NOTES ON THE USE OF RARE EARTHS IN ELECTRIC ILLUMINANTS.[1]

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Received March 24, 1905.

AS SCIENTISTS and engineers have come to a realization of the inefficiency of existing methods of illumination, the problem of improving upon these inefficient methods has received considerable attention. While the element carbon has heretofore been almost exclusively used commercially in both arc and incandescent lamps, the rare earth oxides, so-called, have recently been found to possess desirable properties for use as illuminants.

We are already familiar with the work of Auer von Welsbach in producing gas mantles of thoria and ceria. To use the rare earths in electric illuminants was a logical step. However, the problem presented difficulties not encountered in the production of a serviceable gas mantle. We should remember that an illuminant, to be an improvement over the Edison or carbon filament lamp in the matter of efficiency, must be capable of withstanding a higher temperature than the carbon filament for a length of time sufficient to make it commercially attractive. One might at first suppose that it would be difficult to improve upon the carbon filament in the matter of efficiency, or the ability of the filament to operate commercially at a very high temperature, since carbon is practically infusible and the rare earths are fusible and in a carbon arc. Carbon, however, slowly vaporizes at the temperature at which it operates in the incandescent lamp and, finally, after 400 to 600 hours has depreciated in light giving power to such an extent that it is best to replace it. It is the vaporizing properties rather than the melting-points of the materials with which we are concerned in this problem. It has long been known that substances which are commonly regarded as insulators, such as glass and porcelain, become quite good conductors of electricity at higher temperatures.

Prof. Buff, in 1854, read a paper "On the Conductivity of Heated Glass for Electricity," and Faraday's "Researches" give a number of examples of such conductors. Jablochkoff attempted to use refractory materials, such as lime, to separate and insulate the carbon electrodes of his Jablochkoff candle. He soon found that these supposed insulators in reality became conductors and emitted light by virtue of the current passing through them from one electrode to another. He even designed terminals with which to carry the current of electricity to the lime conductor, with the idea of making a lamp based on this principle. It is safe to say that had it been possible to produce electricity as cheaply then as now, lamps of the Nernst type would have been known commer-

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[1] Read before the Pittsburg Section of the American Chemical Society, March 23, 1905.

cially much sooner than they were, for Jablochkoff's persistent attempts at commercial exploitation were baffled largely by the undeveloped state of electrical engineering.

That the rare earth oxides are exceedingly refractory and do not readily vaporize at a high temperature, makes the Welsbach mantle possible; that these oxides will conduct electricity when hot, makes the Nernst lamp possible. Of all the oxides which conduct electricity but few are refractory enough for an efficient filament of glower. It was in determining the most desirable of these and in fixing the best proportions to use that Nernst did his greatest work.

Ordinary red iron oxide, when formed into filaments and baked, will conduct electricity at ordinary temperatures, but such filaments do not withstand sufficiently high temperatures to be used as light sources. Magnesia and thoria, on the other hand, withstand exceedingly high temperatures, but these conduct electricity only with great difficulty. In general, mixtures of two or more oxides conduct better than a single oxide and, in turn, the fusing-point of the mixture is lower than that of either oxide alone. It seems that the vaporizing point is not necessarily lowered, judging from the fact that thoria and the small amount of ceria used in a Welsbach mantle form quite a stable mixture, or possibly a chemical combination, while ceria alone or uncombined is a somewhat undesirable oxide from its rather marked tendency to vaporize.

