SELECTIVE RADIATION FROM VARIOUS SUBSTANCES, III

By W. W. Coblentz

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I. INTRODUCTION

The present investigation is the beginning of an attempt to supply a long-felt need of an accurate knowledge of the spectral energy distribution, of some standard sources of light, in the visible and in the ultra-violet parts of the spectrum. The problem is a difficult one and heretofore has never been given thorough attention. Once the spectral energy distribution of a standard source of illumination is accurately known, it is possible to obtain the spectral energy distribution of other weaker sources of radiation by indirect methods, such as by spectrophotography or spectrophotometry. The standard sources which are the most easily reproduced are probably well seasoned incandescent lamps.
operated at a given efficiency. For ultra-violet radiation, however, they are quite impracticable on account of the absorption by the glass bulb which will not be sufficiently constant for different lamps. For ultra-violet work, flame standards seem the best adapted; and of these the acetylene flame seems the most useful on account of its high temperature. The effect of variations in atmospheric conditions will probably have but little influence on the spectral energy curve. The black body, while ideally more scientific, is hardly to be classed as a convenient standard. The carbon filament is a good substitute for the black body, since it shows but little selective radiation in the visible spectrum. In certain classes of work the ideal standard is the vacuum tube radiation. Here the radiation from the individual spectral lines is measured, and we are not concerned with spectral purity and other sources of error. The chief error lies in accurately measuring the energy, which is always very weak, especially in the violet.

In making preliminary experiments on the suitability of various sources of radiation as spectral energy standards several new phenomena were observed which required extensive investigation and which diverted the attention from the main problem. The results obtained are unique in themselves and are therefore published at this time, since the rest of the work has been postponed.

It will be shown on a subsequent page that, throughout the visible spectrum, the radiation from the acetylene flame is proportional, within the limits of experimental errors, to the thickness of the flame, so that the values of the spectral energy, given here-with, apply to a flame viewed flatwise or edgewise. This is not true of the infra-red spectral energy curves. Here the emissivity is no longer a simple function of the thickness of the radiating layer, and hence can not be considered a reference standard without specifying the manner in which the flame is used.

II. APPARATUS AND METHODS

1. THE SPECTROMETER

For investigating the infra-red spectrum a vacuum bolometer, a mirror spectrometer, and a fluorite prism were used. The essential features of this apparatus have been described in previous communications.
For investigating the ultra-violet and the visible spectrum, all of the apparatus was of special construction. The spectrometer was of special design, and made in the instrument shop of the Bureau. Not only were short focus lenses of large aperture provided, but the collimator tubes were also designed so as to utilize all the light arriving at the viewing end and to avoid reflected light.

The optical parts consisted simply of two plano-convex quartz lenses 6 cm in diameter and 18 cm focal length, and a large 60° quartz prism. For the visible spectrum triple achromatic glass lenses have been provided. Quartz is transparent to about .25μ, hence the only loss is due to reflection. A light flint-glass prism was also employed as a check on the work. The dispersion was twice as great as in the quartz prism, which reduced the intensity of illumination. Hence the observations are of little value in the ultra-violet, where (at .42μ) the absorption begins to be quite large.

The fewness of the reflecting surfaces reduced the energy losses by reflection. It will be noticed presently that the “scattered” light in the system is very uniformly distributed over the field. Hence while not negligible in the case of an intense source of radiation such as the Nernst glower, this diffuse light simply increases the observed radiation by a fixed amount throughout the entire spectrum. Of course, for a small angular distance from the normal, as obtains in the present experiments, the scattered radiation should be uniformly distributed, but heretofore no very definite experiments have been published to give the desired information.

From the observations of Rosenmuller\(^1\) it appears that the actual loss of light in such an instrument is insignificant out into the extreme violet. For radiometric work this correction would have but little significance and in the present work no correction has been applied.

The collimator tube was provided with an accurately divided scale, which permitted setting the radiation meter in accurate focus at different parts of the spectrum. This scale was calibrated for proper focal lengths by means of the helium lines, which also served as a calibration of the prism. The change in

\(^1\) Rosenmuller, Ann. der Phys., 29, p. 355; 1909.
focal length from .35μ to .75μ was about 15 mm, and at each spectrometer setting the instrument was set to accurate focus as determined from a calibration curve of the scale on the collimator tube. For the region from the yellow to the ultra-violet, however, where the dispersion is large, the matter of accurate focus was unimportant, as was found by actual observation.

The spectral lines are of course slightly curved in such an instrument. The slit which covered the thermopile was therefore made of thin sheet copper cut so as to exactly fit the curvature of the spectral lines.

2. COMPARISON OF DISPERSION OF PRISMS

It is of interest to notice the dispersion of various prisms in different parts of the spectrum. In fig. 1 is shown the width that a bolometer, having an angular aperture of 4° arc, subtends in wave lengths (the "slit width") in different parts of the spectrum when using different prisms having the same angle—60°. These curves show that a carbon disulfid prism is the best for the region to 1.4μ. For most purposes quartz is the best.
In the present work the spectrometer slits were 0.6 mm wide, or about 10 minutes in arc. Even with this wide slit the actual width, subtended in wave lengths, is far less than for similar work in the infra-red, where even greater exactness is desired than in the present investigation. The slit-width correction, i.e., the factors for reducing the prismatic spectrum into the normal spectrum, were obtained from the curve of refracting indices and minimum deviation settings, and also by direct calibration of the prism by means of the helium lines. The values derived by these two methods agreed exactly throughout the whole range, except beyond .69μ, where they began to diverge. From .69 to .75μ the factors determined from the experimental calibration curve were therefore used. This divergence at .75μ is due in part to the fact that the dispersion curve of quartz has a point of inflection in this region of the spectrum, which makes it difficult to determine the slit-width factors with great exactness.

3. THE RADIOMETERS

A special Rubens thermopile\(^2\) of 20 elements of iron and constantan and a new radiomicrometer were provided for this work. The thermopile wires were only .07 mm in diameter and the total resistance was 9.5 ohms. Wires of this fineness rust off very rapidly unless protected. They are therefore given a thin coat of shellac, which is baked. Because of this defect it seems advisable to use copper instead of iron in this form of pile. The thermoelectric power of copper-constantan is not very markedly different from the iron-constantan. The junctions are then painted with a mixture of lampblack and chemically precipitated platinum black, the brush used being an end of a silk thread. This thermopile was entirely free from the usual drift observed in the heavier type of instrument, and it came to temperature equilibrium in far less time than the actual period of the galvanometer. The latter has also been described. On account of the great light-gathering power of the spectrometer, a high galvanometer sensitiveness was not required, and it was generally used on 2.5 seconds single swing, which corresponded to about \(i = 2 \times 10^{-10}\) amp. for a scale at 1 meter.

\(^2\) This Bulletin, 4, p. 391; 1907.
Magnetic and thermal disturbances were inappreciable. In fact, with this apparatus far less difficulties were experienced than in the general infra-red investigations, which is just the opposite from what was expected before undertaking the work. To be able to make a reading in 5 seconds instead of 5 to 10 minutes, as was necessary heretofore, is an important item, especially when examining an open flame subject to various fluctuations in the surrounding conditions.

The thermopile was mounted in a heavy metal case, which was rigidly attached to the collimator arm. It was found that the eyepiece at the rear did not permit setting the thermopile slit upon a spectral line with as high degree of accuracy as was desired. Hence, after the completion of the focal length and the prism calibration the eyepiece was removed. This space was inclosed with black felt, which absorbed the radiation passing by the thermojunctions, and the adjustment of the thermopile slit (the so-called zero setting) was made by viewing it at an angle from the front. Using the intense yellow helium line as a reference point, there was no difficulty in testing this adjustment of the thermopile slit in the spectrum.

A new form of suspension was made for the radiomicrometer,\(^3\) previously described, but on account of its inconvenience and because of the high sensitivity of the thermopile it was not put to extensive use. It has given such satisfaction in other work, however, that it seems worth while to describe it. The suspension, Fig. 2, consists of two junctions of bismuth and silver, with a copper loop, and it was made linear for spectral radiation work. It was found that by dropping the molten bismuth from a height of about 1 m it would spatter out into a thin, well-annealed plate, which could then be rolled to .02 to .04 mm thickness. The dimensions of the present junction were: Bi = 8 x 1 x .03 mm; Ag = 3 x 1 x .01 mm, and copper wire .08 mm in diameter. The central active junctions were painted on one side with a mixture of platinum black and lampblack, with a trace of shellac in alcohol. The window covering the junctions consisted of a film.

\(^3\) This Bulletin, 2, p. 479; 1907.
of glass blown so thin that it showed interference colors. Such a film absorbs but little in the spectrum, except at 8 to 9\(\mu\). For a candle at 3.1 meter and scale at 1 m, with all extraneous light excluded except that which passed through a long blackened tube, the deflection was 22 cm (for a single swing of 25 sec.) or more than 200 cm at 1 meter. For a single swing of 10 sec. the deflection was at least 50 cm. It is therefore apparent that this form of junction is as sensitive as any heretofore described. The weight of the complete suspension was a little less than 10 milligrams. The sensitivity of this suspension was not very much greater than that of a similar suspension having but a single thermo-junction, which is in accordance with the theory.

