explosion except when tubes of very small cross-section are used. The danger of explosion increases very much if the nitrogen peroxide is not dried by distillation over phosphorus pentoxide, as an oxidation takes place when moisture is present, giving rise to a high pressure even when the tubes are cooled in ice before being opened.

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[1] Published by permission of the Director of the Chemical Warfare Service.

[2] Ber. deutsch. chem. Ges., 2, 326 (1869).

[3] Ibid., 35, 1528 (1902).

Quantitative Study of the Reaction

The nitrogen peroxide was obtained by heating lead nitrate in a long, glass tube at about 400°, drying the evolved gases with P_2O_5, and liquefying the nitrogen peroxide by means of ice and hydrochloric acid. Liquid nitrogen peroxide was also prepared by the interaction of arsenic trioxide and nitric acid, and was furnished to us by the small Scale Manufacturing Section; but this had to be dried over phosphorus pentoxide before it would give satisfactory results. The tetrachlorethylene was obtained by cracking carbon tetrachloride.

Six small tubes of about 2 cc capacity were made by fusing ordinary 4 mm soda-glass tubing. Into each was introduced known weights of N_2O_4 and C_2Cl_4, so that three contained an excess of the former, and three an excess of the latter. In each case the volume of the liquid was approximately $^2/_3$ of the capacity of the tube.

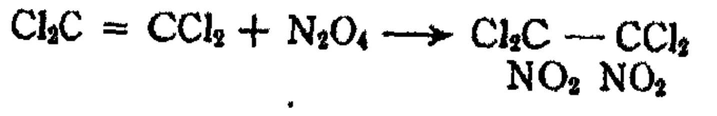
The tubes were divided into pairs, and heated in the water bath. The conditions and results of the experiment are summarized in Table I.

TABLE I

	Temp. °	Time of heating	Yield		Yield
			Theory	Obs.	
(1) N_2O_4 excess	60°	3 hrs.	0.867 g	0.311 g	35.9%
(2) C_2Cl_4 excess	60°	3 hrs.	1.472 g	0.317 g	21.4%
(3) N_2O_4 excess	60°	6 hrs.	1.085 g	0.486 g	44.8%
(4) C_2Cl_4 excess	60°	6 hrs.	1.563 g	0.524 g	33.5%
(5) N_2O_4 excess	80°	3 hrs.	0.716 g	0.570 g	79.5%
(6) C_2Cl_4 excess	80°	3 hrs.	1.152 g	0.758 g	65.8%

In every case a considerable pressure was observed on opening the tubes.

Since the production of tetrachlordinitroethane involves merely the addition of N_2O_4 to C_2Cl_4 and the opening of the double bond as follows:



$$Cl_2C = CCl_2 + N_2O_4 \longrightarrow \underset{NO_2}{Cl_2C} - \underset{NO_2}{CCl_2}$$

it is logical to assume that a diminution of pressure should result in the tube as the reaction progresses. This, as we discovered, was not the case. Nitrogen tetroxide is intermediate in composition between nitrous and nitric anhydride and reacts as follows with cold water:

$$O_2N - NO_2 + HOH \longrightarrow H_2NO_2 + HNO_3$$

If the water is heated, however, the unstable nitrous acid breaks down, giving nitric acid and nitric oxide.

$$\underset{\text{(heated)}}{3N_2O_4 + 2HOH} \longrightarrow 4HNO_3 + 2NO$$

Thus the presence of hot water vapor in the reaction mixture will produce HNO_3 and NO; and an oxidation of C_2Cl_4 with the production of phosgene becomes possible. This would account for the pressure developed.

Four tubes were prepared from 4 mm tubing, and the open ends drawn to a capillary, bent in the form of a U, so that any gas resulting from the heating could be collected over mercury. One cc of a mixture of equal volumes of N_2O and C_2Cl_4 was introduced into each. Two were carefully kept dry, but two were allowed to absorb moisture until the contents became blue when frozen. The conditions of the experiments and results are summarized in Table II.

TABLE II

	Temp.	Time	Volume of gas evolved
(1) Contents moist	60°	3 hrs.	35 cc
(2) Contents moist	60°	3 hrs.	40 cc
(3) Contents dry	60°	3 hrs.	15 cc
(4) Contents dry	60°	3 hrs.	20 cc

The evolved gas was colorless, insoluble in water, and developed a brown color with air. This supports our theory that a part at least of the pressure was due to NO, which resulted from the reaction with moisture.

Further precautions for drying the constituents were taken as follows: An H tube was made of 4 mm tubing.

One end was blown into a small bulb, and the whole carefully dried. A little P_2O_5 was placed in the bulb and covered with equal volumes of C_2Cl_4 and N_2O_4, previously dried over P_2O_5. The openings in the tube were then sealed and the liquid distilled to the second arm by gently heating the bulb, and freezing the second arm with CO_2 snow and ether. The connecting arm was then sealed, and the tube heated to 60° for three hours. It was cooled, opened, and the gases collected over mercury. About 3-5 cc of an inactive gas was evolved. This indicates that careful drying will eliminate the high pressure caused by the side reactions noted above. There remains then only the pressure of N_2O_4 to account for. Its vapor pressure at various temperatures are given in Table III.[1]

TABLE III

Temperature °C	Pressure, atmospheres
54.2	4.10
70.1	7.3
79.7	10.1
87.1	13.0
101.4	20.5
110.8	27.2

Autoclave Material

Since no porcelain-lined autoclave was available at first, a run was made in a phosphor-bronze autoclave. Accordingly 175 g. N_2O_4 and 320 g. C_2Cl_4 were placed in a tall beaker within the autoclave and the whole heated to 80° for three hours. A yield of 195 g. was obtained, 40 percent of the theoretical. The interior of the autoclave was badly corroded and it seems probable that the low yield was due to the nitrogen peroxide reacting with the metal.

We next attempted to use Bakelite varnish as a protective coating, but even when carefully baked it was almost completely destroyed as soon as subjected to the N_2O_4 vapors.

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[1] Zeit. phys. Chem., 81, 308.

We then tried placing the mixture of C_2Cl_4 in a large bottle, the mouth of which was loosely covered with a beaker. The whole was surrounded with sand and a top layer of iron filings. This method had to be abandoned on account of a very considerable loss of product by diffusion through the sand surrounding the reaction bottle.

An attempt was next made to find a metal sufficiently unaffected by N_2O_4. Small pieces of nichrome, copper, and iron wire, and spirals of copper and iron oxide were placed in tubes with N_2O_5 and P_2O_5, and heated to 80° both in the liquid and the vapor for three hours at 80°. The copper and copper oxide were badly attacked, and so heavy a pressure was developed that an attempt to open the tubes resulted in their being reduced to fragments No pressure was developed in the tubes with the nichrome, and the iron and iron oxide, The last two showed no evidence of being attacked, but the nichrome was badly pitted.

Since iron is apparently unattacked by dry N_2O_4, the following series of tests were made to determine the resistance of various kinds of iron when heated in a mixture of C_2Cl_4 and N_2O_4 at 80° for three hours. The results are summarized in Table IV.

TABLE IV

Iron	Condition of	Pressure developed	Condition of metal
(1) Steel	Mixture dry	Slight	Unattacked
(2) Steel	Mixture moist	Very high	Completely destroyed
(3) Wrought iron	Mixture moist	Very high	Completely destroyed
(4) Cast iron	Mixture dry	High	Badly attacked
(5) Wrought iron	Mixture dry		Unaffected

From the above results it seemed probable that a heavy-walled wrought-iron autoclave would prove satisfactory. Accordingly several runs were made using such a container but the efficiency was never better than 50 percent. Even with the most careful drying, the moisture absorbed by the C_2Cl_4-N_2O_4 mixture was sufficient to cause the walls to be badly attacked and hence to contaminate the product with iron. This autoclave was therefore abandoned.

Later a porcelain-lined autoclave was obtained; but it leaked and was not satisfactory. The maximum efficiency obtained in it was 65 percent; but it is believed that this could be increased very materially under more favorable conditions. In Table V are given the yields obtained in the later runs with the three autoclaves.

TABLE V

Autoclave	C_2Cl_4	N_2O_4	(Temperature 85°)		% Yield
			Time	Product	
Phosphor-bronze	300 g	150 g	3 hrs.	205 g	58%
Iron	320 g	300 g	6 hrs.	245 g	50%
Porcelain-lined	400 g	230 g	6 hrs.	410 g	65%

Effect of Catalysts

If the temperature at which the reaction takes place could be lowered by the use of a catalyst, the difficulty in regard to material of construction would probably disappear because nitrogen peroxide makes iron passive at ordinary temperatures.

Four sealed tubes, each containing an approximately equal amount of a mixture of dry perchlorethylene and N_2O_4, were prepared containing the catalysts noted below, and allowed to stand at room temperature for three days. The results are noted in Table VI.

TABLE VI

Catalyst	Amount produced
Purified Dorsey charcoal	Few white crystals
Powdered filtchar[1]	Few white crystals
$AlCl_3$	.....
$ZnCl_2$	.....

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[1] A commercial charcoal.

In no case was the amount produced equal to more than 1 to 2 percent of the theoretical.

Three more tubes were prepared, each containing approximately equal amounts of N_2O_4 and C_2Cl_4, the first two with Dorsey charcoal and filtchar, respectively, and the last without catalyst. They were heated 2 hours at 60° with the results summarized in Table VII.

TABLE VII

Catalyst	Temp.	Time	Wt. $C_2Cl_4N_2O_4$	% Yield
Dorsey charcoal	60°	2 hrs.	5–6 g	9
Filtchar	60°	2 hrs.	4–5 g	9
No catalyst	60°	2 hrs.	6–7 g	6

It is evident from the above results that the efficiency is affected but little by these catalysts.

A column of dried Dorsey charcoal contained in a wide tube, sealed at one end, was covered with anhydrous C_2Cl_4. The tube was surrounded with water at 80°. A reservoir, containing 150 cc of pure N_2O_4, was connected through a trap with a tube reaching to the bottom of the Dorsey column. The latter was provided with a reflux spiral condenser cooled with tap-water. The spiral was connected with another spiral condenser, cooled with water at 5° C, which returned the N_2O_4 liquid to the bottom of the reservoir. A bulb, containing P_2O_5 and open to the air, was sealed into the line immediately below the second condenser. By this means a continuous and rapid flow of gas was passed through the hot C_2Cl_4, and acted as an efficient stirring device for the catalyst. The run was continued for six hours, the apparatus disconnected, and the C_2Cl_4 and Dorsey charcoal separated. The volume of the liquid had increased, rising over 1 cm in the tube. Evaporation yielded 3–4 g of the product, 3 percent of the theoretical.

Although much N_2O_4 was lost through difficulties encountered in keeping the second condenser at a sufficiently low temperature, it seems evident that, even with perfect condensation of the peroxide, this method is impracticable since so long a run would be necessary to produce a noticeable amount of the compound.

It will be observed from the above experiment and others which have preceded it, that the reaction

$$C_2Cl_4 + N_2O_4 \longrightarrow C_2Cl_4N_2O_4$$

only proceeds smoothly under the following conditions:

(1) Temperature of 80°.

(2) Heating 3-6 hours.

(3) Pressure about 10-12 atmos. (See Table III, V. P. of N_2O_4.)

(4) Excess of *liquid* N_2O_4.

The last point indicates, as does the experiment just described, that the reaction takes place mainly in the liquid and not in the gaseous phase, and in consequence the most favorable conditions would be a small gas space, and an excess of N_2O_4, conditions which we were unable to produce in our autoclave on account of the difficulty of obtaining sufficiently large amounts of dry N_2O_4.

Solubility

It was found that 30 cc of dry N_2O_4, distilled from P_2O_5, will dissolve 15.7 g. of $C_2Cl_4(NO_2)_2$ at 0°. The solubility in superpalite and chorpicrin was not determined quantitatively but seemed to be of the same order.

Owing to the signing of the armistice, further work on the preparation and properties of tetrachlordinitroethane was discontinued. This work was begun while the Catalytic Laboratory was under the Bureau of Mines and was continued after the transfer to the War Department. It was carried out under the general supervision of W. D. Bancroft.

NEW BOOKS

The New Physiology. *By J. S. Haldane. 22 × 14 cm; pp. viii + 156. Philadelphia: J. B. Lippincott Company, 1919.* The present tendency illustrated by Loeb and his school, is to consider all physiological phenomena as purely problems in physics and chemistry. This was a natural reaction from the theory of vitalism. Haldane believes that we have gone too far along this line. He points out the immense complexity which one must assume for a given cell in the kidney, for instance, to develop and maintain itself so that it will have a structure which responds to the stimulus of a certain percentage of urea or sodium chloride in the blood and reacts in such a way that energy derived from oxidation is so directed as to perform the work of taking up urea or sodium chloride from the blood and transferring it against varying osmotic pressures from one side of the cell to the other. He prefers to introduce the conception of the living organism which is distinguished by the fact that in it what we recognize as specific structure is inseparably associated with what we recognize as specific activity. Its activity expresses itself in the development and maintenance of its structure, which is nothing but the expression of its activity.

This is a perfectly possible way of looking at things but does not get us ahead very far. The fact is that from any point of view we soon come to what appears to be a blank wall. For any given organism we may perhaps show that the response to any stimulus follows necessarily from the physical or chemical nature of the organism; but that does not tell us how the organism came to develop that particular structure. On the other hand we may say that the particular structure is developed necessarily by the living organism but that is not really explaining. It seems to the reviewer that it may perhaps be a very good thing to emphasize that a study of the physics and chemistry of physiology has not given the results that over-enthusiastic people may have claimed for it. Haldane does not really help us with the problem by his method of stating it and there is the danger that his deliberate vagueness may keep people from establishing quantitative results which can perfectly well be obtained now. In other words Haldane's destructive criticism is much better than his constructive work.

This volume is a series of addresses bringing out the same point of view. The single speeches are entitled: the relation of physiology to physics and chemistry; the place of biology in human knowledge and endeavor; the new physiology; the relation of physiology to medicine; the theory of development by natural selection; are physiological, biological, and psychological categories irreducible?

The last address is summarized by the author, p. 155, as follows: "When we make use of physical categories we are employing simplified maxims or principles which, on account of their simplicity, are very convenient for purposes of prediction, but which can only be used over a limited extent of our experience without gross error. When we attempt to apply them to biological or psychological phenomena, the error becomes apparent; we cannot express biological or psychological experience in terms of physical conceptions. In other words, we cannot reduce biological and psychological to physical categories. Similarly, in biology we are also employing relatively simplified maxims which enable us to predict another large class of phenomena, but cannot be applied to what we distinguish as psychological phenomena without gross error. Hence we cannot reduce psychological to biological categories." *Wilder D. Bancroft*

The Realities of Modern Science. *By John Mills. 21 × 15 cm; pp. x + 327. New York: The Macmillan Company, 1919. Price: $2.50.*—In the preface the author points out that physical science is so subdivided and classified that the sense of unity is obscured. This book is intended for the general reader who is interested in modern science. The titles of the chapters are: the beginning of knowledge; the machines of the ancients; weights and measures; the beginnings of science; the beginnings of experimentation; the realities of science; the molecular composition of matter; the electron; energy; some uses of mathematics; rates; force, a space rate of energy; molecular motions and temperature; motions of electrons; the interactions of moving electrons; the continuity and correspondence of molecular states; molecular mixtures; electrolytic dissociation; equilibria and their displacement; molecular magnitudes; molecular energy; electronic magnitudes.

Man is distinguished as being an animal which uses tools and fire. His first tools developed into machines. Weights and measures were introduced, including a subdivision of time. The introduction of scientific theory is credited to the Greeks on the ground that the Babylonians and the Egyptians merely accumulated data. Gilbert and Galileo are considered as the first logical experimenters in physics. The realities of science are said to be matter and energy. The atomic theory dates practically from Dalton and the molecular composition of matter is considered by the author as becoming firmly established about 1860. The electron of course goes back only to the last years of the nineteenth century. The ninth chapter deals with energy after which comes a chapter on the uses of mathematics. This makes it possible to consider velocity and force.

On p. 153 the author says: "Today the goal of the scientist is not an impossible perpetual motion machine but rather the efficient utilization of the available energy of the universe and that increase in availability which may follow further knowledge as to the composition of matter. Scientifically the aims are radically different, but socially they are identical, for in both cases the aim is to lift man above the struggle for existence. To understand more fully the present limitations which the scientist encounters in making available for man some of the untouched sources of energy in the universe, we need to consider the energy of molecules and electrons. In so far as the energy they possess is potential we are in ignorance of its very existence except in those cases where we have already learned to release it, as in various chemical or electrical actions. In so far as it is kinetic energy we may measure its amount even in cases where we do not as yet know how to utilize it. On the part of the molecules of a substance such a measurement is possible because the energy is manifested as heat."

On p. 183 the author says: "Conduction occurs as the result of the motion of electrons. This may be an actual motion or it may be a motion of what we might call certificates of electronic indebtedness. A positive ion is essentially a certificate of electronic indebtedness which may be transferred at will and may be satisfied at any point in the universe where there is an excess electron. (Sometimes the certificate will call for more than one electron, as is true of the ions of some liquids.) In the transfer of electricity, therefore, between two plates, say A and B, of which B is positive and A negative, it makes no difference whether the transfer is an actual one of electrons moving from A to B, or is accomplished by the motion of certificates of electronic indebtedness from B to A, or in any part by each method."

It is not quite clear what the author means when he says on p. 217: "The statement that matter is molecular in composition implies that no abrupt change takes place when a body of matter undergoes a change from one to another of the three forms—solid, liquid, and aeriform. The changes in state are successive, and continuous." So far as we know there is no critical point for solid and liquid, or for solid and solid. If the solid is polymerized and the vapor is not the change is discontinuous chemically as well as physically. One cannot be enthusiastic over the statement, p. 245, that since hydrogen and chlorine are evolved when a hydrochloric acid solution is electrolyzed, the dissociation which has made conduction possible is that of the hydrochloric acid rather than of the water. This line of reasoning would lead to trouble in the cases of caustic soda and of sulphuric acid, and did in fact mislead Faraday.

The chapters on molecular and electronic magnitudes are very good, and in the chapter on equilibria the author has laid especial stress upon the principle of LeChatelier-Braun. The book as a whole is a good one though not a great one. As might be expected, there is a good deal more physics than chemistry in it.

Wilder D. Bancroft

Qualitative Chemical Analysis. *By W. W. Scott. Third edition. 19 × 14 cm; pp. xi + 350. New York: D. Van Nostrand Co., 1918. Price: $2.50.*—In the preface the author says that the greater portion of the text has been rewritten and new material added, although the general plan of the original work has been retained. The book is divided into six parts: introductory physical chemistry; study of bases; study of radicals; method of analyzing an unknown; tables of reactions for acids and bases; the less common elements. The book contains an immense amount of information. The reviewer doubts whether it is helpful to the student to speak of Na_2^+ and Cl_2^-, or to say, p. 12: "Salts do not have to be extremely soluble to ionize; even a difficultly soluble salt such as silver chloride dissociates to a slight extent in pure water, *e. g.*, AgCl dissolve slightly and forms ions Ag^+ and Cl^-." The next three lines on the solubility product are not as clear as they might be. A more serious error is to include tungsten, tantalum, molybdenum, and tellurium in the hydrogen chloride group as metals whose ions unite with Cl^- to form insoluble chlorides.