It would be a long story to take up the various properties of all the rare earth oxides and the possible combinations with one or more of the others. A mixture which is used largely in lamps of the Nernst type, is composed of 85 per cent. zirconium oxide to 15 per cent. of yttria earths. Zirconium is not properly classified among the rare earths, though it is customary to do so. The term "yttria," as used here, means in reality a mixture of many oxides occurring together in certain minerals and closely allied in physical and chemical properties. Zirconia was used in comparatively large quantities for the first Welsbach mantles and, hence, considerable attention had been given to various methods of producing it for such use. While many of the experimental glowers were made from zirconia bought from chemical supply houses, it was impossible to obtain uniform results from such material. Good zircon ore, which is a zirconium silicate, occurs in abundance in Henderson County, North Carolina, and this ore contains about 67 per cent. of zirconium as oxide. By treating this ore in the following manner quite uniform results are possible:

The ore is ground very fine in a ball mill and mixed with twice its weight of crude acid potassium fluoride. This is placed in an ordinary graphite crucible and heated slowly until thoroughly fused, and the ore is completely dissolved. The fused mass is then ground and dissolved in hot water containing a quantity of crude hydrofluoric acid equal to about one-tenth the weight of the fused mass. The silica remains undissolved as potassium silico-fluoride (K_2SiFl_6) and the potassium zirconium fluoride (K_2ZrFl_6) is drained off while boiling hot into a silver-lined vessel. Upon cooling, the filtrate develops crystals of potassium zirconium fluoride and, doubtless, small quantities of other elements in similar crystal form. Iron and many other impurities which are present in the ore, or have been introduced by the use of the crude reagents, remain in the liquor which is drained from the crystals. The crystallizing process may be much hastened by artificial cooling. Rinsing the crystals with cold water is likewise beneficial in removing all traces of the mother-liquor. The crystals are gathered and fused in a platinum dish. By this means any silica present seems to be vaporized and other impurities, like titanium, are made insoluble. The fused mass is ground and dissolved in hot water and crystallized as before. A few of the first crystals are removed, or, instead, alcohol may be added to the solution until a small amount of crystalline precipitate is formed. These first crystals contain much of the undesirable impurities. They are, therefore, removed and the crystallizing process is continued. The pure crystals are then dissolved in hot water and the solution is made rather acid by the addition of pure hydrofluoric acid. Ammonia is now carefully added to the hot solution until a small amount of precipitate is formed. If the solution of the crystals has been made acid, the addition of ammonia, even until alkaline, will precipitate iron and some other foreign metals, but will leave the zirconia in solution until it is cooled and diluted.

This method was found to be an exceedingly simple one for removing iron from zirconia, which, by other methods is a troublesome operation. The hot filtrate, after removing the precipitate of iron, is dropped directly into a cold ammonia solution which at once precipitates zirconia as a hydroxide. Up to this stage of the process it has been necessary to use vessels and utensils not affected by hydrofluoric acid. The last precipitation may be made in glass or wooden receptacles. The precipitate is washed several times by decantation, and then pressed out on suction filters and, after a thorough drying by heat, is powdered and sifted through fine bolting-cloth and is then ignited in a platinum dish with a very gradually increasing temperature and with constant stirring. The ignition process requires several hours, or sometimes days, the final temperature being a good red heat. Traces of silica are removed by this operation.

The physical condition of the precipitate is dependent to a great extent upon the amount of hydrofluoric acid in excess. When precipitated from an almost neutral solution the precipitate dries into hard pieces translucent in appearance, and which are difficult to pulverize. With the greater excess of acid the material dries in lumps resembling starch, in which condition it is much more suited to our purpose.

The zirconium made by this process seems to be reasonably pure. Precautions must be taken to keep out dirt and to that end it has been found advantageous to purify the air admitted to the rooms where the glower materials are prepared by passing it through a water spray. An absolutely pure zirconia is not required and though a trace of silica improves the efficiency and seems to diminish the initial depreciation of candle-power of a glower, it is a dangerous element to have present, for slightly more than a trace will cause a rapid change in potential difference at the glower terminals besides causing lack of uniformity in the behavior of glowers of one batch, due to the fact that the silica becomes unevenly distributed among the glowers by vaporization and condensation occurring in a roasting process, which will be described later.

Although the purest materials make the best glowers for direct current, it cannot be said that an absolutely pure zirconia is desirable for alternating current glowers. Silica is particularly undesirable in direct current glowers. In general, a glower which operates well on direct current, showing almost no change in potential difference, will show a greater change when operated upon an alternating current circuit.