From the fact that the galvanometer did not have to be forced to its highest sensitivity it is not to be inferred that spectral energy curves in the visible spectrum can be easily observed with ordinary apparatus. The intensity in the yellow is about 400 times and in the red (.725\(\mu\)) it is about 3000 times that at .38\(\mu\). On the large mirror spectrometer, using the small fluorite prism previously described, the Nernst glower gave a deflection of about 2000 cm at the point of maximum emission. With 6 times the light-gathering power, which obtains in this instrument, the deflections would have been 12 000 cm at the point of maximum emission. With the present instrument, using a quartz prism, the intensity of maximum emission (at 1.35\(\mu\)) of the Nernst glower would be about 90 000 times that at .38\(\mu\).

4. THE ROTATING SECTORED DISK

With galvanometer deflections ranging from 70 cm in the yellow to 400 cm in the red it was necessary to provide apparatus to reduce the intensities to a measurable value. This could be done either by throwing resistance in series with the galvanometer, or

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by reducing the incident light with a convenient form of rotating sectored disk. The present sectored disk consists of eleven series of openings at 90° from each other, each opening being 16 mm long, the respective angles being 2°, 3°, 4°, 6°, 8°, 10°, 12°, 15°, 20°, 30°, and 45°. This gives reduction factors ranging from \( \frac{1}{2} \) to \( \frac{1}{45} \) the original intensity, which seemed sufficient as a first experiment. This disk, although 41 cm in diameter, and made of copper about 1 mm in thickness, with aluminum bracing arms 10 cm long and about 5 mm thick, has proven to be thoroughly rigid and free from lateral vibration when in rapid motion. The thickness of the whole framework was kept small, 1 cm, to reduce the air path in infra-red radiation work. The essential parts of this form of disk are (1) a large disk with numerous openings (nothing particularly new about it) which reduce the intensity by an accurate amount at each step; (2) a motor rigidly attached to the frame supporting the disk, and moving with it; (3) a slotted base plate, supporting this framework, and provided with a rack and pinion to move this frame, containing the disk and motor, back and forth in front of the spectrometer slit. A long rod is provided to operate the pinion from a distance. The whole is shown, without details, in Fig. 3 and needs no explanation. From a mechanical point of view it might be better to have the large angular openings nearer the rim, thus reducing the weight, and to increase the accuracy in the small angular openings at the center by using, for example, two 4° openings situated at 180° instead of four 2° openings situated at 90° from each other. This would permit larger angular openings, although for radiometric work a reduction factor of less than \( \frac{1}{2} \) is of little use. Openings both larger and smaller are possible, but previous experience showed that the aforesaid factors would be the most useful as a preliminary attempt. Provision has, of course, been made for substituting another disk with different openings. This experiment shows that still larger disks can be operated without vibration. Of course, where only spectroradiometric work is contemplated with a slit of less than 1 mm wide, more steps can be put in the smaller disk. The present instrument is also useful for total radiation work. The definite openings make errors impossible in setting them before the slit, and they fill all the requirements in
radiometric work where it is necessary to reduce the radiation by a definite amount. A uniformly decreasing angular opening (instead of step-wise as in this case) is easier to construct and would be useful, also, in spectrophotometric work, such as the instrument, recently described by Hyde. But such extreme care is necessary in adjusting and in making settings before the spectrometer slit with the latter form, that at the time when the design of a rotating sector was undertaken no thought was given to the development of such an instrument. These two types of rotating sectors are excellent examples of what may be independently developed by two investigators to fulfill their individual needs.

5. ACCURACY ATTAINABLE

The fact that the galvanometer could be used on a very short period made it an easy matter to investigate the visible spectrum. A casual examination of the records shows that in the yellow and in the red where the deflections (actual or reduced) were from 10 to 20 cm, the individual readings vary by .3 to .5 mm from the mean, or one part in 200 to 400. The intensity of the radiation, falling on the front part of the thermopile case which consisted of a double-walled copper shield with a slit in it to permit the radiation falling upon the active junctions, caused a slight unsteadiness of the zero reading, and hence lowered the accuracy attainable. In the blue and green where the deflections were from 5 to 10 cm the zero reading was not affected by the excessive heating and the individual readings vary by .2 to .3 mm (for example 5.83; 5.82; 5.82; 5.84; 5.85; 5.83 cm), or one part in 200. In the extreme violet and in the ultra-violet (except for the Nernst glower) where the deflections were only from 3 to 5 mm, the accuracy attainable was only from 1 part in 10 to 1 part in 50. In case of the Nernst glower, in the extreme ultra-violet, and in the stray light measurements, where the deflections were 15 mm, the variations from the mean (which includes fluctuations in the glower due to air currents) were less than .5 mm or about 3 per cent. On the whole, this refinement is of minor importance, for the interest lies in the general trend of

Selective Radiation from Solids, III

the energy curve from the extreme ultra-violet into the infra-red. It may be added, in conclusion, that a small fluctuation of .1 to .2 volts, in incandescent lamps, although observable on the spectrophotometer, did not affect the observations by a perceptible amount, except in the case of the Nernst glower, in which a variation of 0.1 volt caused an appreciable variation in the emissivity in the yellow and especially in the red. All the lamps were operated from a storage battery, so that the voltage was easily held constant. The voltmeter was calibrated several times and found to be constant. The incandescent lamps were seasoned by the photometry division of this Bureau, and the voltages specified for obtaining a definite efficiency. For this purpose, a series of efficiency measurements (candlepower and watt-input) were made, varying from, say, 2.3 to 3.5 w. p. m. h. c, and a curve was drawn from which the voltage could be read for the production of, say, 2.5 wpc.

In conclusion, it seems desirable to emphasize the fact that the accuracy attainable in radiometric work is greatly influenced by weather conditions, just as in astronomical work. The present observations were made in the hottest summer months when the temperature within the observing room was closely the same as on the outside of the building. Even then cloudy, wind-free days were the best. In subsequent work, several months later, when it was more windy, and when the room temperature was different from the outside, the thermopile was more unsteady in its action. The galvanometer mirror would also fluctuate a little, due to air currents and probably also to changes in astatacism caused by a slight swaying of the building by strong gusts of wind, so that a precision of only 1 part in 100 to 200 was possible.

III. THE ACETYLENE FLAME

1. HISTORICAL

That particles of incandescent carbon in flames, and especially in incandescent lamp filaments of carbon, can have a sharp band of selective emission just beyond the visible (red) spectrum has always seemed to the writer to be doubtful. The properties of "soot" and "lamp black" are a high absorptivity in the visible
spectrum which decreases rapidly as we go into the infra-red. The experiments of Ladenburg on the incandescent particles in the acetylene flame show a similar property of a high absorption in the visible spectrum which decreases uniformly in the infra-red. In order to have a sharp band of selective emission the flame should show a band of strong, well-defined absorption in this same region. The curves of Ladenburg do not indicate such a condition. From all the experimental data now at hand one would expect a much higher emissivity in the blue, decreasing uniformly into the infra-red, just as obtains in the metals. That this is actually the case for acetylene was found by Dr. Burgess, who kindly made the measurements with an optical pyrometer. The pyrometer showed an emissivity equivalent to a black body at a temperature of 1357° in the red, to 1450° in the green, and to 1475° in the blue, which is the order of the selective emission of metals. In view of the fact that, as will be noticed presently, the acetylene flame seems to show a slightly more transparent region in the violet, it would be interesting to have a comparison of this same region with a sensitive optical pyrometer.

Spectrophotometric intercomparisons of various flames and incandescent lamps seem to show a band of selective emission in the deep red. The acetylene flame was used as a comparison standard. Because of its rapid change in absorptivity (and hence emissivity) in the region of .75μ (see Fig. 9), the slope of the spectral energy curve of acetylene is entirely different from that of an opaque solid, e.g., a carbon filament. Hence the curve of ratios of emissivities of these two substances assumes various forms (depending upon the temperature of the carbon filament) which, combined with errors due to stray light, lack of sensitivity of the eye, etc., give the appearance of a band of selective emission at .72μ when in reality the whole is due to a rapid variation in transparency in the region of .7 to .8μ.

The logical procedure is, of course, to compare such sources against a black body which can not emit selectivity in favor of

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7 This Bulletin, 5, p. 364; Table III.
9 This Bulletin, 5, p. 376; 1909.
some particular spectral region. About two years ago a preliminary spectrophotometric comparison was made of a carbon lamp and of an acetylene flame, with the radiation from a black body. At that time no permanent acetylene apparatus was at hand. A temporary generator and gasometer were constructed, with which acetylene was produced for two series of spectrophotometric comparisons, and for the pyrometric comparisons just mentioned. Because of the difficulty of operation and the lack of assistance further work was discontinued until the completion of the Bureau’s permanent acetylene gas generating apparatus, which now consists of an automatic generator attachable to either a high or a low pressure gasometer.