Wilder D. Bancroft

An Introduction to the Physics and Chemistry of Colloids. *By Emil Hatschek. Third edition. 19 × 13 cm; pp. x + 116. Philadelphia: P. Blakiston's Son and Co., 1919. Price: $1.50.*—There are no important changes in this new edition so, it is only necessary to call attention to the fact that there is evidently a demand for such a book and that this book apparently meets the demand.

Wilder D. Bancroft

SOME STUDIES IN FONDANT MAKING

BY MARY STEPHENS CARRICK

The work to be reported in this paper was undertaken with two points in view: first, to establish a set of directions for making fondant whereby a standard product could always be obtained; and second to explain as far as possible the principles of the process involved. Fondant is made by heating sugar with water and acid, cooling the syrup, and then beating it vigorously. During the heating a portion of the sugar is inverted. It is usually assumed that, if one starts with a given amount of sugar and heats until a given boiling point is reached, the concentration of the final solution is fixed definitely; but this is not necessarily true because the boiling point will vary with the amount of invert sugar present. If the mixture were brought up sufficiently slowly to the final temperature, it would contain only invert sugar. If it is brought up very rapidly, it will contain a relatively small amount of invert sugar. Since relatively small changes in the amount of invert sugar have very marked effects on the quality of the fondant, it is evident that two people may get different results, depending on the size and shape of the pan and on the number and type of burners used. As a matter of fact the difference of boiling point with varying amounts of invert sugar is unimportant under ordinary conditions with the kind of thermometer ordinarily used.

In all the experiments ordinary tap water was used. This may be either hot or cold. The hot water simply dissolves the sugar more quickly. However, cold water was used in all of this work because that is always available.

Various acids were tried at first. Vinegar (acetic acid), lemon juice (citric acid) and cream of tartar (potassium acid tartrate). Cream of tartar was found to be the most desirable, first, because it gave a better texture to the finished product; second, it is a solid form and its composition is more constant than that of vinegar or lemon juice. The amount of acid used can, therefore, be measured more accurately. Third, the tartrate is easier to keep and inexpensive. For these reasons, cream of tartar was the acid used in all of these studies.

Proportion of Ingredients

One cup of sugar by measure was used in all experiments. The average weight of this amount of sugar is about 210 grams. To this weight of sugar varying amounts of water were added.

In the following tables the time of cooking was 15 minutes and the maximum temperature reached was 116° C:

TABLE I—SHOWING THE INFLUENCE OF VARIOUS AMOUNTS OF WATER

Serial No.	Sugar Wt. in grams	Water		Total measure before cooking	After cooking	
		Wt. in grams	Measure		Wt. grams	Measure
1	213.2	251.6	1 cup	1 1/2 cups	224.9	2/3 cup
2	210.7	180.2	3/4 cup	1 1/4 cups	228.3	2/3 cup
3	210.2	115.4	1/2 cup	1 cup	225.1	2/3 cup
4	210.6	59.9	1/4 cup	3/4 cup	229.5	2/3 cup

In the above table 0.30 gram of cream of tartar or 1/8 teaspoonful, and 1 cup of sugar, which varied slightly in the number of grams, were used in all four cases.

These data show that no matter what the amount of water used at the beginning, the total measure after cooking is the same. The differences in the total weight was also very slight. Subtracting the weight of sugar from the total weight after cooking, gives the amount of water in the finished product. The average amount of water present in the fondant is seen to be 15.7 grams, or about one tablespoonful.

Since there is a constant amount of water remaining in the fondant, obviously any difference in the resulting texture must be due to the hydrolysis caused by varying amounts of water and not in the final quantity of water present as such. The speed of inversion is proportionate to the concentration of hydrogen ions present.

A quantitative determination of serial No. 1 made with one cup of water was found to contain 7.88 percent invert sugar, while in No. 2, using 3/4 cup of water, 6.28 percent of invert sugar was formed. The product made from one cup of water was very sticky, due to too much hydrolysis. The most desirable amount was 3/4 cup of water and this gave a smooth, creamy texture to the fondant. Smaller amounts of water as shown in Nos. 3 and 4, were unsatisfactory because they rendered the material too stiff and hard. A smaller amount of water than 3/4 cup can be used if a longer time is allowed and the temperature during cooking is lowered. However, the purpose was to establish a minimum time and regulate the other conditions accordingly. The time element will be discussed later.

Using 3/4 cup of water, one cup of sugar, cooking for 15 minutes and not exceeding a temperature of 116° C, different amounts of cream of tartar were added. These amounts varied from 1/16 to one teaspoonful. Less than 1/8 teaspoonful did not cause sufficient hydrolysis to give the desired texture. More than 1/8 teaspoonful proved undesirable, first, because it formed too much invert sugar, resulting in a very sticky product; and second, because a presence of more than 1/8 teaspoonful of acid gave a disagreeable acid taste to the material. Under the standard conditions mentioned above, 1/8 teaspoonful of cream of tartar gives 6.28 percent invert sugar which amount seems to be the correct proportion to give the optimum taste and texture. If the amount of acid is increased, the hydrolysis is markedly increased. When 1/4 teaspoonful of cream of tartar was used 9.6 percent invert sugar was formed as compared with 6.28 percent invert sugar with 1/8 teaspoonful of acid.

In this connection it is interesting to note that a type of fondant can be made without the use of any acid. However, it is much less desirable than when the acid is added, for a number of reasons. First, because it requires a very much longer time of cooking to secure enough hydrolysis to give it a creamy texture. While the creaminess increases with the length of cooking, it is too slow to be practical. Fondant cooked for an hour to 116° C without acid was much less creamy than when cooked for 15 minutes with 1/8 teaspoonful of acid. When cooked for 15 minutes at 116° C without acid, only 0.45 percent invert sugar was obtained. Under the same conditions with 1/8 teaspoonful of acid, as already noted, 6.28 percent invert sugar was produced.

In the second place, non-acid fondant forms crystals while cooking. These crystals make lumps in the material which do not disappear on standing.

The third objection to fondant made without acid is its taste. The small amount of cream of tartar makes a less surfeiting substance than one in which there is no acid present.

In the fourth place, the lack of acid prevents the fondant from being kept to as good an advantage. This is true because it does not acquire smoothness on standing. This question will be taken up later under the change of texture on standing.

Method of Cooking

The ingredients in the proportions already established were placed in a container and stirred over a flame until melted. This stirring was a precaution against caramelization of the sugar in the bottom of the pan before the water penetrates the sugar. After the syrup began to boil, however, it was not stirred since the agitation might cause the mass to crystallize. Again, stirring would bring the concentrated sugar solution in contact with the sides of the vessel higher up than the boiling syrup. This higher temperature of the vessel would cause crystals to form by the constant drying out of the mixture. The process of boiling does this to a certain extent. Should the crystals, formed on the sides of the container, drop into the boiling syrup as it becomes more concentrated or should they be dislodged in pouring the cooked fondant over them into a plate, it would cause large, coarse crystals to form.

There are three ways in which crystal formation during cooking may be kept down to a minimum. First, the boiling at the beginning should be slow. Second, the cover should be kept on the vessel for the first three minutes. The steam will then dissolve the crystals as fast as they form. The best way, however, is to make a swab by wrapping a small piece of cheesecloth smoothly around a fork. Dip this into cold water and wipe down the crystals formed. Care should be taken not to stir the boiling liquid with the fork.

If in spite of these precautions some crystals have accumulated around the sides of the pan, the hot syrup should be strained through a fine sieve as poured out. This should prevent the growth of crystals in the cooling mixture.

A number of different temperatures for cooking fondant were used to determine, if possible, the optimum degree. The material was cooked from 112° C to 124° C, allowing a difference of 2° in each case. At 112° C the fondant was found to be too soft and sticky to use. This is caused by the presence of too much water. As the temperature was raised the fondant became harder and drier. At 116° C it seemed to give the more desirable texture. At this point about a tablespoonful of water remained in the mixture, as has been pointed out. It seemed better to get the additional softness of the final product from further hydrolysis rather than by the use of more water. With a standard temperature the amount of hydrolysis can be easily regulated by the length of time allowed for the syrup to reach that temperature. The disregard of this last point is the chief cause of failure in fondant making. The popular idea has been that it was entirely a question of concentrating the liquid and that a definite temperature implied a definite result.

In the following table, showing the length of time of cooking, the time was counted from the point at which the mixture was boiling rapidly, or when the thermometer registered 100° C.

TABLE II—SHOWING LENGTH OF TIME OF COOKING

Sugar = 1 cup
Water = 3/4 cup
Cream of tartar = 1/8 tablespoonful
Temperature = 116° C

Serial No.	Time in minutes	Results
1	7	Very sweet, smooth, but stiff
2	10	Less sweet, more creamy, easy to handle and only slightly stiff
3	15	More plastic than above; not too sticky to work and very desirable
4	20	More creamy than No. 3, too soft to work
5	25	Creamier than No. 4 with increasing softness
6	30	Creamier than No. 5, with still more softness

The above data indicate that the optimum length of time for cooking is 15 minutes. Seven minutes used in the first determination was the minimum length of time in which the 116° C could be reached. The gas burner employed contained 44 holes. On analysis 3.2 percent invert sugar was found to be present. This fact explains the sweetness of the taste. Invert sugar is less sweet than cane sugar but the amount here is too small to influence the taste.

The stiffness of the product is also accounted for by the limited amount of hydrolysis. Comparing Nos. 1 and 3, it is seen that the latter, as mentioned, gave 6.28 percent invert sugar, showing almost twice as much hydrolysis. Increasing the time to twenty minutes, 8.14 percent invert sugar was found to be present. This proved to be much too soft to work. A longer time still increased the stickiness. Discarding then, all periods of time longer than fifteen minutes as undesirable, tests were run for every two minutes between seven and fifteen minutes in order to study the intermediate products. Nine minutes and less gave fondant too stiff.

From eleven to fifteen minutes, there was very slight difference in the resulting texture.

From these observations it was concluded that any period of time from ten to fifteen minutes would give excellent results, the fifteen-minute period being slightly preferable.

By standardizing the time and temperature factors in the cooking process, that is, allowing fifteen minutes for the thermometer to reach 116° C, the variable conditions of the size and material of the container and the kind of burner, are eliminated. In the work reported here the burner described above, was turned on a little more than half cock.

After cooking, the syrup was allowed to stand in the pan until all bubbles disappeared from the surface. It was then poured into a plate to cool. The bubbles may cause crystallization. In a readily soluble substance like sucrose any decrease in temperature increases the saturation. Hence, checking the temperature by immediately removing the syrup from the stove and pouring it out while still full of bubbles, would favor crystallization.

The fondant could remain in the pan in which it was cooked and cool there, except for the time gained by more rapid cooling when poured in a shallow dish or plate. In the latter there is also liable to be less waste since it is easier to collect the fondant from a plate than from a deeper vessel. But in any case it should be allowed to cool gradually. Sudden cooling may cause spontaneous crystallization of the undesirable type.

It is necessary to beat the mixture to secure crystallization. This bears out the statement of Young[1] that a solution may be cooled to a temperature noticeably below its saturation temperature without the appearance of crystals of the solute and that mechanical impact is necessary to produce crystals. The stirring or beating acts in this capacity.

In the subsequent table, various lengths of time of beating are shown at temperatures beginning at 20° C and reaching 70° C. Above 70° C the crystals were so undesirable

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[1] Jour. Am. Chem. Soc., 23, 148 (1911).

that no data were recorded. The different temperatures were readily obtained by stirring the mixture over a water bath.

TABLE III—TEMPERATURE OF BEATING

Temperature	Time Minutes	Temperature	Time Minutes	Temperature	Time Minutes
70° C	12	70° C	4	70° C	2.5
65° C	3	65°	3	65°	2
60°	10	60°	3	60°	2
55°	7	55°	3.5	55°	3
50°	5	50°	3	50°	3
45°	3	45°	6	45°	3
40°	5	40°	6	40°	5
35°	7	35°	4	35°	10
30°	13	30°	15	30°	13
25°	23	25°	23	25°	23
20°	20	20°	20	20°	20

It was observed that the higher the temperature the more granular the mixture, due to the hastening of the chemical reaction by the heat. An attempt will not be made to explain why the crystals at the higher temperature formed so quickly. The data, however, show this to be the case. In general the cooler the mixture, the longer the time of beating, and the more creamy the texture. There appeared little difference between the temperatures of 30° C and 40° C. The slight gain in texture at 30° C was not commensurate with the length of time necessary to obtain them. At 35° C good results were obtained in a shorter time, but they could hardly be distinguished from those obtained at 40° C in a still shorter time. Considering that it only took five minutes to get crystals when stirred at 40° C and considering the almost equally desirable texture produced, this temperature is believed to be the optimum.

The lower temperature gave good results with an increasingly smooth texture, but in these instances too much time was employed. The colder the fondant the stiffer the syrup becomes and, hence, the more difficult to beat as well as requiring more time.

To determine the best manner of beating, three methods were tried. In all cases the conditions were the same, excepting the way in which the syrup was beaten. In the first method a wooden spoon was used in beating; in the second, a wooden spoon was used in stirring, making a vigorous circular movement; the third was the "cut in" method. A silver knife was used for this. The "cut in" process consists merely in scraping up the whole mass, folding it over and then cutting it through with a knife. This treatment was suggested by the recommendation of one writer who insisted that it was the only way in which an excellent product could be secured.

Nine determinations of each of the above methods were made. In treatments one and two there was no difference in the texture. In number three, however, in every case the texture was more granular and lacked creaminess. This seemed due to the slower and less vigorous movement employed. The first method was the quickest.

It was observed that in beating the thick syrup small bubbles of air were incorporated into the mass by the process of stirring. An infinitesimal number of these always accumulated before the crystallization began. There are two possible theories, on which to explain this phenomenon. First, there may be a momentarily increased saturation of the surface film, so that the solution is supersaturated with respect to the smallest possible sugar crystals. In the second place, the air incorporated may contain dust. This may start the crystallization. If this is true, dust must have the power of increasing the concentration in the film around the dust particle.

The Effect of Kneading

The usual procedure in making fondant is to beat it until the mixture is stiff and then knead with the hands into a soft, moist mass. Some experiments were carried out to show the necessity of kneading.

From the same cooking of fondant, one-half was kneaded and the other half placed away without kneading at all. On examination of the unkneaded material it was found to be much more sticky than the kneaded. To overcome this stickiness it was cooked to a higher temperature with the intention of removing a little more water. The syrup was cooked to 118° C, 120° C, and 122° C and allowed to cool to 40° C. It was then beaten. It was found that the higher temperature did not remove the stickiness in the unkneaded fondant. At 122° C it was too hard to work.

Later it was discovered that all the stickiness could be "kneaded out" after it had been put away for some time, if it was then kneaded. The product resulting from delayed kneading was identical with the product secured by immediate kneading. The conclusions from these observations were that if the fondant is kneaded before being placed away, little kneading is required when it is worked up later; if put away immediately after beating without kneading, very much more kneading will be necessary at the time of using. In either case, the kneading is necessary to remove the stickiness. It is merely a choice as to when the kneading shall be done, whether before or after standing.

The question then arose in regard to the amount of beating necessary when the fondant was placed away without kneading. The table below gives some data on this point in which the beating was continued from two to five minutes.

TABLE IV—SHOWING THE EFFECT OF THE LENGTH OF TIME OF BEATING ON TEXTURE

Time of cooking = 15 min.
Cooking temperature = 116° C
Temperature of beating = 40° C

Serial No.	Time of beating	Results
1	2	Very hard; a mass of syrup and large crystals
2	3	Excellent product but required longer kneading
3	4	As above but required less kneading
4	5	Harder than No. 3 but required same kneading

In this table the following materials were used in all instances: 1 cup of sugar; $^3/_4$ cup of water; $^1/_8$ tablespoonful of cream of tartar.

From these data it seems better to beat at least four minutes before pouring into a jar, if the material is first to stand without kneading. If beaten less than three minutes unsatisfactory results are obtained.

The Change of Texture on Standing

It has long been observed that fondant becomes more soft and creamy on standing. This fact was first accounted for by postulating that fondant takes up moisture. However, since the same effect is obtained when the material is kept in a moisture-proof container, evidently there must be some other explanation.

On the theory that the larger crystals are cemented together by the smaller ones, any change of temperature would tend to change the texture. If the temperature is raised, the smaller ones dissolve and the larger ones fall apart. This is equivalent to saying that the mass becomes more plastic. Proof of this theory was obtained by a very simple experiment. A square of loaf sugar was placed in a saturated sugar solution in which some sugar crystals were still left in the bottom of the flask. On standing for a week the loaf fell apart. This phenomenon is analogous to the change occurring in the texture of the fondant. The dissolving out of the small cementing crystals leaves the relatively larger crystals free to easily slip about in a syrupy mass. This also accounts for the ultimate disappearance of all lumps present in the freshly made fondant.

In the work on the influence of kneading and not kneading, it was observed that after three or four minutes of beating, the creamy mass was poured into a glass jar, it immediately became very stiff and hard. This was due to an interlocking of the crystals. On standing over night it became very sticky. This was because of the dissolving out of the cementing crystals as described above. The crystals which remain, not having been broken up by any kneading at the time of putting the fondant away, were necessarily larger than the largest ones in the kneaded material. Hence, there was more syrup medium to the surface of the crystals in the unkneaded fondant than in the kneaded fondant in which the crystals were smaller. And consequently, the unkneaded fondant would become even more plastic on standing than the kneaded. The "kneading out" of this excess plasticity is explained on the basis that kneading simply increases the surface of the crystals by breaking them up so that there is relatively less syrup medium to the surfaces; therefore, a less sticky mass. By this kneading, or increasing the surface of the crystals, all the stickiness can be removed from the unkneaded fondant. By the same process any small amount of stickiness found in the fondant, at the time of making, may be removed.

If the fondant is very sticky and longer kneading is required it is better to use a board and a knife as a breaking up of crystals evolves heat. As the fondant becomes warm it is necessary to let it stand long enough before proceeding further, since the heat tends to dissolve the crystals. It is not very desirable to "let it stand" in the hands. Stickiness due to the presence of too much water or to excess of hydrolysis cannot be "kneaded out."

Analysis of Fondant

In making fondant according to the preceding data, one would start with 210 grams (1 cup) of sugar, 180.2 grams (3/4 cup) of water and 0.3 gram (1/8 teaspoonful) of cream of tartar. This mixture should be cooked for 15 minutes until it reaches a temperature of 116° C. On this basis the finished material should contain 15.7 grams of water, 13.188 grams of invert sugar, 196.812 grams of sucrose and 0.30 gram of cream of tartar. This is assuming, however, that the cream of tartar acts as a catalyst and further, that 6.28 percent invert sugar is formed by the process and that this amount remains the same. At this temperature with the small amount of water present invert sugar is not likely to undergo further decomposition.