In the spectrophotometric measurements no selective emission was found in the carbon lamp; but the acetylene flame seemed to show selectivity in the deep red. From a recent study of the original observations it appears to the writer that the conclusions of a true selective emission at \(0.7\mu\) was erroneous. The data then obtained, when properly interpreted, indicates a low emissivity in the region of \(0.7\mu\). But the eye is not sufficiently sensitive to differences in intensity for frequencies beyond \(0.7\mu\) to put much reliance in these spectrophotometric observations. Moreover, from recent experiences with the spectrophotometer then used, the writer feels that even a substitution method of comparison may not eliminate all errors. In the apparatus used by us the photometric field is not evenly extinguished by the rotating sector (in this device the sector is stationary and the beam of light is rotated), the line of extinction being from the lower right-hand quadrant to the upper left-hand quadrant. In the extreme red the eye, therefore, unconsciously tends to wander from side to side and inconsistent settings result. In some recent spectrophotometric work consistent results were obtained only by fixing the eye on the central part of the photometric field. If the same conditions obtained in our acetylene comparisons, the apparent selectivity is easily explained. This same thing, however, should have also appeared in the spectrophotometric comparisons of the incandescent lamps. On a sub-

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10 This Bulletin, 5, p. 376; 1910.
11 This Bulletin, 5, pp. 349 and 376; 1910.
sequent page it will be shown that the previous announcement\(^{11}\) of a selective emission band at .72\(\mu\) was based upon a misinterpretation of a peculiar depression in the spectrophotometric curves of acetylene (compared against a black body) which is not due to a true emission band, but is due to a rapid decrease in the absorptivity of the acetylene flame in this region of the spectrum. Suffice it to say that any selectivity of even a small part of that recorded by us spectrophotometrically could not have, as will be noticed presently, escaped detection radiometrically. The radiometric observations, at any spectrometer setting, are in agreement to at least 1 part in 200 and often to 1 part in 400 (the slight fluctuations in the galvanometer deflections being due to the unsteadiness of the acetylene flame) which accuracy can not be attained with a spectrophotometer, at least not in the extreme red end of the spectrum. As the one principally responsible for undertaking this work, the writer can but express his regrets that anyone should be misled into a discovery of selectivity\(^{12}\) from the preliminary spectrophotometric data then obtained. Other data then at hand was overwhelmingly against our spectrophotometric results and with the new data, to be discussed presently, the writer feels no necessity for changing the views then expressed,\(^{13}\) namely that the apparent spectrophotometric selectivity is not due to a true emission band, but is due to an increase in transparency of the acetylene flame in the infra-red. Previous observations on the distribution of energy in the spectrum of the acetylene flame were described by Stewart;\(^{14}\) but the data is not applicable to the present question of a selective emission in the visible spectrum.

It is to be noticed that in the present experiments the light-gathering power of this instrument was six times that used in previous investigations of acetylene. The dispersion was also considerably greater than used heretofore, being almost five times as great when using the glass prism. Furthermore, there is no uncertain absorption due to silvered mirrors. The instrument

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\(^{12}\) Hyde, Jour. Franklin Institute, 170, p. 29; 1910.
\(^{13}\) This Bulletin, 5, p. 376; 1910.
was capable of collecting sufficient light and in producing a sufficiently long visible spectrum to make observation easy, accurate, and free from doubt. If a band of selective emission, of appreciable intensity, exists at \( .7\mu \), it must, therefore, be observable in the spectral radiation curve.

2. THE VISIBLE SPECTRUM

For the present investigation, the acetylene was produced by a commercial automatic generator. It was burned as it came from the gasometer, without additional drying, and hence was investigated as in previous experiments. For the flat flame, a Von Swarz "Perfection" acetylene burner was used. The rated capacity was \( \frac{3}{4} \) cu. ft. per hour, operated on a pressure of 7 cm (2\( \frac{1}{2} \) inches) of water. A lava tip of a "Naphey" burner was also used. This consumed \( \frac{1}{4} \) cu. ft. per hour. It gave a cylindrical flame about 3 cm high. Spectral energy curves of these two flames were also obtained when burning under a gas pressure of 10 cm (4 inches) of water. It was found that the spectral energy curves of these two flames coincided exactly when operated under the same gas pressure. No data was obtained of the cylindrical acetylene flame when burning under 7 cm water pressure. The observations on the flat flame show that for the same intensity in the violet the intensity in the red is greater on the normal water pressure of 7 cm than on the higher pressure of 10 cm water. In view of the fact that the observations on the flat flame were made on different days with different adjustments of the flame before the spectrometer slit, further observations will be necessary to determine whether this is solely due to a variation in pressure.

In these three series of measurements, using the quartz prism, no selective emission (which should manifest itself as a hump at \( .7\mu \) in the spectral energy curve), could be observed either in the prismatic or the normal spectral energy curve. As a further check on the accuracy, using a larger dispersion, the apparatus was readjusted and a light flint silicate prism substituted for the one of quartz. With this larger dispersion, using the rest of the apparatus as before, the galvanometer deflections were reduced to 5 cm in the yellow and a total deflection of 35 cm in the red. For
accuracy in measuring the galvanometer deflections, all readings were reduced to about 15 cm, and, since the deflection could be read accurately to 0.3 mm, to 0.5 mm, a precision of 1 part in 300 to 400 would easily have been possible. But the flame was subject to fluctuations, due to air currents, of 1 to 2 mm (galvanometer deflection), so that this precision was considerably reduced. The results obtained on the flat flame are shown graphically in Fig. 4, in which the continuous lines (••••) give the observations in the prismatic (glass) spectrum and the dotted lines (○○○○○) give this same data reduced to the (approximate) normal spectrum.

The normal spectral energy curve of the flat flame, obtained by using the quartz prism, coincides within 1 per cent throughout the whole length with the normal curves given in Fig. 4. This is an excellent test of the factors used in reducing the prismatic curves to the normal curve. No correction has been made for change in focal length which would increase the curvature in the red.

In the prismatic curves, Fig. 4, the three dots at each point of observation, for example at .7μ, indicate the maximum, the mean (of 10 to 15 observations), and the minimum deflections representing three series of observations made in rapid succession back and forth throughout the spectrum. The whole time consumed was less than two hours, with the barometer reading 755 mm and a relative humidity of about 69 to 70 per cent. No irregularity is observable in the energy curves, greater than that due to fluctuations in the flame, and it can safely be said that these curves show no band of selective emission, at .7μ to .72μ, in which the maximum rises as much as one per cent above the general trend of the spectral energy curve. The spectrophotometric data would indicate a protuberance at .70μ rising several centimeters above the general trend of the spectral energy curve. Furthermore, the spectral energy curves, obtained with this apparatus, of carbon filament lamps show no selective emission in this region. It is therefore an interesting question why the spectrophotometric intercomparisons of these two sources should indicate an abnormal emission beyond 0.7μ. The very marked difference of their
Fig. 4
emissivities in the infra-red should produce a maximum in their ratios of intensities. This maximum for a 2.5 watt "Gem" carbon filament lies at about .55μ. See Figs. 6 and 8.

In Fig. 5, curve a shows the normal spectral energy curve of the acetylene flame, determined with the mirror spectrometer, fluorite prism, and vacuum bolometer. In order to obtain sufficient intensity, the flame was placed so that it radiated edgewise into the spectrobolometer. The curve has been corrected for absorption by the silver mirrors. The values obtained by Stewart, using a cylindrical flame, have been similarly corrected and reduced to a normal spectrum by means of the writer's slit width factors. The two curves coincide exactly throughout the whole visible spectrum. The lack of coincidence in the infra-red is no
doubt due to the difference in the effective thickness of the two flames, as will be noticed on a subsequent page. The values of the various emissivities (arbitrary units) of the normal spectral energy curve of acetylene are given in Table I. The values at .36μ to .52μ were obtained with the quartz lens spectrometer. They coincide exactly, over the common range from .44μ to .52μ, with the values obtained with the mirror spectrometer having three reflecting mirrors. Using five mirrors, instead of three, the spectral energy curve at .40μ to .44μ falls slightly below the values given in Table I. This is no doubt due to the lack of a proper correction for the absorption by the silver mirrors.

**TABLE I**

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<th>Wave Length in μ = .001 mm</th>
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3. **EMISSIVITY A FUNCTION OF THE THICKNESS OF THE RADIATING LAYER**

The acetylene flame consists essentially of incandescent carbon particles in the process of combustion, suspended in the heated gases, CO₂ and H₂O, which are the combustion products of acetylene. The spectral energy curve therefore consists of a continuous spectrum due to the incandescent carbon particles superposed upon the composite emission spectrum of water vapor and carbon dioxide, which consists of strong emission bands, notably at 2.7μ and 4.4μ.
In order to be able to use the acetylene flame as a standard of reference in spectral radiation work, it is important to know how the emissivity varies with the thickness of the flame. That the thickness of the radiating layer has but slight if any effect on the shape of the (prismatic) energy curve in the visible spectrum is shown in Fig. 5, curve $b$, which gives the radiation from the flat side (xxx and $\cdots$) and the edge (○○○) of the flame. In this experiment the acetylene flame, radiating edgewise into the spectrometer slit, illuminated a width of only about 1.5 cm of the glass prism, which was therefore entirely covered except about 1.5 cm of the central part of the face. In this manner, the flat side of the flame illuminated the same width as the flame turned edgewise. The expectation was to find a marked increase in the emissivity in the red when the flame was radiating edgewise into the spectroradiometer. The deflections were eleven times as large as those from the flat side of the flame, but when reduced to the same scale and plotted, as shown in curve $b$ Fig. 5, they coincide throughout the whole range. In this experiment the radiation from the flat flame (xxxx) was first observed, then the flame was accurately adjusted edgewise (○○○○), and finally the observations were repeated on the flat flame (○○○○). The observations of the flame radiating edgewise were subject to greater variations (due to air drafts which deflected the flame from the 1.5 cm opening of the cover on the prism) than when observed flatwise, and, in all, less observations were made than for the curves in Fig. 4. Nevertheless, there is an exact coincidence of the three series, throughout the visible spectrum, showing the same relative emissivity when viewed flatwise as when viewed edgewise. This is probably to be expected in view of the fact that the variation in the absorptivity with thickness of the flame is not very marked in this spectral region. Moreover, in this spectral region the variation in absorptivity (emissivity) with the wavelength is not so marked as in the infra-red. In this same curve the observations marked with the rectangles (□□□□□) were made with the same apparatus, and a flat flame, a month later when meteorological conditions were different, and when the gas generator contained a fresh charge of carbide. The observations coincide exactly with those previously obtained.
Fig. 6
In Fig. 6, curve a gives the normal infra-red spectral energy curve of the acetylene flame radiating edgewise into the silt, while curve b gives the energy curve of the same flame radiating flatwise into the spectrobolometer. In the latter all the observations were multiplied by the factor, 9.6, which produced an exact coincidence throughout the visible spectrum. In the infra-red there is a wide departure in the lack of coincidence of the two radiation curves. This is especially noticeable in the emission bands of carbon dioxide at 4.4μ. For the flat flame the ratio of the two maxima, $E_{\text{max}} : E(\lambda = 4.4\mu) = 2.05$ while in the flame radiating edgewise the ratio of $E_{\text{max}} : E(\lambda = 4.4\mu) = 5.5$. In other words, in viewing the flame flatwise the maximum emission of the CO$_2$ band is almost one-half as great as the point of maximum emission of the incandescent carbon particles, while in the flame viewed edgewise, the CO$_2$ band is only about one-fifth the maximum at 1.25μ.