Knowing the above proportions, theoretically, it ought to be possible to obtain fondant by mixing these three ingredients together. The practical impossibility comes in not being able to dissolve this large amount of sugar in so small an amount of water. However, if sucrose is ground in a mortar to the degree of fineness of the crystals in fondant and to this is added commercial glucose in the proportion to give the one tablespoonful of water present in fondant, a fondant-like material can be made. The composition of commercial glucose is as follows: Water, 19 percent; glucose, 38.5 percent; dextrin, 42 percent; and ash, 0.5 percent. It can readily be seen from this that it would require about five tablespoonfuls of commercial glucose to keep the water content correct for one cup of sugar. This proportion was tried and a product was secured very much like fondant in texture, but the presence of the dextrin gave it a gum-like taste. This can be partly overcome by the addition of the usual amount of acid.

The question of making fondant without the use of heat is, indeed, an interesting one. Further work along this line may prove of considerable practical importance.

The summary of the foregoing study can best be stated in the recipe for fondant making given below.

Recipe for Fondant

1 cup of sugar; $^3/_4$ cup of water; $^1/_8$ teaspoonful of cream of tartar.

Directions for Making Fondant

1. Put sugar, water and cream of tartar in a container and stir over heat until melted.
2. Carefully remove all crystals from the side of the pan.
3. Allow 15 minutes for the syrup to reach a temperature of 116° C.
4. Remove from the heat without jarring and let stand until all bubbles leave the surface.
5. Pour slowly into a shallow platter.
6. Let stand until cooled to 40° C.
7.[1] Beat for at least 3 minutes after which it can be

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[1] If fondant is put away without kneading, this must be done when ready to use.

poured into a glass jar, covered closely and put away, or beaten until stiff.

8. Knead into a soft, moist mass and put away into a tightly closed glass jar and allow to stand at least 24 hours.

Acknowledgment

The author wishes to gratefully acknowledge her indebtedness to Professor W. D. Bancroft, Department of Chemistry, under whose immediate direction this work was done. His many helpful suggestions are incorporated throughout this study. Thanks are also due Professor Flora Rose, of the Home Economics Department, for her practical suggestions; Professor G. W. Cavanaugh, Department Agricultural Chemistry, who kindly made the determinations of the invert sugar present; and to Professor T. R. Briggs, Department of Chemistry, for the reading of the manuscript.

Cornell University, 1917

THE COLORS OF COLLOIDS. X

BY WILDER D. BANCROFT

Glasses and Glazes

Colored glasses may contain the coloring matter dissolved or in colloidal solution. This seems to be generally recognized because Heaton[1] says that colored glasses may be divided into classes:

1. Those in which the color is introduced by a colored compound of the metal in a state of solution in the glass; in this case the intensity of the color is proportional to the concentration of the solution of coloring material.
2. Those in which the color is due to the optical effect of minute particles held in suspension by the glass; here the color depends upon the size and distribution of the particles.

This is an admirable start; but it does not get us anywhere because we are not told, except casually, which glasses belong in the first class and which in the second. There is also a very great haziness as to the actual nature of the coloring matter in many cases. It will not be possible for me to clear up this matter from the data actually available; but a presentation of the subject will certainly be interesting and should be helpful.

With glasses colored by gold, silver, or copper we know that there is a second phase because the ultra-microscope shows it to us and because the characteristics of the glasses are those of colloidal solutions. The true ruby glass is colored by metallic gold[2] and has some very interesting properties. Fused glass containing a small amount of gold is colorless and remains colorless if cooled quickly. If cooled slowly or if reheated to a temperature well below the melting point, it becomes red owing to the separation of particles of gold of the size to transmit red light. If held too long at a high tem-

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[1] Thorpe: Dictionary of Applied Chemistry, 2, 721 (1918).

[2] Zsigmondy: "Colloids and the Ultra-microscope," 165 (1909).

perature the red color changes to a violet and then to a blue. These are exactly the changes that we get in aqueous solutions and for the same reason, the increase in the size of the particles. It is not quite clear, however, why the rapidly cooled glass should be colorless. The simplest explanation is to say that we have an unspecified salt of gold in true solution. This is the attitude of Wolfgang Ostwald.[1] "Ruby glass owes its red color to the presence of colloidal gold. I show you three specimens which are 'solid solutions' of gold in three very different characteristic degrees of dispersion. The first is an almost clear but slightly yellow mass of glass. This is obtained immediately after dissolving the solid gold salt in the glass. There is obtained in this way a molecularly dispersed solution of the gold in the glass and one which, in consequence, is ultra-microscopically empty. The second preparation is the ordinary ruby glass in which the gold is obtained in a colloidal state. The third specimen is deep blue by transmitted light and orange brown by reflected light. The specimen is also distinctly turbid. It springs from a failure in glass manufacture in that, presumably through a too long heating of the glass, a coagulation of the red gold particles to the more coarsely dispersed blue particles has taken place—just such a change as I showed you in an aqueous dispersing medium when I coagulated the red gold (produced through reduction of gold chloride by tannin) to blue gold through the addition of acid. These same facts as illustrated in the case of glass prove of what little importance is the kind of dispersing medium and how much depends upon the degree of dispersion in determining the variations in color of this substance."

The colorless glass cannot be due to the formation of a gold salt because the same phenomenon is observed when the glass is heated in a reducing atmosphere. Either the gold is in true solution in the glass or it has been peptized so that the colloidal particles are too small to have any effect upon the beam of light. Zsigmondy[2] believes that the colorless glass

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[1] "Theoretical and Applied Colloid Chemistry," 186 (1917).

[2] "Kolloidchemie," 28 (1912).

is a true solution of metallic gold in glass; but he does not give any satisfactory reason for this. It would be interesting to see how glasses richer in gold behaved when heated. The tinctorial power of the gold is very high, 0.01 percent giving a pink color and 0.1 percent a red. The number of colloidal particles is enormous, billions per cubic millimeter according to Zsigmondy. The smallest particles visible in the ultramicroscope have a mass of about 10^{-15} mg.

The cheaper form of ruby glass owes its color to colloidal copper and the red in some glazes is due to copper in some form. The Chinese ox-blood is believed by Lauth and Dutailly to be metallic copper in tin oxide. The copper oxide is reduced to metallic copper, this being dissolved in the glaze and imparting to it on cooling a copper-red color, while on more rapid cooling a colorless glaze is produced, which, however, becomes red on slow gradual heating. Seger[1] does not agree at all that the production of the red color is due to a segregation of metallic copper simply by a strongly reducing firing. His own experiments showed that alternately reducing and oxidizing conditions of the fire gases are required in order to produce the red color. The difficulties of the manufacture lie less in the composition of the glaze than in the composition of the fire gases. Using one and the same glaze, the shade of the color is subject to extraordinary fluctuations running from black through brown to sealing-wax red and light bluish green. Some pieces are colored differently on one side than on the other according to the intensity of the draft through the saggars. With the same glaze some burns may produce a beautiful color while others may not show any red color at all, everything coming out gray or black.

"Now let us see, how cuprous glazes behave in a reducing fire or fusing in a reducing gas, and let us first take such white-ware glazes free from lead, which beside copper oxide contain

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[1] Collected Writings, 2, 734 (1902).

no other metallic oxide that could be reduced. For example, a glaze having the stoichiometric composition

$$0.5Na_2O, 0.5CaO, 2.5SiO_2, 0.5B_2O_3,$$

a glaze which melts smooth at about the melting point of silver, and is made by fritting together

	Parts
Pure sodium carbonate	26.5
Marble	25.0
Ground quartz	75.0
Hydrous boric acid	31.0

and which, after the melting, is ground together with 1 percent of copper oxide. This mixture is put into a small porcelain crucible which is placed in a platinum crucible; the crucible is provided with a perforated porcelain lid and through the opening a thin, porcelain tube is introduced, as in the Rose reduction crucibles of the laboratories. The mixture is not put into the platinum crucible directly in order to prevent the platinum from alloying with the copper of the mixture.

"If we heat the glaze mixture in a stream of hydrogen or carbon monoxide introduced through the porcelain tube, to dark red heat, that is, to 400° or, at most, 500° C, the copper oxide is reduced and the glaze does not melt but is only fritted together. It has a red color caused by the copper segregated out.

"If we now apply a higher heat, maintaining a current of hydrogen or carbon monoxide, about to silver-melting heat—the highest temperature obtained by a Bunsen burner—the metallic copper disappears, the copper flakes dissolve in the melting glaze, the red color vanishes and the completely molten glaze has now received a greenish gray color. If we coarsely powder this gray mass and again melt it together with the same white glaze, to which a trifle of some oxidizing agent is added, say 1 percent of ferric oxide, stannic oxide, or a sulphate, like gypsum, but this time in a stream of air, in the crucible of the test kiln mentioned below, there is obtained a glass of a beautiful red color.

"We must attribute this reaction to the fact that by the oxidizing agents which are contained in the glaze free from copper, the black metallic copper enclosed in the copper glaze is changed to cuprous silicate and this imparts to the glass a red color, for the ingredients react as follows:

$$\begin{aligned} 2Cu + Fe_2O_3 &= Cu_2O + 2FeO \\ 2Cu + SnO_2 &= Cu_2O + SnO \\ 2Cu + SO_3 &= Cu_2O + SO_2 \end{aligned}$$

"The last reaction is remarkable, owing to the fact that a lively evolution of gas takes place in the fusion. If the glass is allowed to cool, before it has become entirely clear, thus still retaining some bubbles, the presence of sulphurous acid can be proved by the smell on opening the bubbles.

"If we now produce a glaze of a higher melting point, mixing the whiteware glaze given with the white porcelain glaze mentioned above,

$$\left.\begin{array}{l} 0.3K_2O \\ 0.7CaO \end{array}\right| 0.5Al_2O_3.4SiO_2,$$

we obtain a glaze which at silver-melting heat only vitrifies but does not fuse. This glaze consists of 25 parts of the above copper whiteware glaze and 75 parts of the porcelain glaze. If we heat this likewise in a crucible, as was done before, at a silver-melting heat, introducing hydrogen gas or carbon monoxide, we again obtain a gray vitrified mass. On heating this in air, that is, in the open crucible, we observe that it assumes after a short time a reddish brown or red color, which, however, fades quickly, and whose place is taken by a light green color. We also observe in this connection that the strongest reducing action of the gases produces a black color, since it causes the reduction to metallic copper; that on admission of air this changes to a red color; that the copper is first changed to cuprous silicate; and that finally the green color of the cupric silicate appears.

"If we heat the mixture more strongly over the blast-lamp, admitting a reducing gas, so that the glaze is fused, the mass thus formed remains gray in color and on heating in the air turns to a reddish color only on the surface, but in the interior it retains its gray color. On the vitrification of the glaze, further oxidation (and with it the red color) is excluded. A striking phenomenon is at the same time caused by the carbon deposited in the glaze. If the reduction is accomplished with illuminating gas instead of with hydrogen or carbon monoxide, a part of its carbon is deposited owing to the decomposition of the gas, which surrounds the glaze particles and thus prevents fusion. The glaze thus becomes apparently less fusible and retains its porous character even at the temperatures which lie above its melting point. If glazes, reduced in this manner, are heated in the air, the carbon is burned out, but at the same time the copper segregated out is also oxidized to cuprous oxide and the glaze is now enabled to fuse. In this manner red glazes are always produced.

"These experiments, performed in the crucible with pure reducing gases, were supplemented by others carried on in the test kiln, using a small test-kiln fired with gas. This little furnace not only increases the rapidity of the experiments, but it also enables the experimenter to effect alternate reducing and oxidizing kiln conditions quickly and to control them by gas analysis. As trial pieces there are used small cups of biscuit-burned porcelain body, coated with a glaze, composed of 25 parts of whiteware glaze compounded with 1 percent of copper oxide and 75 parts of porcelain glaze.

"On heating these in the kiln, first in an oxidizing flame, until a glow is just visible, then in a strongly reducing flame, so that about 10 percent of carbon monoxide is contained in the fire gases, up to a temperature not exceeding gold-melting heat, we observe on pulling small glazed trials from the kiln with a pair of tongs that the glaze as well as the body possesses a dark color due to the deposition of carbon.

"If we now allow the kiln to cool and do not close the damper so the air passes through the kiln for some time, we observe that the vitrified glaze coating has become beautifully red. When we fire under the same conditions, but higher, up to the temperature of cone No. 1, we obtain a fused glaze, gray in color, which, on properly melting the glaze in the oxidizing flame at about cone No. 1, changes more or less to reddish or brownish, but never assumes a fine red color. Repeating the same operation with another small porcelain cup, but with a lower content of carbon monoxide in the fire gases (2 to 3 percent) the gray color appears still more intensely.

"On firing a trial cup so that we first burn with a strongly reducing flame about up to silver-melting heat, and then burn alternately with a strongly reducing and oxidizing fire up to incipient fusion, about five minutes' reducing and two minutes' oxidizing, and after the fusion of the glaze finish the burning of the porcelain in the oxidizing flame, we obtain a fine red glaze. This red glaze is retained quite satisfactorily in the oxidizing fire after once it is fused and it can remain in the latter five to six hours without changing in color, though on the surface it may assume a pale green color due to oxidation. This nearly colorless, extremely thin surface coating produced by oxidation gives to the pottery a special charm. Only when the glaze is very thin is it possible that the change in color might extend through the entire thickness of the glaze on remaining in the oxidizing atmosphere for a longer time, and such thinly glazed places, as well as the edges, and the relief decoration under the glaze assume a green color.

"It is of special importance in the burning of the red glazed porcelain that the fire be very sooty. Between the saggar rings which form the stack of saggars, I have always inserted on top and at the bottom of the ring, at the height of the ware, three small pieces of fire-clay tile of 1.5 to 2 cm. in thickness, so that the flame was freely admitted to the ware, and could always draw freely through the saggars. The deposition of carbon from the fire gases has by no means the purpose of bringing about a very strong reducing effect, for the copper oxide is changed to copper even under weakly reducing conditions, but it should be the function of the carbon to retard the fusion of the glaze by depositing the soot in it. If now oxidizing conditions are suddenly brought about, avoiding neutral firing conditions as much as possible, the copper, during the burning out of the carbon from the glaze, again changes to cuprous oxide and is retained as such by the glaze which is fused soon after this change in firing. When the burning is accomplished without the deposition of soot on the surface of the ware, the red color will never develop, and the copper glaze always assumes a gray color since then the closing of the pores of the glaze is not retarded and the metallic copper segregated out is deprived of the possibility of reoxidizing to cuprous oxide.

"An experiment which I carried out endeavoring to burn a glaze, burning to a beautiful red with wood as fuel in a gas-fired kiln, using coke as a rule, failed entirely; gray colored ware was always obtained.

"Although on following the rules outlined above, a red color can be produced from every cuprous glaze in the crucible or in the small experimental furnace, the conditions in the large kiln are essentially different. It will not always be possible to produce a uniformly reducing atmosphere with a deposition of soot and it is especially difficult to produce strongly oxidizing conditions during a short time interval (one to two minutes); the red color in using any cuprous glaze will be obtained only rarely and in exceptional cases. But the production of the red color may be facilitated by imparting to the glaze a certain chemical and physical constitution.

"The means of accomplishing this purpose consist first of a small addition of ferric or stannic oxide, in order to be independent of the oxygen of the atmospheric air alone for the translation of the copper to cuprous oxide. These metallic oxides are likewise changed to ferrous oxide and stannous oxide, but their re-formation to the higher oxides takes place quickly and thus they are enabled to oxidize the copper. Although an addition of these oxides by no means prevents the formation of the gray color, yet in their presence the red color appears much more readily. The tin or iron oxide is best melted in quantities of not more than 2 percent, together with the copper oxide and the very fusible whiteware glaze which serves as a frit.

"The quantity of copper oxide which is used is also of great importance for the beauty of the color. In my many experiments I have always used a content of copper of from 0.5 to 1 percent and always obtained very good results. The more copper oxide there is in the glaze, the greater is the liability of some of the gray coloring metallic copper to remain in it and to change the sealing-wax-red color, which is produced by the pure cuprous oxide into a brownish color. With a content of 0.5 percent of copper oxide to 100 parts of the finished porcelain glaze, the glaze where it is colored red is perfectly opaque. For transparent red glazes which, on account of their transparency, receive a deeper red color similar to gold-ruby, I have always used 0.10 to 0.15 percent of copper oxide. With this content of copper oxide the glaze tends to produce green colors more readily, but at the same time the portions which have retained the red color are so much more beautiful. In regard to the quantity of the very fusible whiteware glaze (serving as a frit) necessary, this will always depend upon the temperature to which the body must be subjected in order to burn it to good porcelain. It may vary from 12 to 50 percent of the finished glaze. The more fusible the glaze is to be the lower in silica it must be kept, the smaller may be its quantity and the more beautiful will be the red color developed; the less fusible it is, the more difficult is the production of the red and the more readily will the gray color of the ware be shown. As to the composition of the porcelain glaze being a component of the glaze, I have discussed it in the introduction; other porcelain glazes may very well be used, but care must be taken that the mixture remains as porous as possible; fused porcelain glazes cannot be used for this purpose as they are too dense.

"Fluctuations in the composition of the white porcelain glaze are permissible according to the composition of the body, and the temperature it requires; care must be taken, however, that it does not vitrify at too high a temperature, which is controlled by the addition of a very fusible whiteware glaze. Whatever the composition of the glaze for the Chinese-red or ox-blood color may be, a satisfactory result will never be obtained if the firing is not directed in a suitable manner.

"After the ware is glazed, either by dipping or spraying, and has been set so that the smoke can reach it freely, at first, a fire as oxidizing as possible is maintained. As soon as a dark red heat shows in the kiln, as much smoke as possible is to be produced and continued up to a temperature at which the glaze commences to vitrify. This is followed by short periods of oxidizing fire, kept up at short intervals, about one to two minutes for each quarter of an hour; between these, however, a strongly reducing kiln atmosphere must prevail. This mode of firing must be continued until the glaze has become dense and somewhat glossy. Thereupon the burning may proceed with oxidizing or reducing kiln conditions up to the close of the burn. This method of burning, however, will not be easy to carry out in ordinary coal furnaces, especially will it not be possible, as a rule, to produce the oxidizing fire gases for so short a time without maintaining between time a longer or shorter period of neutral conditions. But in furnaces with inclined grates, fired with wood, one is enabled to produce such a change almost instantaneously by opening the air-passages beneath the charge of wood, and for this reason firing with wood will always remain the most satisfactory way of firing for the reproduction of red copper glazes, if for no other reason than that it, more than any other, permits of a uniform and intense evolution of smoke."