Curve c, Fig. 6, gives the ratios of curve a to curve b, and it also shows that the emissivity of the CO$_2$ increased by a much smaller amount than did the emissivity of the incandescent carbon particles.

In Fig. 6 the relative areas of curves a and b are 88 to 74, which explains the wide variations in the various determinations of the luminous efficiency.

4. COMPARISON OF ACETYLENE FLAME AND A SOLID RADIATOR

The wide departure of the acetylene radiation from that of a black body is well illustrated in Fig. 6. For a black body (at the same temperature) there would not be a great depression in the spectral radiation curve, such as obtains in acetylene, between 1.5 and 4.4μ. This is illustrated in the following comparison of acetylene with a Nernst glower. While the Nernst glower at low temperatures departs far from a black body in its radiation, it seemed of interest to compare the acetylene with it when the two were set to the same emissivity in the green. This was done by viewing the Nernst glower against the acetylene flame, using green glass, and varying the current through the glower until its color merged into that of the acetylene flame. The latter was viewed edgewise. The glower was a D. C. type 13 mm long, 1.03 mm diameter and rated at about 73 watts. To obtain a match with

15 This Bulletin, 4, p. 540; 1908.
the acetylene, in the green, an energy input of only 36 watts was required. To the eye, of course, the glower is decidedly reddish in color, due to its greater emissivity in the red. This is well illustrated in Fig. 7, in which curve a gives the radiation from the Nernst glower and curve b gives the radiation from the acetylene flame. The radiation curves are entirely different in these two radiators and while the Nernst emitted the more "light," it was of a type not the most useful to the eye. The ratio of the areas of these two energy curves is \((a : b) = 84 : 34\); the \(\lambda_{max} = 1.35\mu\) and \(1.25\mu\) respectively.
5. ABSORPTIVITY OF AN ACETYLENE FLAME

The general notion seems to prevail that amorphous carbon in the form of "soot" or "lampblack" is a turbid medium, which has the property of an increase in transparency with increase in wave length. The few experiments now at hand on the absorptivity of a layer of soot at room temperatures indicate a high absorptivity in the visible spectrum which decreases uniformly but rapidly as we go into the infra-red. There are so many forms of amorphous carbon that this should hardly be considered a general rule without further investigation. Furthermore, the nature of the medium in which the particles are suspended must also be considered, whether the surrounding medium is a hot or a cold gas, or a liquid, as in the case of asphaltum varnish. In this respect, as will be noticed presently, the incandescent particles in the acetylene flame are not unlike colloidal suspensions of metals in which there is usually a distinct absorption band.

The present examination of the absorptivity of an acetylene flame was undertaken to verify the previous work by Ladenburg, whose absorptivity curve (see Fig. 9) is smooth and continuous in the region of .7μ, where there should be an absorption band, if the acetylene flame has a true emission band in this part of the spectrum. The discovery of a fairly well defined absorption band in the visible spectrum came as a distinct surprise, for it was the expectation to find a uniform increase in absorption as we go into the ultra-violet, as is generally supposed to be the case, and as indicated in Ladenburg's curves, which, however, stop at .7μ. A subsequent search of the literature on the absorption by lampblack shows that, even in the cold state, there are some forms of carbon (or hydrocarbon ?) which exhibit an absorption band in the visible spectrum. In 1886, Nichols published the results of an investigation of two specimens of lampblack, both of which showed a maximum of absorption in the region of .52μ, the transmitting power being considerably greater in the red and in the violet. Subsequently he published measurements upon the age coating.

in incandescent lamps, made by Messrs. Moore and Ling, in which it was shown that the absorption of light by the deposit of carbon upon the glass bulb of a lamp with a treated carbon filament, was greatest in the region of .635μ. It is interesting to note that the age coating on the bulb of an incandescent lamp, containing an untreated carbon filament, did not show a maximum absorption in the visible spectrum, behaving in this respect like lampblack deposited from flames.

The structure of the carbon particles in the acetylene flame with their maximum absorption in the visible spectrum are therefore not very unlike some of the aforesaid "metallic" deposits from such vapors as gasoline or benzine on a treated carbon filament. By heating a strip of platinum in an inclosed vessel and then introducing acetylene, similar metallic films may be formed, which are easily removed and mounted on a glass plate.

The first indication of an increased transparency in the acetylene flame, in the violet, came from an examination of the ratios of its spectral emissivities with those of carbon filaments. These ratios show a decided maximum in the visible spectrum. This is illustrated in Fig. 8, in which curve c gives the ratios of emissivities of acetylene (from Fig. 4) divided by the emissivities of a graphitized carbon ("Gem") filament which was operated on 2.5 w. p. m. h. c. A similar curve, c Fig. 7, gives these ratios to 2.5μ. In this case the flat side of the flame radiated into the spectrometer slit. Curve b gives the ratios of emissivities of the acetylene flame to the emissivities of the graphitized carbon filament, when the

19a Since writing this paper, Dr. Nutting has kindly made a spectrophotometric examination of the age coating on the glass walls of commercial incandescent lamps containing "treated" filaments and graphitized carbon ("Gem") filaments. The lamps were prepared for me by Mr. Mulligan. The deposits were heavy, to avoid errors in observations. In neither case was a distinct absorption band found in the visible spectrum. The absorption decreased uniformly from 49 per cent in the violet (.447μ) to 47 per cent in the red (.7μ) for a sample coating from a "treated" carbon filament. The coating from the graphitized filament absorbed 29 per cent in the violet, which decreased uniformly to 28 per cent in the red. The observation were repeated, with greater thoroughness, on a sample of "treated" carbon deposit, which absorbed 57 per cent in the violet and 51 per cent in the yellow, the accuracy being 1 part in 200.
flame radiated edgewise into the spectrobolometer. In these comparisons a glass prism was used with the quartz spectroradiometer. Using a quartz prism to obtain the two spectral energy curves, curve d gives the ratios of the emissivities of acetylene divided by the emissivities of a treated carbon lamp on 4 w. p. m. h. c. Curve a gives the ratios of acetylene to the emissivities of a Nernst glower, on normal operation. The depression observable at .48μ to .52μ in the preceding curves is also observable in this one; but since it is unknown whether the glower has a band of selective emission in this region the data is not so convincing.

In all these curves the region at .7μ to .72μ shows no sharp changes in curvature, such as would have to obtain in the presence of an emission band in this region. These spectroradiometric ratios are exactly analagous to the spectrophotometric data and since the original observations are accurate to at least 1 per cent (which accuracy can not be claimed with the spectrophotometer at .7μ) it is evident that the accuracy of the spectrophotometric data must be considered in doubt until further work has been done on that subject. In all these curves there is a pronounced maximum in the region of .56μ to .60μ, the variation in the position of the maximum being due to the difference in temperature of the carbon filament.
For curve $d$ the black body temperature $^{20}$ of the treated carbon lamp on 4 w. p. m. h. c. is $1790^\circ \pm 20^\circ$C. This curve at $0.7\mu$ is very similar to the one obtained with the spectrophotometer. $^{10}$ In the violet the spectrophotometric curves previously obtained, $^{10}$ and also those recently obtained by various observers in this Bureau, do not drop so rapidly as the aforesaid curves given in Fig. 8.

In the spectrophotometric comparisons of the acetylene flame against a black body at $1410^\circ$ Abs. (a much lower temperature) Nichols and Merritt $^{21}$ found this maximum shifted over into the blue-green. However, the fact that the acetylene curve and the spectral energy curve of the black body at $1410^\circ$ Abs. do not coincide is hardly evidence of selective emission, for the temperature of the acetylene flame is about $1800^\circ$C and hence would, under ordinary circumstances, emit the more light in the blue and violet part of the spectrum; but the important point is that their energy curve of acetylene shows a marked elevation in the blue-green.

While all this data can now, at the conclusion of the work, be cited as additional evidence of a transparent region in the violet of the acetylene flame, the first discovery of this transparency, by measuring the absorptivity directly, could not be supported by such convincing proof, and three distinct series of experiments were made, during an interval of four months, in order to be certain that the whole is not due to instrumental errors.

In the first series of measurements of the absorptivity of the acetylene flame an image of Nernst glower was projected upon the slit of the quartz lens spectroradiometer (with light flint glass prism) by means of a 15 cm focal length silvered mirror. The flat acetylene flame was placed, in a fixed position, about 3 cm in front of the slit. Two shutters were provided; the one for preventing any radiation from entering the spectroradiometer slit, the other for preventing radiation from the Nernst glower from falling upon the acetylene flame. Suitable shields were of course provided to prevent errors due to stray light. Repeated experiments showed that observations could be repeated exactly on

$^{20}$ This Bulletin, 6, p. 326; 1910.

relighting the flame. The Nernst glower was operated constantly on a storage battery, to keep it at a uniform temperature. The order of observation consisted in (1) setting the spectroradiometer circle to some definite wave length; (2) observing the galvanometer reading due to the acetylene flame; (3) observing the galvanometer reading when both the acetylene flame and the Nernst glower radiated into the slit; (4) with the acetylene flame extinguished, observing the radiation from the Nernst glower; and (5) usually repeating the complete series in the reverse order. From 10 to 15 observations were therefore obtained for each of the three steps, or from 30 to 45 at any spectrometer setting. The absorptivity is \( (2) + (4) - (3) \div (4) \). In this manner curve a, Fig. 9, was obtained. The cone of light from the glower covered the greater part of the thin central portion of the acetylene flame; but only a strip of the flame,
about 5 mm wide, shone upon the prism face. The absorptivities are therefore only relative values. About four months later the work was taken up anew, to verify these observations, by using a thicker absorbing layer, but other instrumental details remaining as before. For this purpose two flat flames were placed as close together as was possible, and the absorption by the two flames was observed. The deflections for the two flames were, of course, much greater and permitted observations farther into the violet than in the previous experiment. The absorption band, curve b, Fig. 9, came out much sharper than with the thinner flame. Moreover, there appears to be an absorption minimum in the region of 0.48\(\mu\) to 0.5\(\mu\). It is important to notice that the depression in the curves, at 0.5\(\mu\), is greatly magnified in Fig. 9, and hence, at a first glance, may appear deceptive. The total variation in the absorptivity is so small that it would be difficult to observe a change in emissivity in this part of the spectrum, because of the smallness of the galvanometer deflections, and the rapid change in the spectral energy curve as indicated in Fig. 4. The slight depression at 0.52 to 0.54\(\mu\) observable in Fig. 4 is probably due to the increased transparency of the acetylene flame, but it is not much greater than experimental error.

There still being reasons for doubt in this matter the work was repeated, using Ladenburg's method in which an image of a thick (2 mm diameter) Nernst glower was projected normally upon the acetylene flame which stood flatwise back of a metal screen, with a slit 10 x 2 mm area. The radiation from the glower and the acetylene flame, passing through this slit was received upon a second mirror which projected an image of the two radiators (the slit) upon the spectrometer slit. The absorption in the second mirror reduced the intensity of the acetylene flame so much that observations were very difficult in the violet. The absorptivity curve c is practically the same as in the previous experiments. The absolute values of the absorptivities in the three experiments are not comparable, because different areas of the (flat surface of the) flame were examined. Ladenburg's curve is also given in this illustration as additional evidence of the absence of an absorption band at 0.7\(\mu\). In order to increase
the absorptivity he placed the flame so that the flat side made an
angle of 45° with the slit.

The sharp turn in the absorptivity curve at .7μ to .8μ must
have a peculiar effect upon the emissivity curve, but it will not
produce a true emission band. As a result of the absorption
(emission) band at .6μ, and of the rapid decrease in absorptivity
at .7μ, the spectral energy curve of the acetylene flame is much
straighter (practically a straight line from .6μ to .7μ) in this
spectral region than obtains in metal and carbon filaments.

It will be an interesting investigation to determine whether
the presence of an absorption band in the visible spectrum is a prop-
erty of all flames containing incandescent carbon particles. In
the low temperature flames, e. g. benzine, amyl acetate, etc., the
difficulty will arise in obtaining sufficiently large deflections to
make the test conclusive. A qualitative test may be obtained
by simply taking the ratios of their emissivities against an untreated
carbon filament. See Fig. 8. A special form of optical pyrometer
would be the simplest instrument to use, provided it can be made
sufficiently sensitive in the violet.

Heretofore it has generally been supposed that flame spectra 22
exhibit but two types of emission bands; (1) the sharp emission
bands of the gases which are the heated combustion products of the
gas used (e. g., the emission bands of CO₂ at 4.4μ, Fig. 6), and (2)
the radiation from the incandescent carbon particles which, as in
the case of the lamp filament, covers a wide portion of the infra-red
spectrum with a maximum in region of 1.2μ to 1.5μ. But no
really convincing data was at hand which indicated a true emission
band in the visible spectrum. All the data herewith presented
indicate such an emission band in the acetylene flame. The next
question is the probable cause of this band. Some of the experi-
ments on lampblack just quoted seem to indicate that the absorp-
tion is caused by the carbon particles (probably hydrocarbons)
suspended in the heated gases. There seems to be a difference in
the structure of the carbon (lampblack) deposited on a cold
surface, which shows no absorption band in the visible, 19 and in
the structure of carbon (hydrocarbon?) deposited on hot surfaces,

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22 See The Illum. Eng., London, 3, p. 261, etc., 1910, in which the various types
of emission spectra are illustrated.
e. g., a deposit on the "treated carbon" filament of an incandescent lamp. The latter form when condensed on the walls of the lamp sometimes shows an absorption band in the visible spectrum. The broadening or the sharpening of bands in various substances in solution, with change in temperature, does not seem to follow the same law. It is therefore possible that the broad region of absorption caused by the cold carbon particles is narrowed down into a sharp band when the particles are in a highly incandescent state.

The theoretical temperature of combustion of acetylene gas is of the order of 4000° to 5000° C at the moment of disruption of the acetylene molecule. Such a high temperature can not, of course, be maintained on account of the heat lost by conduction, convection, and radiation, so that the mean thermal temperature of the acetylene flame is about 1800° C. Similar emission bands in other substances have been ascribed to thermoluminescence and no doubt some will be willing to consider the selective emission in the visible spectrum of acetylene to be due to the emission of the acetylene molecule. By luminescence is meant an emissivity greater than that of a black body at the same temperature. An interesting case of a supposed thermoluminescence is the peculiar diaphanous white light emitted by oligoclase when heated to a mean thermal temperature of 800° to 1000°. However, the incandescent carbon particles are at a temperature of at least 1800°, which fact, taken in connection with the experiments on the variation of emissivity with thickness and the comparison with the Nernst glower just described, seems sufficient evidence that the selective emission in the acetylene flame can be explained on a purely thermal basis, without invoking the hypothetical and unproven assumption of the presence of "luminescence."

6. SUMMARY

The present investigation of the acetylene flame had for its main object the exact determination of the emissivity and absorptivity in the visible part of the spectrum. This has required a special equipment of spectroradiometric apparatus and gas gene-

rators. The present results show that the earlier spectrophotometric data was misinterpreted; that the peculiar change in curvature in the spectrophotometric ratios at $.72\mu$ is not due to a true emission band but is due to a rapid increase in the transparency of the flame in the region of $.7\mu$ to $.8\mu$. The various curves herewith presented show no selective emission at $.7\mu$ in the sense of a true emission band or protuberance, rising sharply above the general trend of the spectral energy curve and merging into the latter at near-by regions—for example, at $.67\mu$ and $.73\mu$. The acetylene flame has a band of selective absorption (hence also of emission) extending throughout the visible spectrum with a maximum at about $.6\mu$. This absorption becomes more uniform beyond $.75\mu$, at which point there is a rather sharp turn in the absorptivity curve. This produces a much straighter spectral energy curve in the visible than obtains in carbon and metal filaments, and also results in a greater deficiency in the radiation in the infra-red. This is difficult to show in the spectral energy curve of acetylene, but is emphasized by taking ratios of emissivities by comparison with a radiator, which is more nearly like a black body. This procedure brings out small changes in curvature in a manner similar to the magnification of transformation points in cooling curves of a substance by using two thermocouples, the one of which is imbedded in a substance not having such transformation points. The method of taking ratios therefore commends itself in searching for a selective emission in the visible spectrum of low temperature flames.

IV. SELECTIVE EMISSION OF THE WELSBACH MANTLE

1. HISTORICAL

It is beyond the scope of the present paper to give a complete account of the various experiments that have been made to explain the selective emission of the gas mantle perfected by Auer von Welsbach. A fairly complete account may be found in a recent paper by Fulweiler.\textsuperscript{24}

That many of these experiments have been misdirected is evident; and it is equally true that the results obtained often seem to be seriously misquoted by subsequent writers. In view of the fact that even as late as the year 1895 the properties of the radiation from a uniformly heated enclosure were none too well understood, the experiments of St. John on the selective emission oxides 25 were novel. Two years prior to his work Violle 26 examined various oxides, heated to incandescence in a uniformly heated enclosure, and found that they all appeared at the same brightness, following Kirchoff's law. In the same manner Bunte 27 heated various oxides, including cerium and thorium, to 2000° in an electric furnace and found no special emissivity. In St. John's experiments the oxides were also heated in a furnace and after reaching a thermal equilibrium he observed their true emissive properties by introducing quickly, through the observing window, a cool porcelain tube at the end of which he could observe simultaneously his platinum comparison standard and the oxide. Since he received radiation only from the platinum and from the oxide and nothing from the enclosure, the black body effect was eliminated and he could observe their true emissive properties at known temperatures measured by the furnace.