Stokes[1] has discussed the properties of a certain sample of glass colored by copper in a very thin stratum on one face. "By transmission it cut off a great deal of light and was bluish. By reflection, especially when the colorless face was next the eye, it showed a reddish light visible in all directions and hav-

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[1] "Mathematical and Physical Papers," 4, 245 (1904).

ing the appearance of coming from a fine precipitate, though it was not resolved by the microscope, at least with the power tried. It evidently came from a failure in an attempt to make one of the ordinary red glasses colored by suboxide of copper and the only question was as to the state in which the copper was present. It could not be oxide, for the quantity was too small to account for the blueness, and in fact the glass became sensibly colorless in the outer flame of a blow-pipe. Analysis of the transmitted light by the prism showed a small band of adsorption in the place of the band seen in those copper-red glasses which are not too deep and therefore a small portion of the copper was present in the state of suboxide, *i. e.*, a silicate of that base. The rest was doubtless present as metallic copper, arising from over-reduction in the manufacture; and accordingly the blue color, which would have been purer if the suboxide had been away, indicates the true color of copper by transmitted light, quite in conformity with what we have seen in the case of gold. Hence in both metals alike, the absorbing and the reflecting powers are, on the whole, greater for the less than for the more refrangible colors, the law of variation with refrangibility being of course somewhat different in the two cases."

Rosenhain[1] seems to be quite uncertain whether the color of copper ruby glass is due to metallic copper or to cuprous oxide. In Aventurine glass, the second phase comes out in spangles presumably of metallic copper. Zulkowski[2] believes that copper ruby glass owes its color to cuprous oxide; but the general opinion is against him,[3] though the evidence is not very conclusive. Zsigmondy[4] says in regard to this: "Colloidal copper is interesting because of its relation to copper ruby glass. The constitution of this glass has long been under dispute. Some authors have held that the copper

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[1] "Glass Manufacture," 182, 184 (1908).

[2] Jour. Soc. Chem. Ind., 16, 284 (1897).

[3] Williams: Trans. Am. Ceramic Soc., 16, 441 (1914); Thorpe: Dictionary of Applied Chemistry, 2, 721 (1918).

[4] "The Chemistry of Colloids," 127 (1917).

is in the form of cuprous oxide while others believe the free metal is present. The deciding of this point is scarcely possible by analysis; but light has been thrown on it since colloidal copper has been made having the same color as copper-ruby glass. Lottermoser[1] and Billitzer[2] obtained brown and Gutbier[3] blue hydrosols by the reduction of copper salts or by electrical disintegration. Paal and Leuze[4] have prepared both red and blue hydrosols by the reduction of colloidal copper oxide with hydrogen or hydrazine hydrate. The necessary copper oxide was made from copper sulphate to which potassium hydroxide and the sodium salt of lysalbinic or protalbinic acid had been added. The resulting dark blue liquid was dialyzed and evaporated. The reduction of copper oxide in the wet way by means of hydrazine takes place in two stages. At first an orange-colored milky liquid is obtained that doubtless contains cuprous oxide. On further reduction the liquid becomes clear and is colored deep red. Paal and Leuze obtained liquids in this manner that were quite black in reflected but deep red in transmitted light. This agrees perfectly with the color of copper ruby glass. The author was able to convince himself with a preparation of his own make that the red liquid gives the absorption lines near line D that are characteristic of copper ruby glass. The absorption lines are somewhat wider and the maximum is displaced slightly towards line C, which would indicate that a partial coagulation had set in, whereby flocculent complexes were formed, similar to the use of gold gelatine solutions on evaporation. Copper hydrosols should be investigated further with the ultra-microscope and also from the standpoint of spectrum analysis. Red copper hydrosol behaves differently, depending upon whether it is made with the sodium salt of protalbinic or lysalbinic acid. The first gives an olive green color with sodium chloride, a phenomenon that has been ob-

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[1] Jour. prakt. Chem., (2) **59**, 489 (1899).
[2] Ber. deutsch. chem. Ges., **35**, 1929 (1902).
[3] Zeit. anorg. Chem., **32**, 355 (1902).
[4] Ber. deutsch. chem. Ges., **39**, 1545, 1550 (1906).

served in the case of copper ruby glass. The second becomes blue when treated in a similar manner."

All that this shows is that colloidal copper may exist and that it is red, which nobody denies. The implied statement is that colloidal cuprous oxide is orange; but that is not necessarily true. Hydrous cuprous oxide is orange but anhydrous cuprous oxide is red and the colloidal precipitates would differ in the same way. The real question is whether cuprous oxide could exist as such in glass for there is no reason to suppose that cuprous silicate is red, although it must be admitted that anhydrous potassium cuprous chloride is red, which is a bit unexpected. So far as a red color with copper is concerned, it is not impossible that we may get metallic copper in one case and cuprous oxide in another; but it would be very important to know whether cuprous oxide can exist as such. This ought not to be difficult to determine experimentally because a cuprous silicate glass should be practically optically empty while a cuprous oxide glass should scatter light. Berry[1] reports on the occurrence of a red slag from a copper refinery containing some metallic copper but not much. Treatment with acids dissolved 27 percent Cu_2O, leaving a pale yellow slag containing 8.64 percent Cu_2O, 11.69 percent FeO and 49.24 percent SiO_2, the percentages referring to the original composition. Berry considers that the pale yellow is the resultant of green due to the iron and red due to the copper.

Rosenhain[2] says that silver is never introduced into glass mixtures, the reason being that it is so readily reduced to the metallic state from all its compounds that it cannot be retained in the glass except in a finely-divided form, causing the glass to assume a black metallic appearance resembling the stains produced by the reduction of lead in flint glasses. On the other hand, silver yields a beautiful yellow color when applied to glass as a surface stain and it is widely used for this purpose.

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[1] Am. Chem. Jour., 8, 429 (1887).

[2] "Glass Manufacture," 185 (1908).

This is not at all what Rosenhain really meant. Silver is not reduced so readily as gold and the trouble is not that it comes down in a finely divided state, but that it comes down in so coarse a form as to be pulverulent silver. The yellow stain is the color which the most faintly divided colloidal silver shows by transmitted light. The best yellow stain is obtained with potash-lime glasses. With the hard glasses silver tends to come down metallic. In the case of enamels, silver is added to the mass of the material.[1] Silver carbonate with bismuth oxide gives an intense blue. One function of the bismuth oxide is to hold the silver to the body; but it must also cause a partial agglomeration of the silver because the lustres are blue to green instead of yellow to brown. Experiments should be tried on precipitating silver oxide with bismuth oxide and then reducing the silver oxide, so as to keep the laboratory experiments in close connection with the technical methods. A yellow stain of silver on a blue cobalt enamel gives a green tint.

Platinum and iridium oxide can be used to give grays, especially in enamels, but they are expensive. Glass can be colored yellow by suspended carbon, the color of thin films of so-called carbon being yellow. Carbon cannot be used in lead glasses because of its reducing action.

Glasses containing no heavy metals are colored yellow to yellowish brown by sulphur; but this is apparently due to formation of polysulphides because these glasses are optically empty.[2] In calcium glasses addition of sulphur gives a blue color, apparently due to the presence of colloidal sulphur. We do not know at all why colloidal sulphur should ever be blue but apparently it may be. Wolfgang Ostwald[3] states that blue and green (colloidal?) solutions of sulphur can be obtained by introducing sulphur into molten sodium chloride, into a borax bead, into liquid ammonia or into hot organic liquids like glycerine. He considers that this blue colloidal

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[1] Franchet: Ann. Chim. Phys., (8) 9, 37 (1906).

[2] Fenaroli: Zeit. Kolloidchemie, 16, 53 (1915).

[3] "Theoretical and Applied Colloid Chemistry," 187 (1917).

sulphur is the cause of the blue color of ultramarine. "Of the many facts which confirm this view, I would like to emphasize the analogy between the production of ultramarine and the production of ruby glass, of blue rock salt, etc. In making ultramarine the necessary salts are melted together at high temperature. This yields the gray to white or yellowish 'mother of ultramarine.' This product is then reheated, cooled and reheated again, just as in the case of ruby glass, until the requisite color is obtained. The original product is obviously a molecularly dispersed solution, the particles of which, through reheating, are permitted to condense to colloid dimensions. Support for the correctness of this view may be found in mineralogy. Mineralogists are familiar with a complex sulphur-rich silicate compound known as hauynite, which appears in different colors ranging from colorless to green and blue. It has been shown that the colorless varieties may be colored blue or green by heating them with sulphur in a closed tube, an experiment entirely analogous to the production of blue rock salt by heating this with metallic sodium."

In strongly alkaline glasses selenium gives a chestnut brown color and the glasses are then optically empty.[1] In moderately alkaline glasses the color is red to pink and submicrons can be seen. Potash glasses give a purer red than soda glasses. If the red glasses are heated to 620°, the color becomes a pale brownish yellow. Sodium borate glasses containing selenium are often yellow, but turn red when annealed. Colloidal selenium solutions can easily be prepared which are red by transmitted light,[2] almost exactly the color of arterial blood.

Tellurium in low concentrations colors glass coral to purple-red, in higher concentrations a steel blue. I have not been able to find any reference to a coral-red colloidal tellurium, but the blue one is easy to obtain. In aqueous solution tellurium seems to come down either brown or blue. The blue

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[1] Fenaroli: Zeit. Kolloidchemie, 16, 53 (1915).

[2] Schulze: Jour. prakt. Chem., (2) 32, 390 (1885).

is obtained by reducing a dilute boiling mixture of sodium tellurate and sodium protalbinate with aqueous hydroxylamine hydrochloride. The reduction takes place slowly, the solution becoming first brown and then opaque and the color changing gradually to brownish violet, bluish violet and to indigo blue. It will clearly be necessary for somebody to make a red colloidal solution of tellurium or to show that the coral color is due to something else.

Enamels[1] are "vitreous compositions capable of adhering by fusion to the surface of metal or of pottery. The base of the enamel is generally a colorless glass in which are suspended particles of an opaque metallic oxide or salt generally stannic oxide. Up to about 900° tin dioxide exists finely suspended in the enamel, but at a higher temperature combination or solution may occur and opacity is diminished. Titanic oxide has been used in place of stannic oxide, and antimony compounds have been employed. Opacity may also be obtained by the use of arsenious oxide, calcium phosphate, cryolite, or fluorspar. A preparation known as artificial cryolite sometimes replaces the mineral. When bone-ash is used, a little nitre may be added to remove the color."

The opacity produced by these added white compounds is due to the difference in refractive index. Natural tin oxide for instance, has a much higher refractive index for yellow light than glass. While titania has been used as a substitute for stannic oxide, it is not a very good one because it gives a yellow tint. Haber[2] states that six million kilos of stannic acid a year were used for enamelling iron and that this amount was halved when people stopped mixing and melting the oxide with the other constituents of glass and merely added to it the enamel just before baking. In the old process a great deal of the stannic oxide was actually dissolved in the glass and consequently did not increase the opacity. Impure zirconia is now being used as a substitute for tin oxide in producing opacity. If the zirconia goes into solution as oxide or as

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[1] Thorpe: Dictionary of Applied Chemistry, 2, 333 (1918).

[2] Jour. Soc. Chem. Ind., 33, 49 (1914).

silicate, it does not cause opacity.[1] Of five crystalline titania glazes which were examined,[2] four contained rutile and one probably asgenite. Practically all the titania had crystallized. In a crystalline zinc glaze the crystals resembled willemite. An opaque yellow lead glass is obtained with antimony oxide, the second phase being apparently lead antimoniate, sometimes called Naples Yellow. The black lustre of the Greek and Roman pottery has been reproduced[3] in an oxidizing fire at 850° by fluxing 55 parts of quartz sand with 45 of sodium carbonate and grinding the frit with an equal weight of magnetite. Artificial ferroso-ferric oxide does not yield the black color which is probably enhanced by traces of manganese in the natural ore. The opacity of the enamel is caused by the presence of more stain than will dissolve in the flux. Franchet states that the black enamel was known to the Egyptians and consequently was not discovered by the Greeks. Foster[4] considers that ferrous iron, presumably as ferrous silicate, is the cause of the black color; but Franchet's experiments seem pretty conclusive.

According to Seger,[5] "bluish black paving and roofing tiles are made in the lower Rhine districts and in Flanders by a special process called blue-smoking. As soon as the finishing temperature has been reached the flues on top of the kiln arch are uncovered at the places where they connect with the openings in the arch, and the openings themselves (excepting two or three) are stopped tightly with bricks and clay. Thereupon green alder wood is charged into the firing flues, about eighteen sticks per burn for a kiln of the dimensions given, and the fire-holes as well as the ash-pit doors and the upper flue openings are walled up and daubed as rapidly as possible. The action of the heat on the green wood results in a large volume of gas and a thick smoke fills the entire kiln. These gases cannot burn since the necessary

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[1] Grünwald: Jour. Soc. Chem. Ind., **30**, 210 (1911).

[2] Endell: Jour. Soc. Chem. Ind., **30**, 210, 489 (1911).

[3] Franchet: Comptes rendus, **152**, 1097 (1911).

[4] Jour. Am. Chem. Soc., **32**, 1259 (1910).

[5] Collected Writings, **2**, 767, 802, 920 (1902).

air is lacking and they now burn partially at the expense of the oxygen taken from the ferric oxide of the clay; the red ferric oxide combinations are thus changed to the black ferrous compounds.

"Since this process through which the clay assumes the blackish blue color is reversed as soon as the evolution of gas from the wood ceases, the black ware is liable to turn red again as soon as air enters through the cracks of the kiln which can never be avoided. This is prevented by cooling the kiln as rapidly as possible after charging the wood, which is accomplished by evolving steam in the kiln from water poured on to the arch. In order to avoid a direct flow of water through the cracks of the kiln the sand covering the arch, the latter being 18 cm. thick, is moistened by sprinkling and is solidly tamped. Small dams of soft clay are put up around the arch holes and water is pumped or carried up so that it stands several centimeters deep on the arch and thus maintains a steady evolution of steam in the interior of the kiln which prevents the admission of air. It is obvious that such a radical procedure is bound to injure the kiln and arch seriously, and it is readily understood why the kilns undergo general repairs twice a year.

"The roofing tiles thus blue-smoked withstand weathering much better than the red ware, and for this reason the wise council of the city of Ghent has decreed that all roof areas fronting the streets must be covered with blue tiles, and the use of red tiles is permitted only for back buildings and the sides turned towards the yards.

"It is not absolutely necessary that alder wood be used for the process described; it may be replaced by other fuel, giving off a large volume of similar gases; for instance, the same effect could be produced by the introduction of coal-tar into the kiln, after the latter has been closed up air-tight; likewise in place of wetting the arch, the part of the kiln most easily injured, the kiln could be cooled rapidly by injecting a spray of water into the kiln, say, in the ash-pits."

"The manufacture of black vitrified bricks is one branch of the English brick industry, which has become very important in regard to brick architecture, though in Germany it appears to be entirely unknown thus far. The desire to employ these black bricks is spreading among us. Like the English architect, the German builder requires a black material to produce certain contrasts; but the material which the brickmaker furnishes for the purpose differs so much in the two countries that it is well worth the trouble to examine the difference more closely and see if anything of value can be drawn from the English process.

"Where black bricks are required for architectural ornament with us they are made by boiling ordinary face-brick in coal-tar. These bricks are no doubt improved in weathering qualities by the tar, but as dust soon collects on them they present an unsightly appearance; the original, intense, somewhat glossy black in time passes into a disagreeably dead color—a gray. Many such tar-coated bricks are also to be seen in England, as this method is cheap; but in the better class of brick structures their use is excluded and they are replaced by a material that is incomparably finer and more durable. Our medieval structures extensively employ brick coated with a black lead glaze for the same effect, but the glittering surfaces of glaze offend the eye. As regards appearance the English products stand midway between the two.

"The reader may recall the process of blue-smoking employed in the manufacture of black roofing tiles and brick and described in an account of the Belgian clay-working industry. A similar process is again met in English brickmaking, save that the effect of the dark color is enhanced by a kind of glaze possessing a matt luster, not to be confounded with the appearance of our glossy lead glazes.

"The process for the production of the brick in question, styled 'blue Staffordshire bricks,' or 'iron bricks,' from their appearance and hardness, has its home in the center of the Staffordshire potteries, and in the south, in Bishops-Waltham not far from Southampton. The clay used is a ferruginous but rather refractory clay; the bricks produced from it approach in appearance closest those known in the Berlin market as Rathenow bricks, or those that are made from a clay originating from the weathering of the red carboniferous sandstone in the Saarbrücken coal basin. The clay for the brick is generally well prepared, usually by slumming. To produce a denser and more finished surface the better grades of brick are always re-pressed. Burning is carried on to vitrification either in the ordinary Staffordshire kilns previously described or in smaller ones similar to them, of round shape about 3.5 meters in diameter and 2.5 meters high, arched over, and fitted with six fire-boxes distributed around the circumference, and four to six small chimneys set on the semi-circular crown for the exit of fire-gases. The bricks are set in them in such a manner that six flues are spared out, starting from the fire-boxes and meeting in the center in a vertical flue, and the faces which are intended to become black are left exposed in the setting. Thus for building purposes the bricks are set flat, for paving on edge, always so that those faces laid outward in the construction are left uncovered in the kiln.

"When the heat in the kiln has risen so high that the bricks have passed into the vitrified state, several shovels of salt are thrown into every flue. In the intense heat the salt vaporizes at once and covers the exposed faces of the brick with a very thin, hard glaze. At the same time a fresh charge of coal is supplied, and before the coal is completely ignited the fire-doors and chimneys are tightly closed and daubed up.

"The smoke thus produced has an effect similar to that in the blue-smoking of the Belgian roofing-tiles with alder wood, though it is less intense. A blackening of the clay to the depth of several millimeters due to the reduction of the iron takes place; this action is augmented by the fluxes from the salt fumes that are filling the kiln, and a very dense and hard coating, dull glazed, and of the appearance of graphite, is produced on the faces of the bricks, thus creating a perfectly weather-proof exterior. This process is employed with brick not for the sake of the color effect alone, but also on the most extensive scale for those products where the first consideration is resistance to weathering influences and mechanical abrasion, such as roofing and floor tiles."

"Some of the Rhine and Lorraine establishments make a yellow flooring tile, colored with iron, consisting of a plastic refractory clay with sand and a large amount of lime as a flux. When these are smoked in saggars, a very good black is obtained. The addition of calcium carbonate in the shape of chalk or similar material, not only adds a flux to the body but also prevents warping and makes possible the production of exact surfaces. Experiments have shown the remarkable fact that mixtures of fire-clay with chalk show a minimum shrinkage when there is about 25 percent of calcium carbonate."

Egyptian blue[1] is crystallized $CaO.CuO.4SiO_2$. It is formed between 800° and 900°, above 900° a green glass being obtained. The reaction is reversible, for blue crystals are formed if the green glass is held at 850°.

Glass can be colored yellow with colloidal cadmium sulphide and Horner[2] has produced a yellow of this sort in a boric acid bead. It really would be a good thing if somebody were to take up the whole question of colors in the borax bead so as to determine which were due to colloids and which to true solutions; and also to find out definitely what chemical compounds cause the color in each particular case.

Coming back to the glasses and glazes, we know that at certain concentrations of the coloring oxides, a second phase appears. Thus it is possible to make a chrome Aventurine glass in which one can see the second phase, though we do not know definitely whether the new phase is chromium oxide or a chromium silicate. It should be a relatively simple matter to settle this question once for all.