In the experiments of Le Chatelier and Boudouard 28 they compared the brightness of different spectral regions of various oxides which they heated in a bunsen flame. To measure the temperatures they covered a thermojunction with the oxide under examination. They concluded that the Auer mantle emits no more than a black body, at the same temperature, and that the high emissivity in the visible is due to the coloring matter, cerium oxide, which is added to the thorium oxide.

Nernst and Bose 29 made a spectrophotometric comparison of the light from the Welsbach mantle with an incandescent lamp which was operated at different temperatures. They showed that

26 Violle, Compt. Rend., 117, p. 33; 1893.
28 Le Chatelier and Boudouard, Compt. Rend., 126, p. 1861; 1898.
29 Nernst and Bose, Phys. Zs., 1, p. 289; 1900.
the emissivity is low in the red, which imparts the greenish tint to the emitted light. In order to show that the flame gases have no influence on the light emission they formed the material, composing the Welsbach mantle, into a thin rod which they heated to the same temperature either in an oxyhydrogen flame or by means of an electric current. For thin threads of the material the ratios of the emissivities was practically constant throughout the visible spectrum. But for thick rods the ratios varied, which they explained by the fact that in the flame the rod is heated from without, while the electric current heats the rod from within. Unfortunately no spectrophotometric comparisons were made of the Auer mantle with the heated rod, which, as will be noticed in the work to be described presently, are decidedly different in their emissivities. Furthermore, no mention is made of the marked yellowish-green color which appears on warming the homogeneous rod of the mantle constituents.

In the aforecited papers the general conclusion arrived at was that the high light emissivity of the Welsbach mantle is due to the finely divided particles of cerium oxide which are held in suspension, or perhaps in solid solution, in the thorium oxide. Since the cerium oxide has a high absorption for wave lengths shorter than the yellow, which would produce a high emissivity throughout this whole region, this is not an unreasonable conclusion. However, arguments have been presented to support the view that catalysis in the gas flame causes a localized and more rapid combustion, and therefore causes a higher temperature than would be possible in the mantle of pure oxide. Here the catalytic action is supposed to be something similar to that of a jet of gas impinging upon a piece of hot platinum, which is then heated to a higher temperature by the unignited gas. In the mantle the most efficient mixture is about 99 per cent thorium oxide and 1 per cent of cerium oxide, and it is not clear why this particular ratio should be most efficient for the catalytic action. On the other hand, this optimum ratio makes the explanation tenable on the emissivity basis; for when the proportional part of ceria falls below the above

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amount the absorption, and hence the emission, would not be so complete in the region of the blue and the green, while if the per cent of ceria exceeds this optimum value the emissivity in the long waves becomes more prominent, as has been shown by experiment. Simply increasing the thickness of the radiating layer should have this same effect (if this is the true explanation of the observations), as shown in the experimental part of the present paper. If catalytic action has any marked effect, locally, in raising the temperature of the oxides then the mean temperature of the flame should be increased. This is contradicted by the experiments of White and Travers $^{31}$ who showed that the thoria-ceria mantle is at a lower temperature than a mantle of pure thorium, and that in general the mantles were about $130^\circ$ C below the temperature of the flame.

Previous experiments on the spectral energy distribution of the Welsbach mantle, of interest in the present work, were made by Rubens $^{32}$ who showed that in the region of $1\mu$ to $5\mu$ there is but little energy emitted, while in the green and yellow the spectral energy curve corresponds closely with that of a black body at 1800 Abs.

2. THE VISIBLE SPECTRUM

The strong selective emission in the visible spectrum of the Welsbach mantle is well known from previous spectrophotometric comparisons and from the recent spectroradiometric work of Rubens just quoted. The applicability of the mantle as a standard of radiation will require an extensive investigation of various mixtures of thorium and cerium. Even after specifying the relative proportions of the oxides used, the rate of gas consumption, etc., it does not appear, without further investigation, that conditions can be repeated with sufficient accuracy, so that it will probably be necessary to determine the spectral energy curve of a sample of each lot of mantles manufactured.

The peculiar energy distribution in the visible spectrum of the Welsbach mantle (of unknown composition) is illustrated in Fig. 10. The strong selective emission in the yellow-green, and the weakness of the radiation in the red ($0.70\mu$) is very marked. The


$^{32}$ Rubens, Ann. der Phys. (4) 18, p. 725, 1905; 20, p. 593; 1906.
low emission in the red continues so throughout the infra-red. There is no marked maximum in the region of 1.2\(\mu\) to 1.3\(\mu\) as was supposed to be the case from the measurements made by Lummer and Pringsheim (Zs. für Beleuchtungwesen, vol. 10). It will be an interesting problem to determine the variation in the energy distribution in the visible spectrum with variation in the amount of cerium oxide used in the mantle.

3. COMPARISON OF GAS MANTLE WITH A SOLID GLOWER

The oxides are well adapted to the investigation of the variation in emissivity with the thickness of the radiating layer of the substance.

In a previous paper, the writer \(^3\) gave the emission spectrum of a glower composed of 99 per cent thorium oxide and 1 per

\(^3\) This Bulletin, 6, p. 318; 1909.
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cent cerium oxide, which are closely the constituents of the Welsbach mantle. To verify these observations and to obtain quantitative data, the investigation was undertaken anew. The material used was obtained from new Welsbach mantles, which were ignited, to remove the organic matter, and the fine powdered oxides were squirited into glowers, which were then roasted in the same manner as is done with the commercial Nernst glower. This work was very kindly performed by the Westinghouse Nernst Lamp Company. Duplicate mantles were kept for the experiments on the spectral energy distribution of the mantle itself.

For the experiments on the gas mantle material (thoria ceria mixture) used as a glower, the solid rods were made into suitable lengths (12 mm long between the terminals and 0.77 mm diameter) and provided with platinum terminals. They were operated on the secondary of a transformer as in the previous work on the radiation from electrically heated oxides.

In order to have some rational basis for comparison, the glower was placed a short distance before the gas mantle (at a sufficient distance so that its conductivity was not affected by the mantle radiation) and the temperature of the glower was varied until it showed the same color as the hottest part of the mantle when viewed through monochromatic red, green, or blue glass. This calibration was done by two observers, and in three ways, to eliminate the effect of the structure of the mantle. In the first calibration (which consisted in noting the current and voltage in the primary of the transformer which was necessary to heat the glower to a certain temperature) the glower was brought in line with the vertical edge of the mantle, which avoided sighting on the open spaces in the mantle. In the second series, the observer stood at a great distance so that the eye could not distinguish the structure of the mantle. In the third calibration a metal screen was placed between the observer and the glower. The screen contained an opening of such a size as to cut off the view of the glower terminals. The three series of calibrations were in excellent agreement, as was also the various settings for intensity match by the two observers. The emissivity of the mantle in the red is so much less than that of the identical material when squirited into a solid homogeneous rod that an energy input of 22 watts
sufficed to bring the glower to the same emissivity as the mantles in the red, while 24 watts were required to obtain the same emissivity as the mantle in the green. This low emissivity in the red of the Welsbach mantle is illustrated in Fig. 10. The maximum at .66μ varies with the composition of the mantle. The infra-red spectral energy curves were obtained with a fluorite prism and a vacuum bolometer. The problem consisted in observing the spectral energy curve of (the hottest part of) the Welsbach mantle heated by the usual gas burner. The mantle was then removed, the electrically heated glower was placed before the spectrometer slit and two series of spectral energy curves of the latter were obtained, the one series being for the same emissivity as the mantle in the red, and the second being for the same emissivity in the green.

The remarkable difference in the spectral energy distribution in the Welsbach gas mantle and the same material when operated as a solid glower is shown in Fig. 11. Curve c gives the spectral energy of the Welsbach gas mantle used without the glass chimney. The emission bands at 2.8μ and 4.4μ are due to the heated water vapor and CO₂ which are the products of combustion of a bunsen flame. The radiation from the mantle itself at 3μ corresponds somewhat with the dotted lines, curve c, which is essentially the same as previously observed by Rubens. Curve a gives the spectral energy distribution of the glower when operated on 24 watts (46 volts at terminals; .52 amp) which gave the same emissivity as the mantle in the green. Curve b shows the energy distribution of the same glower when operated on 22 watts (55 volts; .40 amp) which was the energy input required to give the same emissivity as the gas mantle, in the red.