The general question of the ordinary coloring oxides in

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[1] Laurie: Proc. Roy. Soc., 89A, 418 (1914).

[2] Chem. News, 29, 66 (1874).

glass is a puzzling one, however. Spring[1] says that glasses colored by silicates of iron, chromium, manganese, and cobalt are optically empty, in which case they must be true solutions either of the oxides or of the silicates. On the other hand we have seen that stannic oxide, zirconia, titania, magnetite, and probably cuprous oxide can exist as second phases under certain conditions and it is consequently by no means certain that Spring's observations apply to all glasses. Wolfgang Ostwald[2] states that the artificial rubies owe their color presumably to a colloidal chromium as do the Alexandrites, etc.; but this is somewhat vague.

While it is very probable that many of the colored glasses are true solutions, the chemistry of the subject is so much up in the air and the problems have been side-stepped so skilfully in the books that it seems worth while to jot down some of the things that we do not know about the subject even though it may not come strictly under the heading of the colors of colloids. Iron usually colors glass green or yellow; in glazes one may get blacks, blues, browns and reds. If we consider the iron as dissolved in the glass we should expect to get a green with ferrous salts and a yellow with ferric salts by analogy with aqueous solutions and that is what we actually do get. There are difficulties in regard to this, however. While ferrous sulphate with seven of water is green, the salt with one of water is colorless and it is a question how far one is justified in reasoning from the aqueous solution to the silicate solution. Copper sulphate is blue when dissolved in water and green when dissolved in glycerine. The yellow color of the ferric salts is also a little troublesome because ordinary ferric oxide is red and the yellow is found usually as a hydrous form. This difficulty is not necessarily serious because a yellow ferric oxide is said to be obtained by the oxidation of ferric sulphide,[3] and we get yellow bricks when we burn a highly calcareous clay contain-

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[1] Rec. Trav. chim. Pays-Bas, **19**, 339 (1900).

[2] "Theoretical and Applied Colloid Chemistry," 186 (1917).

[3] Diamond: Jour. Soc. Chem. Ind., **37**, 451R (1918).

ing iron.[1] It seems probable that a finely-divided and porous ferric oxide may be yellow and not red though this has not yet been proved.

In glazes where the red color is due to iron, the ferric oxide is present as such and is not in solution. At high temperatures ferric oxide is instable and either breaks down or goes into solution. In the latter case it gives a pale yellow color. The stability at high temperatures is increased very much if the ferric oxide is mixed with chrome oxide. The native chrome iron ore has the composition $FeO.Cr_2O_3$, and is a magnetite in which the ferric oxide has been replaced by chromic oxide. The synthetic mixture probably does not form this compound at all. With high chromium content the color is greenish black and with increasing content of ferric oxide it passes through brownish black to reddish brown and then to a light yellow brown. As has been pointed out, one also gets a black with magnetite which is intensified by the presence of manganese oxide. We do not know to what the blue is due, though it is possible that a suitably finely divided magnetite might give a blue, in which case the cyanogen radical might not be the theoretically important factor in the ferrocyanide and ferricyanide blues.

Solutions of cobaltic salts are blue and so are concentrated solutions of cobaltous salts. It is quite possible that finely divided cobaltous oxide is blue. There is one characteristic of cobalt[2] which "causes difficulties in its use as an underglaze color, namely, that of taking up more oxygen on being heated in contact with air than corresponds to the blue oxide. At the moment of fusion the excess of oxygen is given off and is very apt to cause bloating of the glaze. The best protection against this danger consists in combining the cobalt with alumina. In this way a blue substance is obtained which is much less sensitive to a continued excess of oxygen as well as to reducing influences than pure cobalt oxide. The latter,

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[1] Keane: Jour. Phys. Chem., 20, 734 (1916); Scheetz: Ibid., 21, 570 (1917).

[2] Seger: Collected Writings, 2, 654 (1902).

as well as the cobalt oxide-alumina complex produce a dark blue color. If a light blue is desired, an addition of zinc oxide must be made. The more intense the ignition the lighter it will be. Various tints can be produced from the colors of the cobalt oxide by adding other metallic oxides. An addition of nickel oxide gives grayish blue tints as well as that of iron and manganese oxide, the latter two being less intense in their effect. Uranium oxide acts similarly. By means of chromium oxide all tints of bluish green can be obtained."

Manganese colors glass amethyst to violet.[1] "The full color is only developed when the manganese is in a fully oxidized condition (Mn^{IV}) and can be altered or discharged by introducing reducing substances." This sounds well, but it is a little confusing to turn to the article on "Manganese" and be told that the color of the amethyst[2] has been attributed to the presence of Mn_2O_3 and that pyrolusite has been used to form a black enamel. It is true that in the last case the MnO_2 is in suspension; but there seems to be nothing to show definitely to what the color of the amethystine glass is due. There is still a great deal to be done in the chemistry of the subject. Mixed oxides of manganese and iron give an amber to brown glass.

Schenck[3] found that when hydrous manganous oxide was precipitated with an excess of hydrous aluminum oxide and the mass heated, it was at first pink, as one would expect, and then changed to brown. He did not determine whether the brown color was due to manganous oxide or to a higher oxide.

Manganese oxide behaves to some extent like cobalt oxide, taking up oxygen to form a peroxide and losing the oxygen on fusion. This characteristic is less marked when the manganese oxide is precipitated with alumina or with

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[1] Thorpe: Dictionary of Applied Chemistry, 2, 721 (1918).

[2] See also Scholes: Jour. Ind. Eng. Chem., 7, 1037 (1915); Jour. Soc. Chem. Ind., 35, 318 (1916).

[3] Jour. Phys. Chem., 23, 283 (1919).

phosphoric acid and tin oxide; also when it is ignited strongly and thus made denser.

According to Wicks and Mellor[1] nickel oxide may give blue, green, yellow, and brown colors in glazes, the color varying with the composition of the glaze. Increase of alumina makes the color more stable, with a wider margin of safety in firing. Silica and boric acid deepen the tint and increase the solubility of the oxide. With the alkalies, nickel gives a brown tint which deepens in passing from lithium to potassium. The alkaline earths cause deepening of the brown from calcium to barium. Beryllium gives yellowish brown, magnesium green, and zinc blue. When used as underglaze, nickel colors are attacked by lead glazes, forming the common brown of nickel-lead silicate, which bears a similar relation to nickel-zinc blue, that violet cobalt silicate bears to Thenard's blue and Rinmann's green. The nickel colors are not very good.

Perry[2] reports that nickel oxide with basic oxides alone or with silica gives colors varying from pale brown to dark olive green. Magnesia produced a strong yellow green ($NiO : MgO$) and a brilliant light green when stannic oxide was added. Zinc with silica and nickel oxide gave a dark blue powder. Whatever the basic oxide present, introduction of alumina induced a light matt blue. Titania and nickel oxide with or without other basic oxides produced yellow. Stannic and zirconium oxides gave buff or brownish colors. When fired under glazes the behavior of these stains varied considerably. Colors made from nickel and another basic oxide gave straw brown. The higher the firing temperature and the more energetic the flux, the darker was the brown color produced. Addition of silica to the powders lightened the colors and imparted a greenish tinge. Blues produced by addition of alumina were very instable under the action of glazes. The zinc-silica dark blue was also instable under glaze. A high content of zinc in the glaze tended to preserve

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[1] Trans. Eng. Ceramic Soc., 13, 61 (1913).

[2] Ibid., 13, 67 (1913).

the alumina and zinc blues; but as soon as action began the color changed to gray and then to brown. Magnesia greens were also readily destroyed. Titania yellows were fairly stable both as regards firing temperatures and difference in glass compositions. The most stable colors were those produced by stannic and zirconium oxides. In all glazes of the earthenware type nickel tended to give a brown coloration and was only safe for underglaze use when brown tints were used.

Schenck found that when the hydrous oxides of nickel and aluminum are precipitated together the mass is green and turns yellow on heating. It is probable that with a higher nickel content the mass would have turned brown when heated. Nickelous oxide is said to be a green crystalline powder which turns yellow on heating. There is no special difficulty with the greens, yellows, and browns if we assume that finely divided nickelous oxide is green and that as it agglomerates, it becomes yellow and then brown, brown being merely a dark yellow. It is possible of course that the brown is due to the formation of nickelic oxide; but that is a point which can easily be settled experimentally.

The cause of the blue color is not known. The simplest explanation is to refer it to presence of cobalt in the nickel salt; but there are difficulties about that. Pence[1] worked with a nickel salt which he bought as free from cobalt though he did not test it himself. With increasing zinc content the color due to the nickel changed from brown through purple to blue. To complicate matters still further, the blue is said to be obtained under reducing conditions. It is, of course, possible, though not very probable, that very finely divided nickelous oxide is blue and not green; but that would have to be proved.

Cupric oxide gives blue or green. Solutions of most copper salts are blue and concentrated solutions of cupric chloride are green. From Schenck's experiments with copper oxide in alumina, it seems probable that finely divided copper

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[1] Trans. Am. Ceramic Soc., 14, 143 (1912).

oxide is blue. We do not know whether the blue color is due to dissolved copper oxide or to a cupric silicate and we do not know to what the green color is due; but there seems to be some regularities in connection with it. Boeck[1] found that a turquoise blue enamel from a Persian mosque owed its color to copper. When duplicating it in the laboratory, it was found necessary to add soda and potash in a definite ratio. Too much soda makes the color too green and too much potash makes it too blue. Since this was a tin oxide enamel, it is probable that the copper oxide was not present as a silicate. The Egyptian blue to which reference has been made changes to a green glass when heated above 850°. In order to facilitate the making of this compound alkalies were added to the mix. It would be very interesting to know whether the glass would be blue if only potash were used. Granger[2] reports that in a lime-soda or lime-potash glass, addition of a small amount of copper gives a blue which changes to green as the concentration of copper rises. Granger seems not to have noticed any specific difference between soda and potash. Substituting boric acid for silica gave first a peacock blue and then a greenish color. While there may be no connection, it is worth noting that the green due to ferrous salts becomes bluer[3] when potash salts are substituted for sodium ones.

Chromium oxide gives either green or reds. The green is what one would expect from the color of chromium solutions. If hydrous chromic oxide is peptized by caustic potash we get a beautiful green color. The chrome-pink has not been accounted for successfully. It was originally obtained with lime and stannic oxide, but can now be made in various ways. In regard to it Seger[4] says: "The red colors show many peculiarities which must be considered. They are obtained when a small addition of potassium bichromate is made to a mixture of marble and tin oxide, and the mass is ignited

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[1] Jour. prakt. Chem., (2) 40, 158 (1889).
[2] Bull. Soc. chim. Paris, (4) 15, 116 (1914).
[3] Thorpe: Dictionary of Applied Chemistry, 2, 721 (1918).
[4] Collected Writings, 2, 654 (1902).

strongly. Quite a number of salts besides potassium chromate produce the same effect, but it is safest to work with this one. If too much potassium chromate is used (over 3–4 percent) the resisting power of the underglaze color is decreased considerably. If silica is added to the mixture, the color turns towards red and towards lilac if the lime is decreased, while the color becomes a pure lilac if the lime is omitted entirely. A very strong fire is necessary. The red chromium colors require oxidizing conditions and are destroyed by reduction though restored on continued oxidation."

Mellor[1] says that the tint of chrome-tin pink is the same no matter what chromium compound one starts with, provided the mass is not underfired. Ramsden[2] says that lime is essential to the chromium red glaze to prevent decomposition of the stain. The basic oxides in the glaze should consist largely of lead oxide which helps to form a translucent yellow glass imparting a blood-red tint to the crimson stain. This does not sound as though the color were due to basic lead chromate or anything of that sort. On the other hand, Büttner[3] seems to take the other view because he says that only small amounts of the alkalies and alkaline earths can be introduced into a red glaze containing CrO_3 because chromium trioxide plays the part of an acid only in presence of much lead. If too much silica is present, green and yellow tones appear. The fact that the color is due to oxidation is brought out by Rhead,[4] who states that a green glass is obtained if a mass corresponding to a complex chrome pink formula is melted in a fritt kiln, whereas the red is developed in a muffle kiln. While tin oxide is the usual thing for getting a chrome pink, Watts[5] states that in an oxidizing atmosphere chromic oxide with alumina gives a pink with some gray in it. Addition of zinc oxide improves the color giving finally a delicate

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[1] Trans. Eng. Ceramic Soc., 15, 131 (1915).
[2] Jour. Franklin Inst., 177, 263 (1914).
[3] Jour. Soc. Chem. Ind., 30, 1386 (1911).
[4] Trans. Am. Ceramic Soc., 13, 324 (1911).
[5] Ibid., 13, 301 (1911).

peach-blow pink. Boric acid counteracts the effect of zinc oxide. Under reducing conditions a bright chrome green is obtained. Too much alumina destroys the crimson color.[1] Glasses rich in silica tend to acquire a green tint. At cone 0.5 the order of oxides is CaO, Bi_2O_3, PbO, B_2O_3, SiO_2, Na_2O, K_2O, and Al_2O_3, the lime is being the most favorable to the production of the red color. Starting with Al_2O_3, the oxides become more harmful to the red color in the following order: Al_2O_3, BaO, ZnO, SrO, P_2O_5, MgO, and Sb_2O_3, the oxide of antimony being much the worst.

With alumina and silica constant[2] an increase of boric acid changes the color from a raspberry red to a cherry red. In the overburned glazes containing boric acid, a second boiling or evolution of gas takes place and a green is formed. Glazes in which lead replaces calcium change from raspberry red to a lilac when properly matured. In overfired glazes lead has practically the same effect as boric acid, the production of green or mottled green or red colors.

Purdy[3] reports that brown pinks and brown reds are obtained with high lime; lilac pinks and reds with low lime. Pure pinks and reds are obtained only with the equivalents of CaO 2.0 and 1.5 in the stain. With increase in chromium in the Cr_2O_3 and $K_2Cr_2O_7$ stain glazes, the tints pass from pink to red and then to green, while in the lead chromate glazes the tints pass from pink to brown reds. The best reds were obtained with $K_2Cr_2O_7$ and the darkest pure red with Cr_2O_3 and lead chromate.

From all this it is certain that the chrome pink is due to an oxide of chromium higher than chromic oxide and that the color is not due to a chromate; but that is about all we know. Silverman[4] has made a green chromium glass which is red in greater thickness; but this can hardly have anything to do with the problem of the chrome pink because that is ob-

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[1] Ramsden: Jour. Franklin Inst., **177**, 263 (1914).

[2] Radcliffe and Walduck: Trans. Am. Ceramic Soc., **17**, 278 (1915).

[3] Trans. Am. Ceramic Soc., **14**, 172 (1912).

[4] *Ibid.*, **16**, 548 (1914).

tained in glasses low in chromium. Increasing the chromium content makes the glass green. The most plausible hypothesis seems to be that the color is due to chromic anhydride, CrO_3; but in that case it must be stabilized by something. This is quite possible, for the color develops only in the presence of stannic oxide or some similar substance, which would naturally increase the stability. Also Heidingsfeld[1] gives a formula for a chrome pink which is said to be stable at higher temperatures than usual and which is essentially a chrome alumina containing iron. This is interesting because we have already seen that chromic oxide stabilizes ferric oxide. The important thing, however, to keep in mind is that we have no proof of what actually causes the pink color and that the best we can do is to guess.

Of course it is possible to postulate hypothetical compounds in difficult cases and to let it go at that. We can say that cobalt aluminate is blue, that cobalt zincate is green, that cobalt magnesiate is pink, just as we say that potassium cobalto-nitrite is yellow; but to do that one should show that the definite compounds exist and that they do account for the color changes. That has not been done and we are left with such empirical summaries[2] as the following: "With chrome-alumina calcium gives a fine green while calcium and barium give dark green. Calcium and increasing amounts of zinc give pink to brownish shades. Calcium and magnesium give brown shades, while calcium and lead give fine bright greens. Zinc alone gives light fawn shades, zinc and barium give brown shades, zinc and magnesium give pinkish browns, while zinc and lead give brown and strong pink shades. Barium alone produces yellowish or hedge apple greens, while barium and magnesium give grayish colors. Magnesium alone produces fawn shades and seems to exert a stronger effect upon Cr_2O_3 than zinc does."

The actual experimenting is not difficult because one does not have to work with actual glasses and glazes. One

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[1] Trans. Am. Ceramic Soc., 15, 140 (1913).

[2] Minton: Ibid., 16, 248 (1914).

can start with borax and phosphate beads and one can precipitate the oxides together, the hydrous oxides of alumina, tin, zinc, and magnesium. That would give fairly definite substances which could be analyzed and to which one could apply the phase rule. It is work that anybody could do anywhere and it would be certain to increase our knowledge very much. It is not merely a problem of the ceramic industry. We tell the freshmen every year that manganese colors glass pink and we ought to know something about the chemistry of it.

The general results of this paper are as follows:

1. In glasses and glazes, gold, silver, copper, platinum, iridium oxide, selenium, tellurium, sulphur, carbon, lead antimoniate, magnetite, ferric oxide, stannic oxide, zirconium oxide, titanium oxide, arsenious oxide, calcium phosphate, and cryolite occur usually as a second phase. Chromium occurs in some form as a second phase in chrome Aventurine glass and copper in Egyptian blue.

2. Some glasses colored by iron, chromium, maganese, and cobalt are optically empty. In the enamels the coloring matter is probably chiefly adsorbed by the substance causing the opacity.

3. We do not know what compound produces the pink color with manganese or with chromium. Some of the nickel colors are unexplained, notably the blue. We have no satisfactory way of accounting for the copper glazes being blue in one case and green in another.

4. We cannot predict that cobalt will give a blue with alumina, a green with zinc oxide, and a pink with magnesia.

5. The whole subject of the coloring materials in glasses and glazes needs a careful revision so that the chemistry of it can be put on a sound scientific basis, which is not the case at present.

Cornell University

EMULSIFICATION BY ADSORPTION AT AN OIL-WATER INTERFACE[1]

BY S. E. SHEPPARD

In the course of some experimental work it was desired to prepare a relatively fine grained and stable emulsion of nitro-benzene in aqueous sulphuric and hydrochloric acids, respectively. Certain ultimate conditions of the problem precluded the use of ordinary emulgents (protective colloids, as gelatine, gum arabic, etc.), or of finely divided powders, as used in Pickering's experiments, even if it should be possible to use these with relatively strong acids present.

On considering the theoretical conditions for stable emulsification, it appeared that there were two principal conditions favoring stability, provided a fine subdivision of phase were brought about mechanically.

These conditions are:

1. Approximate equality of the specific gravity of the two phases.
2. Formation of a zone of chemical instability at the boundary or interface.

The presence of a protective colloid of the first type tends automatically to fulfil the second condition. Further, it appears probable that the emulsifying effect of finely divided solids (Pickering) involves more than their mechanical aggregation about an oil particle, that is, it involves their surface catalytic and adsorptive power. In the present case the attempt was made to satisfy the second condition outlined, and influence the interfacial tension, by loading the continuous or external phase (aqueous acid solution) with salts likely to be adsorbed, above all, as incompletely formed complexes, at the interface. This attempt, in combination with specific gravity equalization, was fairly successful. It was found in fact possible in

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[1] Communication No. 82 from the Research Laboratory of Eastman Kodak Company.

this way to prepare quite stable emulsions of nitro-benzene in sulphuric and hydrochloric acid solutions.