The relative areas, as found with a planimeter, are: a = 118 units, b = 55, c = 14 (c = 8.5 units by omitting the emission bands). From this it appears that the solid glower emits about 8.5 times (a ÷ c) as much energy as the gas mantle in order to attain the same emissivity in the green. Of course, the glower emits the more "light." (The relative areas are: a = .5 and of c = .2 unit in the "visible spectrum.") But it is of a quality that is of little use in high efficiency illumination. To the eye such a glower appears a low red. It was therefore of interest to compare the
mantle material in the form of the solid rod with a regular Nernst glower, which is composed of zirconium and yttrium oxides. The

Nernst glower used was the D. C. type, which was operated on 103 volts, 0.62 amp (64 watts) in order to obtain the same energy
curve in the visible spectrum as a tungsten lamp operated on 1.2 w. p. m. h. c.—See Fig. 14. Viewed through either red, green, or blue glass, the regular Nernst glover and the rod of mantle material showed no marked difference in their emission. The rod of mantle material was therefore brought to the same emissivity as the Nernst glover, using red glass for the viewing screen. In making the equal emissivity setting the same results were obtained by viewing the two glowers placed side by side or so placed in the line of sight that they slightly overlapped.
The spectral energy curve of the Nernst glower, on practically normal operation (103 volts, D. C.; .62 amp) is shown in curve b, Fig. 12. The wave length of maximum emission lies at about \( \lambda = 1.3\mu \). The spectral energy of the mantle material is shown in curve a. The energy input for the same emissivity as the Nernst glower was 56 watts (22 volts at terminals; 2.55 amp). Curve c is curve a of Fig. 11 drawn to the same scale. The maximum emission lies at 1.7\( \mu \). The relative areas of these curves are: \( a = 78 \), \( b = 64 \), and \( c = 12 \) units. On a subsequent page it is shown that from the spectral energy curves of a Nernst glower and a tungsten lamp (the latter operated on 1.2 w. p. m. h. c.), set to the same emissivity in the visible spectrum, the Nernst glower is operating on about 2 w. p. m. h. c. No exact comparison can be made with the gas mantle because the quality of its light is so different in the red. The illustrations, however, show the great advantage which the mantle has over the thick glower of the same material. The latter must be heated to a much higher temperature to attain a luminous efficiency comparable with that of the gas mantle. It is to be noted, however, that in commercial operation the luminous efficiencies of the Welsbach mantle, the Nernst glower, and the tungsten filament are not markedly different, being of the order of 3 to 5 per cent of the total energy radiated. It may be noted that while the gas mantle has a higher luminous efficiency than a solid rod of the same material and also more efficient than a Nernst glower set to the same emissivity, the latter is the more efficient of these two kinds of glowlers.

The Welsbach mantle consists essentially of a woven framework of the purest cotton thread which has been boiled in potash to remove the silica. On ignition there is practically no ash. This cotton framework is impregnated with a solution of the nitrates of cerium and thorium and the cotton is removed by ignition. Thorium nitrate when heated expands into thin-walled tubes of considerable strength. This property, in addition to the removal of the numerous filaments composing the cotton threads, leaves the finished mantle of these oxides in an extremely porous state, which permits the particles to easily assume the temperature of the flame. Thorium oxide being white in color can emit but little
in the visible spectrum. Cerium oxide is a rich yellow, absorbing all the violet, the blue, and into the green, and hence must emit the most energy in this region of the visible spectrum. If the thickness of the radiating layer of cerium oxide is small, then the effect of the selective emission is not noticeable in the spectral energy curve. If the thickness of the radiating layer is larger, the band of selective emission extends farther into the infra-red, and the flame temperature is lowered. In the mantle material, in the form of a solid rod, this excessive radiation is very apparent. For use in the bunsen flame, the Welsbach mantle of thoria and ceria in the ratio of about 99 to 1 seems to be the proper proportion for the most efficient illumination. When concentrated into a solid rod the low temperature of the flame and the rate of gas supplied is not sufficient to produce a satisfactory light, and, as noticed in the present illustrations, the temperature must be raised to that of the Nernst glower—2000° C—to produce an efficient illuminant. The specific emissivity is of course entirely different in the two cases, although their luminous efficiencies are not markedly different.

In conclusion it may be added that, while it is highly probable that the radiation from the Welsbach mantle is purely thermal, the problem being chiefly one of thickness of the radiating layer (concentration of the ceria particles), as illustrated in the present experiments, the question of the physical structure of the cerium oxide at high temperatures needs further consideration. In this connection, several observations may be recorded of the influence of temperature on the color of pigments.

It is a familiar fact that zinc oxide, which is perfectly white at room temperature, becomes a rich yellowish-green when heated above 400°. This change in its pigment color is due to a broadening of its absorption band from the ultra-violet into the visible spectrum. Cerium oxide has this same property to a very marked degree. This was first observed in the glower of the mantle material.

It was found that the solid rods of the Welsbach mantle material, used in the present experiments, emit (reflect) a yellowish green light when warmed to 400° to 500°, the color of the cold rod being white. The powdered mantle material does not show
this effect to a marked extent. Thinking that this change in color might be due to some impurity in these particular rods, the glowers made directly from the pure thoria and ceria, described in a previous paper, were examined and found to exhibit this same property. Finally, the pure cerium oxide was examined. In spite of its rich yellow color, which made observation difficult, it turned to a decidedly yellowish-brown on warming. Other yellowish oxides, such as yttria, do not show this property (to a marked degree), which seems to belong to only certain substances. However, this is not a property of colored oxides, as shown by the behavior of zinc oxide, already cited, which at room temperatures is a pure white but which changes to a rich yellow or yellowish-green when heated above 400° to 500°. It is to be noted, however, that this is not a true light emission, such as obtains in the thermoluminescent fluorites (e. g., chlorophane) as may be easily shown by warming these oxides in a dark room, but is due to a change in the absorption of the incident white light and hence a change in the pigment color with change in temperature. This may account, in part, for the yellowish color often observable in street gas mantles when burning low in the daytime. In cerium oxide there seems to be merely a broadening of the absorption band, toward the red, with rise in temperature, and the interesting question is the magnitude of the effect of this temperature coefficient of absorption upon the emission of the gas mantle in the visible spectrum. If this change in absorption contributes (in emission) to more than the visible spectrum then some other yellow oxide, e. g., yttria, might be equally efficient. In this connection an investigation of the variation of the color of pigments with temperature might be useful.

The broadening of the absorption band in cerium oxide is similar to the previous observations on the broadening of the infra-red emission bands of the Nernst glower, with rise in temperature. Heretofore this change in emissivity, due to a broadening of the absorption band of cerium oxide (and hence a change in its pigment color), seems to have been overlooked. It seems evident that this broadening of the absorption (hence emission) band will contribute more to the emissivity in the visible spectrum than would a similarly colored substance in which the
absorption band does not have such a large temperature coefficient. Hence the luminous efficiency of the Welsbach mantle is higher than it would be if the cerium oxide did not have the property of a change in pigment color, hence in its emissivity, with rise in temperature.

The facts just quoted, taken with the present experiments, seem to place the radiation of the Welsbach mantle on a purely thermal basis and renders it unnecessary to introduce the highly improbable hypothetical assumption of a catalytic action to account for the high light emissivity of the gas mantle. At the most, the effect of catalytic action is to raise the temperature of the gas, but it can hardly affect the spectral energy distribution. On the other hand, the thickness of the radiating layer (and perhaps the concentration of the cerium particles) has a very marked effect on the spectral energy distribution. In this connection it would be desirable to find the variation in emissivity of a given thickness of a solid rod in which the concentration of the cerium oxide is varied to compare with similar data on the mantle.

In connection with the foregoing experiments it is of course desirable to obtain quantitative data on the emissivity of some (pure) oxides with thickness. For this purpose samples of the same kind of glower material, squirted into rods varying from 0.2 mm to 3 mm in diameter have been prepared under standard conditions, and it is hoped that it will be possible to gain data on this question in the near future. These glowers also show a change in absorptivity (change in pigment color) on warming, but it is not so marked as in the glower of Welsbach mantle material. The pigment color is brownish, the color of the yttrium oxide, used in the glower, being a rich buff color, thus differing from the cerium oxide, which is a rich lemon tint. In previous communications attention was called to the fact that in metals the high light efficiency is due to a high emissivity (low reflectivity) in the visible spectrum, and a low emissivity (high reflectivity) in the ultra-red. In nonmetals the reflecting power is low, and the absorptivity is not dependent upon surface conditions of the substance. The emissivity is dependent mainly upon the absorptivity which in turn depends upon the thickness of the radiating layer. Ideal
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conditions would be fulfilled by a colored substance (e. g., cerium oxide) having a low absorption coefficient throughout the ultrared, at low temperatures, but in which the absorption in the visible spectrum has a high temperature coefficient (as well as broadening of the absorption band, noticeable by a change in pigment color), so that at high temperatures the emissivity has increased enormously in the visible spectrum with only a moderate increase in the emissivity in the infra-red. This condition is partly fulfilled by the finely divided cerium oxide in the Welsbach mantle, but this condition is not fulfilled in the thick glower. This condition is partly fulfilled in thick layers of perfectly transparent substances, such as quartz, oligoclase, and aluminum oxide described in previous communications. In this case it was noticed that at low temperatures the spectral energy curves of these substances showed but little radiation at $1.5\mu$ to $2\mu$; but at high temperatures the region in the visible spectrum to $1.5\mu$ in the infra-red was suddenly filled up by a strong emission band. The aluminum oxide was the most remarkable of all, with an almost entire absence of radiation in the region of $3\mu$ and with but a small emission in the region of $1.5\mu$ where other substances, emitting a similar intense white light, have a strong emission band. Unfortunately the melting points of these substances are too low to make them useful illuminants.

V. MISCELLANEOUS SUBSTANCES

1. EMISSION OF ARC OF NERNST GLOWER MATERIALS

In the preceding experiments on the Welsbach mantle material used as a solid glower the rod broke, thus forming a high potential arc. Aside from a general increase in the spectral energy due to the radiation from the hot electrodes there seemed to be nothing unusual in the emissivity curve. The energy input remained practically unchanged.

In view of the fact that the radiation curve of the glower consists of emission bands which merge into a continuous spectrum, at high temperatures, it was of interest to determine whether these emission bands are observable in the vapors formed in the arc of these oxides. For this purpose an ordinary Nernst glower, which was broken through the center, was used. It was attached to the
secondary (2000 volts) of a transformer and started by placing the two parts in contact and by heating them externally. After the glower became conducting, the two parts were separated, thus becoming an arc with electrodes of glower material. These electrodes were separated from 5 mm to 10 mm and an image of the arc vapor, which was a very faint white, was projected upon the spectrobolometer slit by means of a short-focus mirror.

The results obtained were entirely negative. Although the sensitivity of the vacuum bolometer was much higher than ordinarily used, neither selective emission bands nor regions of continuous radiation could be detected throughout the infra-red. The slightest trace of radiation from the hot electrodes was sufficient to produce large deflections even in the visible spectrum. The arc vapors were barely visible, and the absence of emission bands is probably to be ascribed to the thinness of the radiating layer.

2. COLOR MATCH VERSUS SPECTRAL INTENSITY MATCH

In a previous paper 34 experimental data was given indicating the spectral range in which there is at the same time a color match and a spectral intensity match. The importance of the work is evident from a consideration of the well-known fact that the eye is very sensitive to variations in color (comparisons in heterochromatic light, using an ordinary photometer) but is not so sensitive to variations in intensity (comparisons in monochromatic light, using a spectrophotometer). Hence, in comparing two widely different sources (e. g., carbon and tungsten), the estimation of a color match may be affected by the great difference in emissivities of the two sources in the deep red, and one can not be certain that their spectral energy curves coincide over a great length of the visible spectrum. It was found by Hyde 35 that on a color match the spectrophotometric curves of tungsten and carbon lamps coincide within the narrow spectral region of .5μ to .66μ. In this region it is an extremely easy matter to make spectrophotometric measurements. But if the attempt is made to extend the spectrophotometric comparisons toward the red, it is found that abruptly at .69μ to .70μ (at least for the writer's eyes)

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34 This Bulletin, 6, p. 301; 1910.
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it is very difficult to make an accurate intensity match. Spectro-

photometrically the region beyond .69μ can not be considered

"well within the visible spectrum," because the eye is not sensi-
tive enough for intensity comparisons in the deep red. But, as

already stated, the eye is very sensitive to differences in color, and

the light from .69μ to .75μ mixed with the blue and yellow may

play an important part in the color match. The object, therefore,
of the writer's experiment was to determine the magnitude of the

departure in intensity match beyond .7μ when two lamps are set
to a color match. In the previous work the spectrobolometric

measurements at .69μ to .7μ were fraught with great difficulty,

and the observed difference in intensity match, amounting to 1 to 2

per cent at .7μ, would have been given but little weight if it had

not been for the more conclusive measurements at and beyond

.75μ, where the intensity match was off by more than 5 per cent.

This is well illustrated in Figs. 10 and 11 of the paper just quoted.34

The graph of ratios of emissivities, Fig. 11, is apparently a

straight line, at .5μ to 2μ, inclined to the horizontal axis and inter-

secting it at an imperceptibly small angle in the visible spectrum;

so small, indeed, that it can not be detected spectrophotometrically

or radiometrically. If we do not admit this to be the case then

we must assume that the ratio of emissivities is the same through-

out the visible spectrum to .75μ, where the graph changes suddenly

from a horizontal to an inclined position. This would necessitate

the presence of a strong selective emission in the region of .7μ to

.75μ (not unlike that which obtains in the visible spectrum of

incandescent gold and copper), in order to keep the ratios the

same as at .5μ to .66μ where no difference in intensity could be

observed. Now the reflection curves of tungsten and carbon36

show no indentations (such as occur in copper at .55μ) in the

region of .75μ from which one can infer an extra emission in this

region. The writer therefore concluded that the departure in

intensity match already becomes perceptible at .7μ as observed.

In one case34 (see lower curve, Fig. 11) the intensity match seemed
to continue out to .8μ, but since the color match was obtained

without special care with an Ives colorimeter no great reliance

was placed on the observations. Whether the graphs of ratios,

34 This Bulletin, 7, p. 55; 1911.
Fig. 11, are straight lines throughout the spectrum will probably depend upon the temperature (maximum emission with respect to the reflectivity curves) of the filaments. The comparison of these lamps for intensity match when on a color match was a piece of pioneering work which has opened up a field requiring further investigation. For the first time it gave us some idea, however crude, of the behavior of the eye in judging differences in color, and differences in intensity, of radiation lying in the extremes of the visible spectrum. But few seem to realize how limited the "visible spectrum" is in comparison with the total range of frequencies radiated by most solids. It is therefore possible to establish relations, e.g., color match, which immediately become inapplicable when we extend our observations beyond what we call the visible spectrum, especially beyond the region of .5μ to .66μ.

The previous investigation arose from the writer's doubts as to the extent of the spectral region in which there is at the same time a color match and an intensity match of two substances, such as carbon and tungsten which (from a consideration of their reflectivities) must have very different spectral energy curves. The spectroradiometric apparatus described in the present paper is better adapted than that previously used to solve the color match problem and hence further data has been obtained.

It has always appeared to the writer that in a color match and in a spectral intensity match, of two sources having widely different spectral emissivities, the spectral energy curves really intersect at an extremely small angle so that, extending over a short spectral region, the two curves appear to be superposed, within the experimental errors of observation. The following experiments give further evidence to support this view.

The present experiments consisted in obtaining a spectral intensity match in the visible spectrum by means of a Lummer-Brodhun spectrophotometer, with a rotating sector (sector stationary and the beam of light is rotated) mentioned on a preceding page, and comparing this with a spectral energy match obtained radiometrically. The two sources selected were the Nernst glower and the tungsten lamp. The visible spectrum was examined with the quartz lens spectroradiometer; already described, while the
infra-red was examined with a large mirror spectrometer and vacuum bolometer. The Nernst glower was the ordinary D. C. type, 13 mm long, 1 mm diameter, operated on 110 volts (at terminals), 0.67 amp. (74 watts), which is practically the normal operation. The tungsten lamp was the ordinary 110-volt type, which was operated on 1.2 w. p. m. h. c. The tungsten lamp, which
had been carefully seasoned for a standard source of radiation, was made the standard in the spectrophotometric comparisons. The voltage of the Nernst glower was varied until the same photometric ratios were obtained throughout the visible spectrum to .69μ. This could be done with an apparent accuracy of 1 per cent. The spectral energy curves were then observed at the voltages required for a spectrophotometric match.

The prismatic energy curves for the visible spectrum are given in Fig. 13, the observations on the Nernst glower being represented by the dots ( . . . . . ) and those on the tungsten filament by the circles (⊙⊙⊙⊙⊙⊙). The galvanometer deflections for the Nernst were 16 times as great as those from the tungsten lamp. When the two curves are superposed they coincide throughout the spectrum from .46μ to .66μ, where they begin to separate by a small amount, not greater than 1 per cent. At .68μ this lack of superposition amounts to 3 p. c.; at .74μ it amounts to 4 p. c.; and at .75μ it amounts to about 5 per cent. In the extreme violet the two curves also show a slight separation which probably would not be observable with the spectrophotometer. Exactly similar results were obtained with another glower. The main interest in the present experiment lies in the extreme regions of the "visible" spectrum. The results obtained verify the writer's previous conclusion that, in a color match or in a spectrophotometric match, there is no true superposition of the spectral energy curves, but that the two curves intersect at an extremely small angle, so that it is possible to have an apparent superposition within the narrow confines limited by the maximum sensibility of the eye.

Curve c, Fig. 13, gives the spectral energy distribution of the Nernst glower in the ultra-violet and of a second glower (xxxx) similarly calibrated against the tungsten lamp. The spectral energy curves of these two glowers coincide throughout the visible spectrum. If properly seasoned, the glowers promise to be useful reference standards if not put to hard usage. The interesting point about curve C is the horizontal part between .24μ and .34μ, which is a measure of the scattered light in the instrument. This scattered light is supposed to be uniform over the whole field. For wave lengths less than .2μ the deflections increased somewhat. Whether this was due to extraneous light or due to radia-
tions of wave length greater than 50μ, caused by the anomalous dispersion in quartz which would refract the extremely long rays into this spectral region was not determined, the significance of the observation not being noticed at the time when the work was done.

![Graph](image)

Fig. 14

The very marked difference in the emissivity of these two sources, already noticeable in Fig. 13, is illustrated in Fig. 14, in which curve a gives the spectral energy distribution of the tungsten lamp on 1.2 w. p. m. h. c. and curve b gives the spectral energy of the Nernst when it has the same energy distribution as the tungsten lamp in the visible spectrum—see Fig. 13. In the Nernst glower curve the $\lambda_{\text{max}} = 1.3\mu$ and in the tungsten curve
the $\lambda_{\text{max}} = 1.22\mu$. The relative areas are: Nernst = 66, tungsten 37 units. This would make the glower about 2 w. p. c., but without proper reduction factors this can not be considered a fair rating. The interest in these curves lies in the illustration of the great difference (about 50 per cent) in the emissivities to produce the same spectral energy distribution in the visible spectrum.

The spectral energy curve of a "gem" (graphitized) carbon lamp on 2.5 w. p. m. h. c. is given in curve c, Fig. 14. The maximum emission is at $\lambda_{\text{max}} = 1.35\mu$, which is not very far removed from the Nernst glower.

WASHINGTON, November 8, 1910.