In the following table, r. t. is the time of separation into distinct phases and hence a measure of stability:

SERIES I

System	Nitro-benzene Water Sulphuric acid				
No.	Temp.	S. G. Nitro-benzene	S. G. H_2SO_4 aq.	% by vol. of nitro-benzene	r. t.
1	15° C	1.230	1.140	50	3 mins.
2	15° C	1.230	1.230	50	30 mins.

It will be seen that equalization of the gravities favors stability.

SERIES II

Using equal density nitro-benzene and sulphuric acid, various colloid emulgents were tried.

No.	Temp	Emulgent	% by volume nitro-benzene	r. t.
1	25° C	1% tannin	50	2 mins.
2	25° C	½% dextrin	50	2 mins.
3	25° C	1% dextrin	50	12 mins.
4	25° C	1% gum arabic	50	12 mins.
5	25° C	1% carragheen moss	50	6 mins.
6	25° C	2% gelatine	50	30 mins.
7	25° C	2% lampblack	50	5 mins.

In all cases except with gelatine the emulgent was coagulated and thrown down.

SERIES III

Experiments were now tried with salts of low solubility in water but likely to form complexes with the acids.

No.	Temp.	Addition	% nitro-benzene	r. t.
1	25° C	$CaSO_4$ to saturation	50%	730′ to ∞
2	25° C	$PbSO_4$ to saturation in distilled water	50%	730′ to ∞

In each case, the solution was made up to equal gravity. The emulsions formed were only relatively stable, *i. e.*, on standing were indefinitely slow in separating, but demulsified more readily on slowly shaking.

Series IV

In this hydrochloric acid s. g. 1.19 was used, saturated with the respective additions.

No.	Temp.	Addition	% nitro-benzene	r. t.
1	25°	Nil	50%	2 mins.
2	25°	NaCl	50	2 mins.
3	25°	$PbCl_2$	50	∞

The emulsion No. 3 in course of two months aged to a relatively stable but coarse grained system, quite visible to the eye, and partially separating, as shown in Fig. 1. Before noticing more fully some properties of the outer layer of the globules formed, the influence of some other factors may be presented.

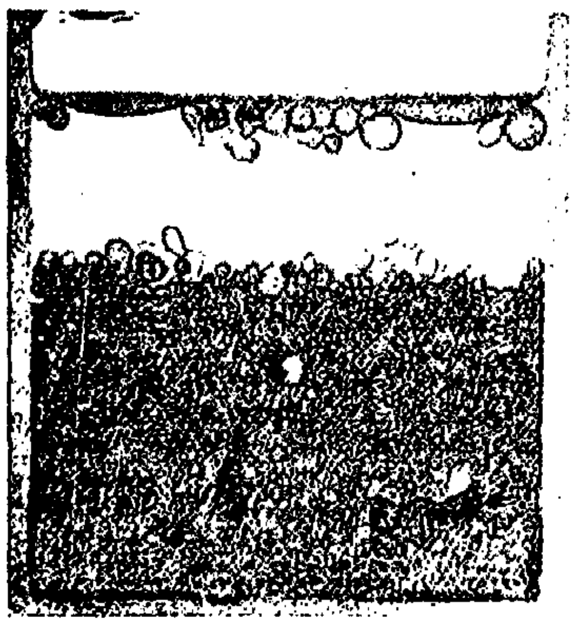

Fig. 1

Influence of Relative Proportions of Acid and Oil

SERIES V

Addition: Water saturated with $PbSO_4$ made to equal gravity with H_2SO_4.

No.	Temp.	S. G.	% by vol. nitro-benzene	r. t.
1	25° C	1.23	5	30 mins.
2	25° C	1.23	10	30 mins.
3	25° C	1.23	25	30 mins.
4	25° C	1.23	40	30 mins.
5	25° C	1.23	45	∞
6	25° C	1.23	50	∞

The relative proportions thus had a marked influence on the stability, which increased greatly in the neighborhood of equal parts by volume.

Influence of Frequency and Duration of Shaking

In the early experiments shaking was done by hand in cylinders, for a period of three minutes. Experiments with a mechanical shaker showed no appreciable difference in result for thirty to one hundred oscillations per minute, nor for times from five to thirty minutes, the stability appearing the same. That an influence exists, particularly on ageing, appears certain, but it is difficult to define.[1] Demulsification was accelerated by slow shaking or even a single vibration in certain cases, for emulsions which remained stable at rest, while shaking gently at a slightly higher frequency would re-emulsify to a system again stable at rest.

On the Nature of the Interface

In the original emulsions (all of which were of the oil in water type) no evidence of separation of a new phase at the interface could be observed. In the aged, granular systems, however, the globules appeared to be covered with semi-

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[1] Cf. also W. D. Bancroft and Newmann: "Experiments on Emulsions," Jour. Phys. Chem., 18, 41 (1914).

elastic membrane or skin, as shown in the micro-photograph at 10 X in Fig. 2.

Fig. 2

On still higher magnification (100X) this membrane is seen to consist of or contain small particles (Fig. 3). As

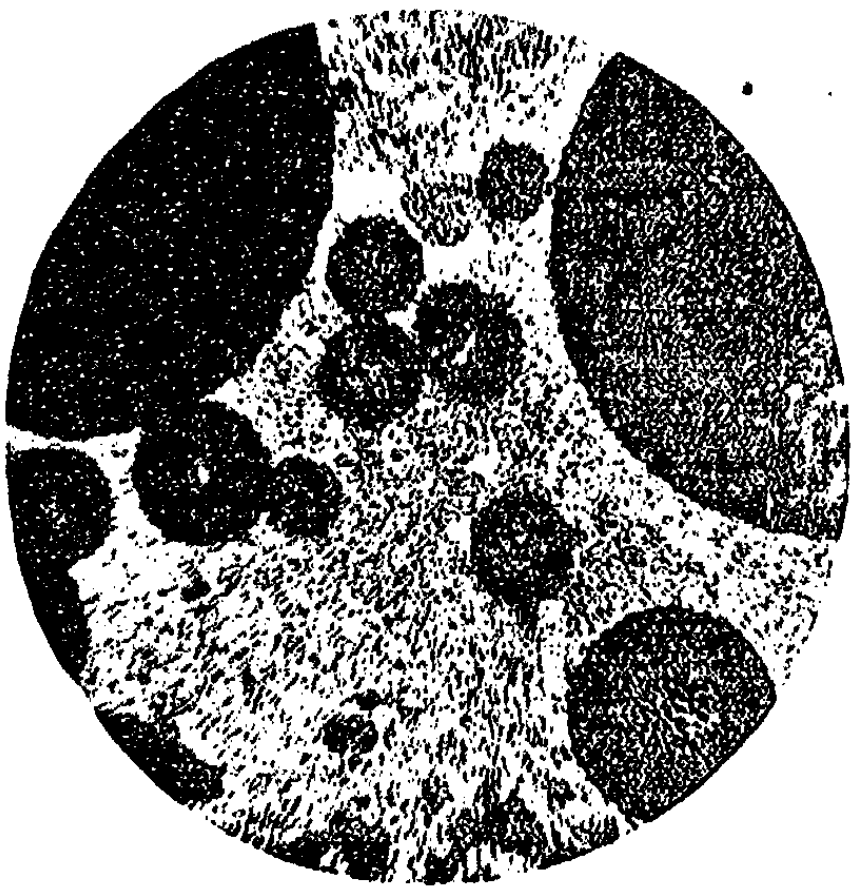

Fig. 3

opportunity did not develop to examine these further, their nature cannot be definitely stated. The nitro-benzene was specially purified, as also the acids and salts, and the interfacial substance is probably a lead compound.

Conclusion

Provisionally it appears, in agreement with Bancroft's general theory of peptization, that adsorption at a liquid, liquid interface is capable of procuring emulsification. The system tried passed on ageing into a condition approaching Pickering's emulsions, but with a great diminution of the dispersity.

Rochester, N. Y.
August 2, 1919

THE COLORS OF COLLOIDS. XI

BY WILDER D. BANCROFT

Gems

In the preceding paper[1] it has been pointed out how little we know about the chemistry of colored glasses and glazes. The matter is still worse when we come to gems, because we do not even know in many cases what substance constitutes the coloring matter, let alone in what form it is present. The only thing to do will be to make synthetic substitutes and show that they exhibit the same color changes as the real gems. There will be a good deal of experimenting necessary because the coloring matters in gems do not behave like any known substances, at least when present in mass. Consequently we are forced to conclude either that gems are colored by unknown elements which behave normally or by known elements which behave abnormally because dispersed through or dissolved in the mass of the gem.

Many years ago Hamlin[2] called attention to the effect of heat on certain gems. "The vivid as well as the more delicate hues of the red tourmaline vanish like magic almost at the first touch of the blow pipe flame; while the green and the blue are not much affected at a higher temperature. The charming tints of the emerald are completely destroyed at a red heat, while the green sapphire and the green diamond are unchanged. The garnet loses its red hues by heat; but the green are preserved. The Saxon yellow topaz changes to white when exposed to a high degree of heat; but the Brazilian topazes, of darker hues, become a beautiful rose-pink at a low temperature; but if the heat is continued to a certain degree, neither hue can be recalled and the stone becomes colorless. The red sapphires often gain a deeper tint; while the bluish in color sometimes become snow-white. Most of the sapphires

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[1] Bancroft: Jour. Phys. Chem., 23, 603 (1919).

[2] "The Tourmaline," 87 (1873).

retain their hues even after having been submitted to a very high degree of temperature. Berzelius found that the red spinel of Ceylon, when exposed to the action of fire, became brown, then black and opaque; but, when cooling, it changed to green; then afterwards became limpid; and finally was restored to its original color. The diamond, when heated, gradually becomes pink; which color gradually fades away on cooling. The hues of the amethyst and zircon are completely destroyed at a red heat. The chlorophane from Siberia exhibits an emerald-green when heated; and still another variety from the same locality, when heated to 212° F, phosphoresces, and becomes green; but, when heated to a still higher temperature, it becomes blue. In all cases with the fluorspar, when the phosphorescence ceases, the color of the mineral disappears, and never returns. In the outer and inner flames of the blow-pipe may be seen remarkable effects, which are not clearly explained by the oxidizing and deoxidizing power. Protoxide of iron with the fluxes gives brownish yellow in the outer light, and a light green in the inner. Oxide of copper with borax gives a green light in the outer flame, and a red in the inner. The oxide of nickel with borax gives a red bead of glass in the outer flame which becomes white when cool. Binoxide of vanadium gives a yellow bead in the outer flame, which turns to green when cool. The globule of glass formed with borax and titanium is often emerald-green; but with a greater quantity of borax added to it, the bead becomes red, which passes to blue or white, according to the degree of heat to which it is exposed."

Hamlin, of course, did not know about the effect of X-rays and ultraviolet light on gems and consequently he did not realize how often the changes may be reversible. Doelter[1] points out that we can divide pale gems into two glasses, those which become colorless at the same time in all gases and those which behave differently in oxidizing, reducing, or neutral atmospheres. With the second class we should

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[1] "Das Radium und die Farben," 69 (1910).

naturally conclude that there had been a chemical change in the coloring matter; but some other explanation is necessary in order to account for the first class. Unfortunately, it is not clear from Doelter's book what substances belong in the two classes. He implies that the colored forms of quartz belong in the first class and everything else in the second class; but the data he gives do not warrant any such conclusion. The color of the yellow diamond seems not to be affected by the nature of the gas in which it is heated and the same is true of the ruby. The sapphire becomes colorless when heated in oxygen, nitrogen, or carbon dioxide which would seem to put it in the first class; but after it has been turned yellowish brown by exposure to radium, it becomes colorless when heated in oxygen and bluish when heated in nitrogen. Topaz becomes pink if heated in oxygen, lilac if heated in nitrogen, and green if heated in sulphur vapor.

While there does not seem to be much to be made out of such fragmentary information as this, the action of heat, ultraviolet light and radium on the colors of gems is very interesting and opens up a broad field for research. Pale amethysts become darker when exposed to radium, while ultra-violet light has no effect. When heated to redness in hydrogen or oxygen, the pale amethysts become colorless while they turn yellow if heated in ammonia. The decolorized amethysts regain their color when treated with radium. Rose quartz is made colorless by ultra-violet light and blackish brown by radium. It is not changed when heated in ammonia. Smoky quartz loses its color when heated and radium brings it back, while hydrogen peroxide tends to make the color yellower. Colorless topaz is made yellow to orange by radium and is decolorized when heated. Ultra-violet light tends to change the orange produced by radium to lilac. Kunzite changes from lilac to green under the influence of radium and is changed back by ultra-violet light. It becomes colorless when heated to 400°; but exposure to radium brings back the blue-green color. Corundum occurs as blue, green, violet, yellow and white sapphires and as ruby. The Oriental sapphire is said by Verneuil[1] to be colored by iron and titanium while the clear sapphire is colored by iron only. Blue sapphires are changed to yellow or yellowish brown by radium, the blue-green sapphires to green and the white sapphires to yellow. Violet sapphires become pure red and natural rubies lose any violet tinge. Artificial rubies and sapphires are not changed by exposure to radium, but their coloring matter is chromium or cobalt. Ultra-violet light makes yellow sapphires blue and violet ones more violet. Heating sapphires in air makes them colorless.

The general result seems to be in all cases that heating makes the gems more nearly colorless and that the action of radium and of ultra-violet light is antagonistic. The only possible explanation seem to be that radium increases the dispersity of the colloidal particles while ultra-violet light decreases it or vice-versa. We know that β-rays increase the agglomeration of sulphur and that they change a selenium hydrosol into crystalline selenium. It should be possible to test this explanation on synthetic materials, using perhaps borate glasses. For instance, radium produces no change in pure chromic oxide but turns it brown when the chromic oxide is dissolved in borax. Ultra-violet light changes the brown to yellow and when a chromium oxide borax glass is heated in ammonia it becomes pale. Alumina is not changed by radium but hydrous aluminum oxide sol is turned blue by it. If cases of this sort should be studied carefully it would probably give us the necessary data to straighten out the question of the colors of gems without any difficulty.

It is quite possible that it might be simpler to start with rock salt and explain the color changes there. Rock salt occurs in nature colored yellow, pink, brown, violet, bluish green, blue, and blackish blue. Some of these colors may be due to iron or to other substances and the most interesting one for the moment is the blue. Rock salt can be colored yellow and blue by the action of sodium vapor, while cathode rays color it yellow to brown, though when heated, the brown

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[1] Comptes rendus, 151, 1053 (1910).

often changes to blue. It seems to be fairly well established that the blue color is due to metallic sodium, though Doelter[1] is a bit unhappy over it. When heated the blue salt becomes colorless because the sodium oxidizes. The color change takes place at a lower temperature in chlorine than in oxygen and in oxygen than in carbon dioxide; but different samples show very large temperature variations. Radium tends to make rock salt red or yellow, and ultra-violet light seems to make this color paler and carry it over somewhat towards blue. The whole subject is very confused and contradictory, so that one is not quite certain exactly what happens or to what extent changes in color are due to unmentioned impurities.

While the changes in the colors of gems when exposed to radium and to ultra-violet light are very probably due in part to changes in dispersion, it must be admitted that the experimental evidence for radium and ultra-violet light actually doing what is expected of them is very slight indeed. To some extent this is because people have not known what to look for; but there is no question but that a study of the color of gems is a fascinating problem in colloid chemistry which somebody ought to attack systematically and intelligently.

Cornell University

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[1] Das Radium und die Farben, 68 (1910).

THE EFFECT OF CHLORINE ON PERIODIC PRECIPITATION

BY MISS A. W. FOSTER

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In the course of some experiments on the absorption of ions by colloids, for which the Liesegang phenomenon was used, some interesting results were obtained when chlorinated tap water was used instead of distilled water.[1]

The rings were formed by the action of silver nitrate on a thin sheet of solid gelatine, which had been impregnated with a small quantity of potassium chromate. To a 4 percent gelatine solution was added potassium chromate to make up $\frac{1}{200}$ gram molecular weight per litre. Two ccs of this solution were poured on a glass plate ($3^1/_4'' \times 4^1/_4''$) kept perfectly level and after the gel had set, a drop of 10 gram molecular weight per litre of silver nitrate solution was allowed to fall on the centre of the gelatine film.

When distilled water was used the resulting ring formation was as shown in Fig. 1, with slight magnification and in Fig. 2, with magnification 25 times. Fig. 3, magnification 25 times, shows the effect produced by using tap water instead of distilled water. As the tap water was known to be chlorinated, it was thought that chlorine might be the cause of the grouping of the rings. To test this, a gelatine solution was made up using pure water, and to part of it was added a drop of the calcium hypochlorite solution used for chlorination (0.960 percent free chlorine). Fig. 2 shows the nature of the precipitate formed in the simple gelatine solution, and Figs. 4, 5, and 6 that of the precipitate formed in the chlorinated solution. It is evident that the chlorine and the grouping of the rings is in some way connected.

When the silver nitrate drop was added to the film a short time after pouring the gelatine on the glass, the rings produced were very close together, both the width of the rings and the spaces between them increasing slightly with the distance from the centre (Fig. 4). If, however, the gel was allowed to set for a longer time before the addition of the diffusing reagent, the rings appeared as in Fig. 5; and if a still greater interval elapsed before the diffusion began the

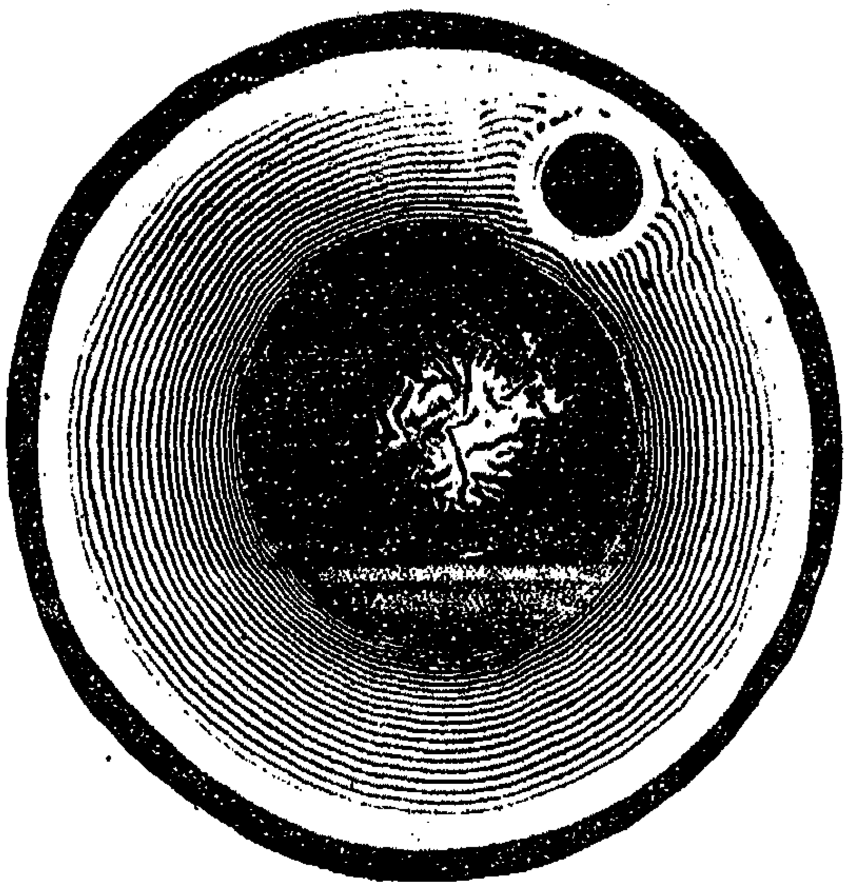

Fig. 1
Diffusion of silver nitrate solution into gelatine solution made with pure water

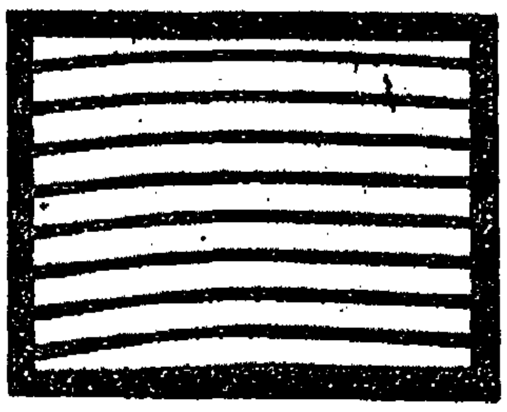

Fig. 2
Diffusion of silver nitrate solution into gelatine solution made with pure water. Magnification 25

rings were in groups like those of Fig. 6. When the diffusion began at a certain stage in the setting of the gel, all trace of

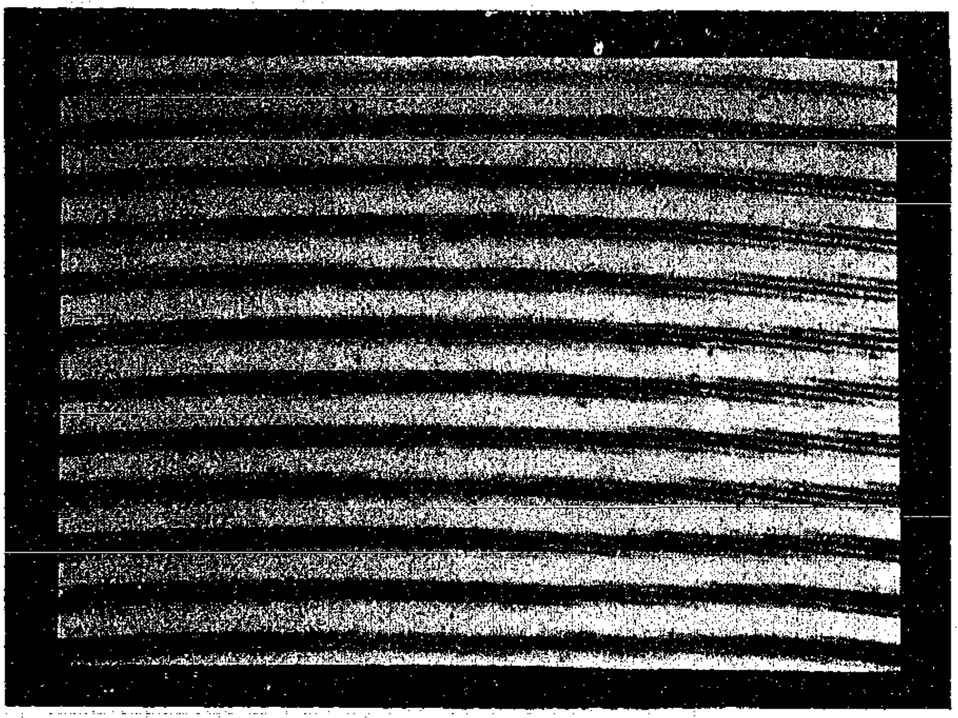

Fig. 3
Diffusion of silver nitrate solution into gelatine solution made with tap water. Magnification 25

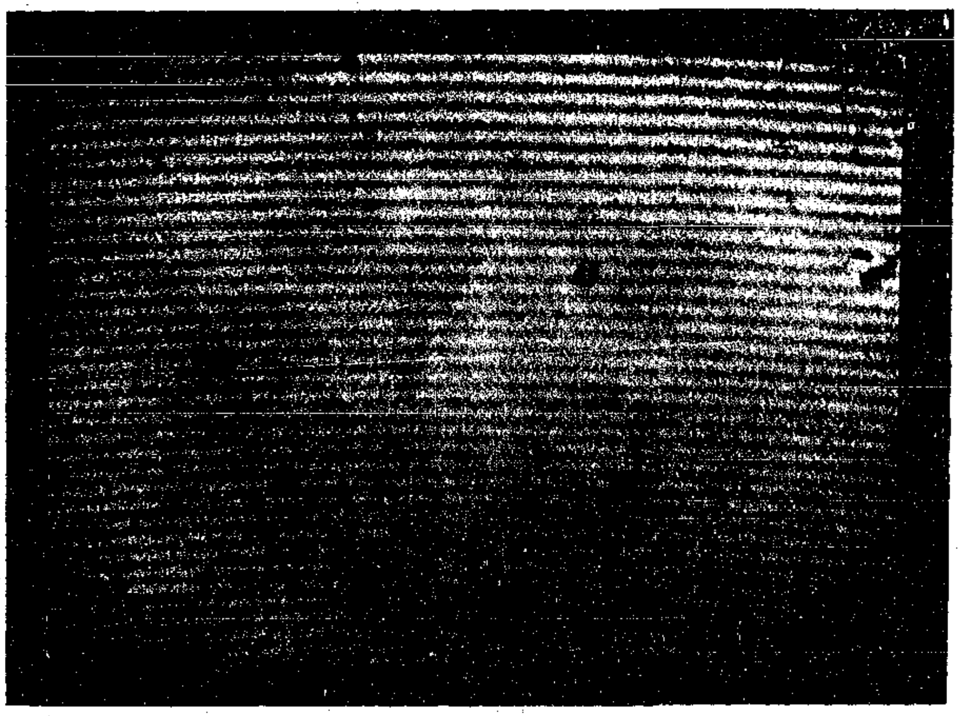

Fig. 4
Diffusion of silver nitrate solution into pure water gelatine solution containing a trace of calcium hypochlorite. Interval between making of film and addition of drop, 1 hour. Magnification 25

the intermediate rings disappeared and the precipitate was in bands made up of groups of rings, the width of each band being, approximately, the same as those produced in the other

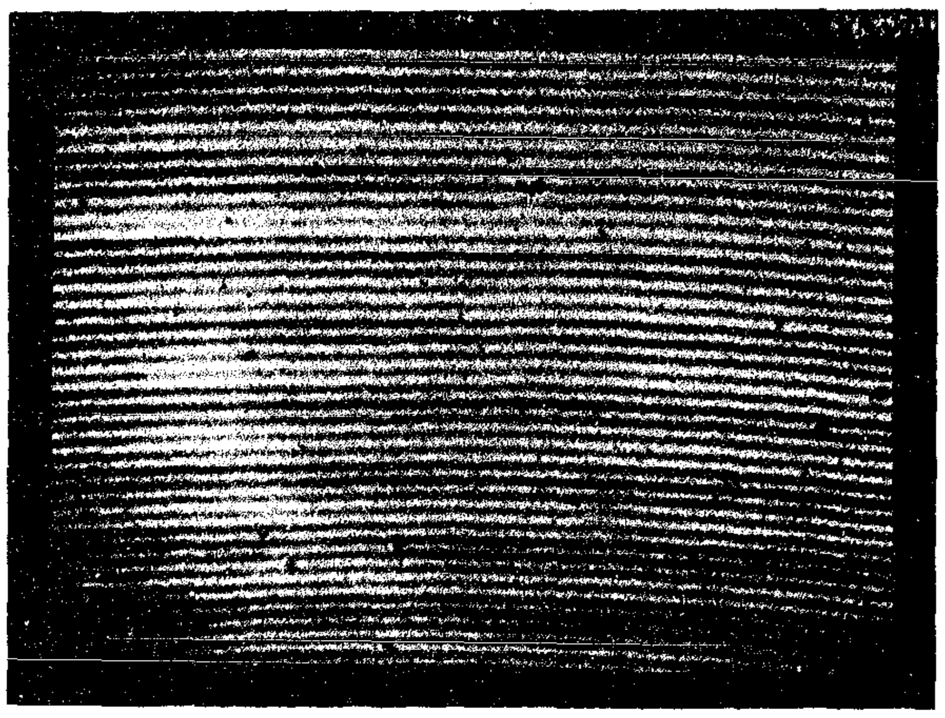

Fig. 5
Same solutions as in Fig. 4. Time interval $1^1/_2$ hours.
Magnification 25

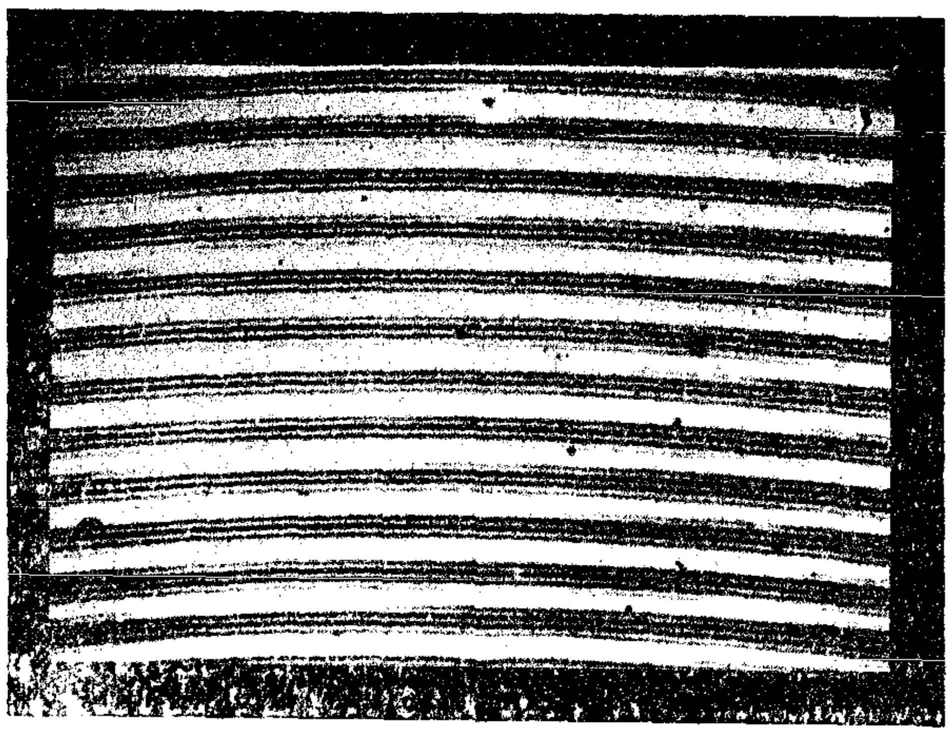

Fig. 6
Same solutions as in Fig. 4. Time interval 4 hours.
Magnification 25

films made from the same gelatine dissolved in pure water and poured out at the same time. The softer the gel, the greater the area of diffusion.

Observations made by means of the microscope during the formation of rings like those of Fig. 4 brought out the fact that the fine bands were to be seen only faintly at first and, under the high power, the tiny crystals could be seen coming into view, the growth of the ring being lateral. Upon these faint bands a second precipitate was formed so that, when diffusion was incomplete, two distinct areas were to be seen, the inner one having rings much darker than the outer one.

For rings obtained by adding the diffusion reagent after a longer time had elapsed from the pouring out of the gelatine, the same kind of thing occurred, except that in the inner area of diffusion, the secondary precipitate formed only on alternate groups of rings (Fig. 5).

The growth of the rings in the film which had set longest before the addition of the silver nitrate drop (Fig. 6) was the same as in the other films, *viz.*, some crystals suddenly appeared in the field of view and in a very short time others appeared beside them so that under the low power the rings were to be seen stretching out lengthwise. These last rings, however, did not form a continuous series but were like those formed last in the softer gelatine, the only difference in their formation being that there were no primary rings upon which the precipitation took place.

In order to show the significance of these results some account of the work which has been done upon the subject of periodic precipitates must be given.

The first explanation, and the one most generally accepted is that due to Wilhelm Ostwald.[2] He said: "By the diffusion of the silver salt into gelatine containing chromate, precipitation does not take place until the metastable limit has passed. This naturally happens in a circle concentric with the drop. Silver chromate in relation to which the neighborhood of the ring is supersaturated, deposits on the precipitate already formed and strengthens it; this continues until the whole of the soluble chromate has been removed from the neighborhood and deposited on the precipitate. The silver salt diffusing on further, supersaturates a new circular strip and the process repeats itself. Since the silver nitrate becomes more dilute by diffusion, the critical concentration at which precipitation begins is reached later and later and the rings form further and further apart."

Morse and Pierce[3] carried on an extended investigation of this phenomenon using capillary tubes and based their explanation upon Ostwald's supersaturation theory. They calculated that when the precipitation takes place the concentrations one seventy-fifth to one two-hundredth of normal for the chromate. They obtained precipitates in pure water but found the rate of diffusion less than for gelatine.

Hausmann[4] suggested that the compounds are present in the colloidal state before supersaturation is reached and precipitation occurs. He showed that the reaction depends only on the ions involved in the precipitate and not on those combined with them and that the speed of the reaction depends on the ion which diffuses into the gel and not upon the one which is present in the gel. He found that $\frac{\text{distance}}{\sqrt{\text{time}}}$ is constant as had Morse and Pierce.

Hatschek[5] used preparations of gelatine containing lead iodide and potassium iodide and diffused a solution of lead into it. The rings of lead were formed as though no lead iodide were already present in the gel which would indicate that supersaturation does not wholly explain the periodicity of precipitates.

Liesegang[6] considered that the spiral forms which he produced in place of concentric rings and which he regarded as being due to some slight disturbance were in no sense at variance with the supersaturation effect. He also showed that a certain amount of acid and gelatose is necessary for the formation of periodic precipitates and that commercial gelatine usually contains these in about the right proportions.

Stansfield[7] worked with gelatine films and in the main the reagents used were potassium chromate and silver nitrate of different concentrations. He strongly endorsed the supersaturation idea and enlarged upon it somewhat; he showed that, according to it, the bands may be equally spaced or at diminishing or increasing distances apart. He emphasizes the fact that the rate of diffusion is an important factor in the formation of rhythmic precipitates.

Bradford[8] proposed the theory that the Liesegang phenomenon might be due to gradual adsorption of the potassium chromate solution in the gel by the growing precipitate so that, the adjacent layers of gel becoming weak in the chromate solution, the silver nitrate would be able to diffuse further into the gel before commencing to form a fresh band of precipitates.

We shall now consider the bearing which the previously described results have upon the theories brought forth by these different workers.

The finer rings are what Liesegang calls the silver chloride precipitates and those of spacing such as is found in gelatine washed in pure water and containing only potassium chromate he calls silver chromate precipitates. In his work the two types seem to have been quite distinct and to have shown no interaction such as suggested by Fig. 5. In the work done to date rings were not obtained in the gelatine solutions except in the presence of the chromate so that the "silver chloride" rings could not be accounted for either on the basis of supersaturation or adsorption as these hypotheses are presented by Stansfield and Bradford. The finer set of bands would seem to have a catalytic effect upon the secondary precipitate so that the characteristic "silver chromate" band is subdivided.

Neither the supersaturation theory nor the adsorption theory takes into account the medium in which the diffusion takes place and that appears from this series of experiments to be of paramount importance. Periodic precipitates were not produced except when the gel was in a particular state. If too much or too little acid was present in the gel the precipitate was uniformly distributed around the central part of the drop because the molecular constitution of the gel is altered

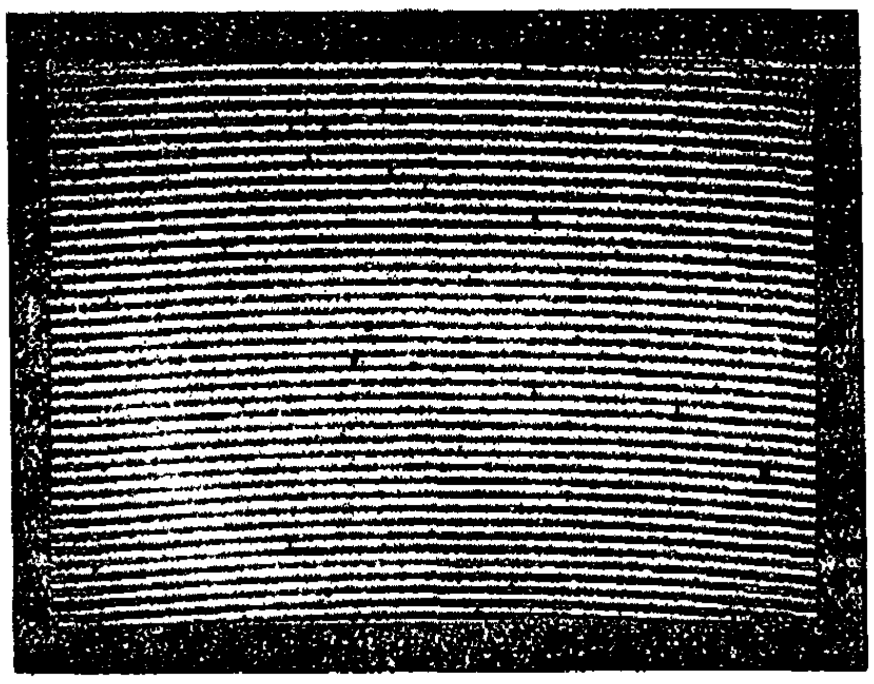

Fig. 7
Diffusion of silver nitrate solution into pure water gelatine solution containing a trace of common salt. Interval between making of film and addition of drop, 1 hour. Magnification 25

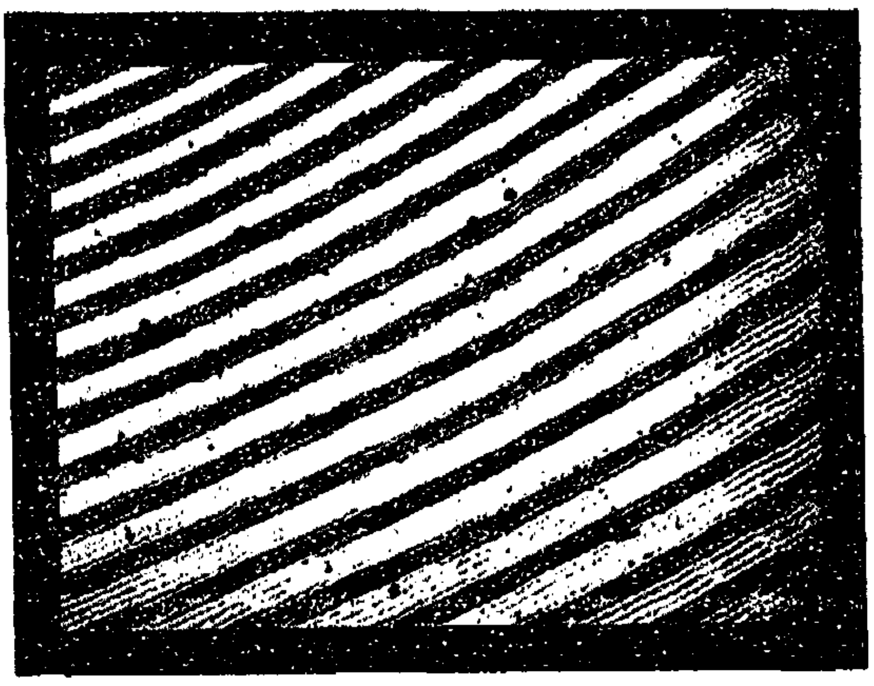

Fig. 8
Same solutions as in Fig. 7. Time interval 3 hours. Magnification 25

so that the rhythmic effects do not appear. That the addition of the trace of the calcium hypochlorite solution or common salt to the gel produces a change of state is evidenced by the fact that gelatine solutions to which these have been added set more quickly than the stock solution and kept longer without liquefying. This change of state is accompanied by a change in the nature of the precipitate. Even the change in the gel due to hydration produces a difference in the rings as is shown in Figs. 5, 6, 7 and 8. Rings were produced in agar when chlorine was present and showed the same spacing as in the gelatine and a certain state of the gel can probably be found such that the precipitates corresponding to the larger rings also appear. Any theory which does not take into account the medium in which the diffusion takes place is not conclusive. For instance, if the gelatine in hardening, forms larger and larger globules, such a circumstance may determine whether the rings are closely spaced as in Fig. 4 or widely distributed as in Fig. 6.

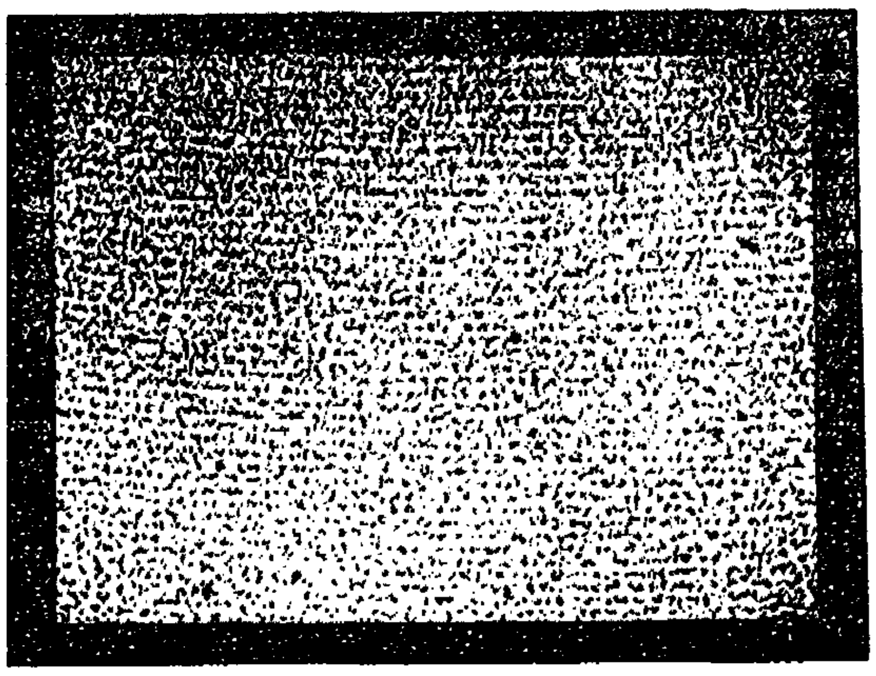

Fig. 9
Silver nitrate diffusing into pure agar water solution containing trace of calcium hypochlorite

TABLE 1
Explanation of Figures Accompanying the Paper

Figure No.	Magnification	Contents of the gelatine solution	Time between formation of film and addition of nitrat	Character of the precipitate
1	1·5	Gelatine, distilled water and potassium chromate	Characteristics independent of this interval	Single wide rings decreasing in width with distance from the centre
2	25	Same as above	Same	Same
3	25	Gelatine, chlorinated tap water and potassium chromate	3 hours	Rings in groups of three, spiral in form
4	25	Gelatine, distilled water calcium hypochlorite solution and potassium chromate	1 hour	Narrow rings, close together, formed by two precipitations
5	25	Same as 4	1 1/2 hours	Narrow, faint rings close together alternating with darker rings formed by two precipitations
6	25	Same as 4	4 hours	Dark rings in groups of three or four, spiral in form, formed by a single precipitation
7	25	Gelatine, distilled water common salt and potassium chromate	1 hour	Rings similar to those in 4 but darker and narrower
8	25	Same as 7	3 hours	Rings of the secondary set in two or threes rather than threes or fours as in 6

This work was carried out under the direction of Professor E. F. Burton.

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NEW BOOKS

Études de Photochimie. *By V. Henri. 25 × 16 cm; pp. vii + 218. Paris: Gauthier-Villars et Cie, 1919. Price: 18 francs.*—Before the war the author had planned to write a large and comprehensive text-book on photochemistry. In 1915 he was sent to Russia where he is now apparently the head of the laboratory of the Scientific Institute at Moscow. Some of the results obtained before the war have been put into shape and are now published in this first number, which contains a study of the absorption of the infra-red and the ultra-violet rays, the calculation of the absorption spectra in the ultra-violet, and a theory of the structure of molecules. The various chapters are entitled: introduction; methods of measuring absorption in ultra-violet and infra-red, and of measuring dispersion in the ultra-violet; effect of different groups on the absorption in the ultra-violet and the infra-red; relation between structure of molecules and absorption in the ultra-violet and the infra-red; absorption of the ultra-violet and infra-red by compounds having several chromophoric groups; calculation of the ultra-violet absorption spectrum from the chemical composition.

Absorption spectra have been obtained for 240 substances and the conclusions are based on the study of about 50,000 observations. For the panchromatic plates used, the law of Schwarzschild was found to hold quite accurately, the exponent n being 0.9μ. The source of ultra-violet light was the high frequency spark from aluminum electrodes under water. A Nernst filament was used as the source of light for studying the absorption in the infra-red. By using fluorite vessels it was possible to work down to 12–14 μ.

The author points out, p. 25, that if dispersion and absorption are simple resonance phenomena, a few measurements should enable one to calculate the absorption and dispersion curves. As a matter of fact the formula of Ketteler-Helmholtz-Drude gives the infra-red absorption for alcohols remarkably well. Since the absorption in the ultra-violet is due to the vibration of electrons and since the molecule is electrically neutral, the part of the molecule carrying the positive charge is supposed by the author to furnish the resonators for the ultra-red absorption, p. 49. This does not necessarily cover the whole ground because one might also have non-polar dissociation which might give rise to resonance, as is known to be the case with anthracene. The author finds that the results can be calculated if we assume that the number of resonators, p, of a given frequency in a primary alcohol is one for every CH_2OH group and three for every CH_3 or CH_2 group. The assumption in regard to the number of electronic resonators, p. 51, seem very far-fetched.

On p. 166 the author deduces the two general laws that the frequencies of the ultra-violet absorption bands are multiples of the frequencies of the infra-red absorption bands, and that the substances which have several absorption bands in the infra-red have also several absorption bands in the ultra-violet, the frequency of each of these latter being some multiple of the frequency of the corresponding band in the infra-red.

On p. 215 the author puts forward the interesting hypothesis that when rays of a frequency v are absorbed, they excite resonators having a lesser frequency v_1, and the molecules emit rays having the frequency v. If rays having a frequency of 1109×10^{12} fall upon acetone, a part of the absorbed energy will be utilized in exciting the infra-red resonators of acetone and the liquid will emit infra-red rays having a frequency of 36.5×10^{12}, or a wave-length of 8 μ, which are the rays which raise the temperature of the liquid. It follows from this that illumination of acetone by the ultra-violet light should cause the emission of infra-red rays. This experiment has not yet been tried.

A measure of the stability of a molecule can be obtained directly by measuring the energy of the radiation necessary to decompose it.

Wilder D. Bancroft

Molecular Physics. *By J. A. Crowther. Second edition. 19 × 13 cm; pp. viii + 190. Philadelphia: P. Blakiston's Son & Co., 1919. Price: $1.75.*—The subject is treated under the headings: introduction; the physics of the electron; the positive particle; the new method of analysis; the nature and size of an electron; the structure of the atom; the electron theory of valency; the atom in vibration; the molecular theory of matter; the atom in dissolution. The chapter on the structure of the atom is new in this edition and the chapter on the electron theory of valence has been rewritten completely.

On p. 90 the author says: "An atom consists of a central nucleus of small dimensions in which practically the whole of the mass of the atom resides. This nucleus is positively charged as a whole, and the mass of the nucleus is most probably entirely due to the charge which it carries. Outside this nucleus, and probably at comparatively considerable distances from it, are sufficient negative electrons to make the system as a whole electrically neutral. These electrons occupy the space which we know as the volume of the atom, not by filling it with their bulk, but either by moving about in it, in somewhat the same way as the molecules of a gas occupy the space in which they are confined, or by the electrical forces which they exert. Our different probings of the atom have revealed nothing apart from these two sets of particles. We must, therefore, picture the atom as a sort of void in which a comparatively few, minute, negatively charged planets circulate around a small positively charged sun. The number of the electrons which make up the planetary system of the atom of a given element is not yet determined with the certainty which is desirable; but is, at any rate approximately, one-half the atomic weight except in the case of hydrogen which almost certainly contains only one. If a table of the elements is consulted, in which the elements are arranged in order of their ascending atomic weights, and if the elements are numbered consecutively beginning with hydrogen as number one, it will be noticed that the number of the element on the list, the atomic number as it is called, is very approximately equal to one-half its chemical atomic weight. Van der Broek has made the ingenious suggestion which is almost certainly correct, that the number of electrons surrounding the nucleus of a given atom is exactly equal to its atomic number, and that consequently the positive charge on the central nucleus is also equal to the atomic number multiplied by the atomic unit of charge. Thus a hydrogen atom would consist of a single electron and a single positive charge. The atom of helium would have two electrons and a doubly charged nucleus, while lithium would have three electrons, beryllium four, and so on. Thus each element would differ from the one immediately preceding it in the table by containing one more electron in its planetary system and one more unit of charge on its central nucleus. The atoms of each element would differ from those of the element immediately preceding it in the table in the simplest possible way, the electrons and the central charge each increasing by unitary steps. It would follow from this that, at any rate in the earlier part of the table, all the elements possible on the system which we are discussing actually exist and have been discovered. The facts of the periodic classification of the elements certainly warrant this assumption."

Wilder D. Bancroft

The Life of Matter. *By Arthur Turnbull. 22 × 15 cm; pp. xviii + 324. Philadelphia: J. B. Lippincott Company, 1919. Price: $3.00.*—According to the author "the work purports to supply—in illustrative, though sketchy, form—a reliable guide and insight into observational method and experiments. It attempts to interpret the general body and bearings of the more important principles of knowledge to the average young man or woman entering college or naturally keen, and to provide a stimulus to any ordinary individual desirous of understanding the widespread applications of modern science to the necessities of real life. It endeavors both to appreciate past workers in their results and also to suggest fresh fields for inquiry and discovery."

The book is written in a queer, jerky style as though it were merely a collection of lecture notes. There is also a touch of mysticism to it which may or may not appeal to the reader. The separate chapters are entitled: elemental matter; from element to plant and animal tissue; tissue plant and animal; the spirit of search; the method of search; the need for inquiry; difference; the fluidity of tissue; continuous oneness of nature and man; definition; change of man; the law of activity; life of man; the growth of water; the origin of cancer; training; activity of body.

The book is intended to interest a great number of people; it covers much ground; and it is very suggestive, all of which are good things. The reviewer does not feel that the presentation of the subject is as satisfactory as it should be; but he may have misjudged the audience.

When one man tries to cover a wide range of subjects, he is pretty certain to slip up on some of his details and the author has suffered in this respect. Glass is not silicon, p. 8; tin does not change in weight when undergoing an allotropic change, p. 13; the splitting of rocks by wetting wedges of wood is not an osmotic pressure phenomenon, p. 30; a wire changes in density but not in weight when drawn, p. 31. It is not true that electro-magnets attract iron but repel aluminum, p. 34, though it is possible to arrange a striking experiment in which the induced currents do cause a repulsion. It is not true, p. 43, that "gold and iron in watery suspension take opposite directions on electric shock;" the author probably means ferric oxide and not iron. While it may be true, p. 52, that "in a part of Virginia the pigs are all black, for the white ones lose their hoofs by feeding off the poisonous roots of certain plants," it is not clear whether the black pigs do not eat the poisonous plants or whether they are immune to the poison. One does not like the illustration of the connection between motion and heating, p. 88. "The hub of a bicycle is hot to the touch after climbing a stiff hill. Conversely, when the water in a kettle is boiled, it bubbles—motion related to heating." It is certainly not accurate to say, p. 164, that bones are fixed with lime just as a photograph is fixed with "hypo."

Wilder D. Bancroft

Introduction to General Chemistry. *By Herbert N. McCoy and Ethel M. Terry. 23 × 15 cm; pp. x + 607. Chicago: University of Chicago Press, 1919. Price: $2.50.*—The first chapter deals with the measurement of gases and with the gas laws. In the next five chapters the authors discuss: indestructibility of matter; idea of a pure substance; decomposition of pure substances; elements; analysis of substances and percentage composition; the law of definite composition; derivation of formulae. The next three chapters deal with acids, bases and salts, and with water solutions, after which come chapters on kinetic-molecular and atomic hypotheses, chemical equilibrium, oxidation and reduction, heat and energy; the ionic hypothesis, and electrochemistry. Five chapters are devoted to nitrogen, phosphorus, sulphur, and carbon compounds. These are followed by chapters on the theory of dilute solutions, disperse systems, and the atmosphere. One chapter then deals with some additional elements and their compounds, one with the classification of the elements, and the final one with radioactivity and the nature of matter.

The book is interesting and the plan has been carried out well. The idea is that the college freshman will study this book as an introduction to general chemistry. This is all very well if we need an introduction to general chemistry; but it is not clear why one should not begin with general chemistry at once without any introduction. While the reviewer has never given a course in general chemistry, it seems to him that a knowledge of chemical facts is very desirable before taking up reaction velocity, equilibrium, electrochemistry, etc. It has always seemed to the reviewer that it was very important for the man who lectures freshman chemistry to be thoroughly familiar with physical chemistry, so that he can present his subject in such a way that many things will not have to be unlearned later.. It does not follow by any means that a great deal of physical chemistry should be injected into the first course in chemistry. This whole question is so fundamental that it seems a pity that the teachers of chemistry should not get together on it a little more than has been done.

There are one or two minor slips. The increased number of collisions is not sufficient to account for the increase in reaction velocity with rising temperature, p. 112. It is unfortunate to suggest, p. 232, that sodium is the primary cathode product when an aqueous sodium chloride solution is electrolyzed. In the statement of Faraday's law, p. 239, no reference is made to the case of cuprous salts. It does not seem satisfactory from any point of view to take up the Bunsen burner on p. 501.

The reviewer was naturally interested in the chapter on colloid chemistry though doubtful whether anything more than a reference to this subject should be included. This book is admirable if there is a need for a book of this type. The reviewer is by no means certain, however, whether there is any legitimate place for it in the college curriculum. *Wilder D. Bancroft*

A Laboratory Outline of General Chemistry. *By Herbert N. McCoy and Ethel M. Terry. 27 × 21 cm; pp. 130. Chicago: University of Chicago Press, 1919. Price: $1.00.*—This is a collection of mimeographed sheets giving laboratory instructions and experiments for use in connection with the text-book by the same authors. The first experiment is on the use of the Bunsen burner, a matter which is taken up near the end of the text-book. After that the laboratory experiments follow the book very closely. There are nearly two hundred exercises and they seem to be well selected, although one cannot help wondering what laboratory work a student will do when he actually takes general chemistry. *Wilder D. Bancroft*

What Industry Owes to Chemical Science. *By Richard B. Pilcher and Frank Butler-Jones. 19 × 13 cm; pp. xiv + 150. New York: D. Van Nostrand Company, 1918. Price: $1.50.*—The contents of this volume appeared first as a series of articles published in the Engineer mostly during the first half of 1917. The object was to take each industry in turn, and to show by examples how science had advanced the methods and processes of production and had laid the foundation for the establishment of new manufacturers. The titles of the chapters are: minerals and metals; heavy chemicals and alkali; coal and coal gas; dyes, explosives and cellulose; oils, fats and waxes; leather; rubber; mortar and cement; refractory materials; glass and enamels; pottery and porcelain; chemical products; photography; agriculture and food; brewing; alcohol, wines and spirits; tobacco, inks, pencils, etc.; gases; government chemistry.

It is interesting to note that nearly all of the topics belong essentially in colloid chemistry. In the twenty pages devoted to minerals and metals the authors discuss iron and steel, copper, lead, nickel, sodium, aluminum, magnesium, molybdenum and tungsten, chromium, thorium, vanadium, gold, the platinum group, and ore flotation. It follows that the information given in regard to any one topic is very limited even though presented in a condensed form. The information is presented clearly and the book is interesting in its way though it will hardly do what is claimed for it in the introduction, that it will furnish teachers of chemistry with abundant material for a wisely directed study of the achievements of science and industry. *Wilder D. Bancroft*

Lecture Demonstrations in Physical Chemistry. *By H. S. van Klooster. 20 × 14 cm; pp. vi + 196. Easton: The Chemical Publishing Company, 1919. Price: $2.00.*—In the preface the author quotes Arrhenius as saying that there are very few doctrines in exact science where so few lecture experiments are shown as in physical chemistry. This volume has been prepared in order to make it easier for the lecturer to show experiments in his courses. The experiments are grouped under the following headings: general properties of matter in the liquid and solid state; diffusion; osmosis; vapor pressure and determination of molecular weights; chemical equilibrium and the law of mass action; catalysis; electrochemistry and ionic theory; solubility and its changes; colloids and adsorption; actino-chemistry; flame, combustion and explosion; liquid air experiments.

Under catalysis the author gives experiments illustrating the seven types of catalytic reactions distinguished by Noyes and Sammet and adds experiments illustrating the three new types of autocatalytic reactions, reactions with intermediate formation of catalytic agents, and reactions catalyzed by germs. The book is full of good experiments and the directions are clear, making the volume one of great value to the teacher. The reviewer would have liked to have seen included an experiment on the reversal of electrodes in cells of the Daniell type and the experiment with the luminous mercury anode, both of which are very striking, though in different ways. *Wilder D. Bancroft*

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