The purity of the zirconia may be controlled, to some extent, by the number of times the material is crystallized during the purifying process, though each operation is attended with some loss of material. Physical properties are quite as important as chemical properties and the procedure above described was evolved to give proper physical, as well as chemical, properties to the material.

After all—''Handsome is as handsome does''—and the real test for the glower material lies in its ability to make good glowers. Test glowers have been made from hundreds of lots of zirconia and these, together with careful chemical records of each lot, have been the guide in developing the chemical process necessary for the production of good glowers. For direct current glowers a crystallizing process is also considerably used, but from a solution of zirconia in hot dilute hydrochloric acid. After two or three such crystallizations it is necessary to precipitate from a hydrofluoric acid solution, as in the first process, to get the material into proper physical shape.

As to the yttria used, this is principally obtained from the minerals gadolinite or yttrialite. Gadolinite is found in Norway and Sweden, and also in Llano County, Texas. The Texas deposit seems to be confined in a very small district and there is every evidence that it is a result of a volcanic eruption. It is found in crystalline form associated with yttrialite, cyrtolite, fergusonite, rowlandite, allanite, and other minerals. The ores from the Llano County district are radioactive and the presence of a pocket in the quartz is generally indicated by bluish discolorations radiating from the pocket through some distance of the surrounding quartz. It is also claimed that the ores contain small quantities of confined helium gas. Gadolinite contains, roughly, 42 to 45 per cent. of yttria earths, 23 per cent. of silica, 13 per cent. iron as oxide, and 9 to 12 per cent. of beryllia. Yttrialite contains 43 to 47 per cent. yttria earths, 30 per cent. silica, 5 to 6 per cent. ceria, didymia, and lanthan, as well as small percentages of urania. Fergusonite contains 32 to 42 per cent. yttria earths and 32 to 46 per cent. columbic oxide. Rowlandite contains 47 to 62 per cent. yttria earths, 26 per cent. silica, and small percentages of iron and magnesia. Allanite contains 20 per cent. ceria and dydymia, with a small percentage of yttria earths and considerable percentages of iron, calcium and aluminum.

It is a comparatively simple matter to obtain and purify the yttria earths from gadolinite and yttrialite so that they are suitable for glower-making. About 1,000 grams of ground ore are dissolved in crude aqua regia. The residue is filtered off and the solution evaporated to dryness, repeating this operation several times, or until all silica is removed. The neutral solution is then diluted to several liters and the addition of a hot solution of oxalic acid to the hot solution containing the earths brings down the rare earths as oxalates, leaving iron and other impurities in solution. The oxalate is washed thoroughly with hot water and ignited, and the crude yttria earths are dissolved in dilute hydrochloric acid, just sufficient in amount to dissolve the oxide. To the rather dilute and neutral solution, which is cold, crystals of potassium sulphate are added in excess. After standing twenty-four hours the cerium group has been quite thoroughly separated as double sulphates and the filtrate is then treated with ammonia to bring down the hydroxides of the rare earths, thus freeing them of the great excess of potassium sulphate. The washed precipitate is dissolved in a quantity of pure hydrochloric acid, just sufficient to dissolve it, and again treated with boiling oxalic acid solution, as before. This brings down the rare earth oxalates in sufficiently pure form. The oxalates are thoroughly washed wtih hot water and ignited, and any remaining potassium is separated from the ignited oxides by washing upon a filter with hot water.

With the yttria, as well as the zirconia, physical properties are important, and the oxalate method gives an exceedingly fine precipitate which requires no mechanical treatment.

Experiments indicate that the yttria earths of the greatest atomic weights give the most satisfactory results in glowers. In other words, ytterbia is better than yttria. Owing, however, to the great difficulty of separating the yttria earths from each other, which is so far possible only by laborious fractionation processes, entailing great losses, not much has been done toward using the higher atomic weight yttria earths beyond selecting ores which are rich in these earths.

The Llano County ores seem to be superior to the foreign ores in this respect, the atomic weights being yttrialite 115, rowlandite 107, fergusonite 103, and gadolinite 100, while the foreign ores may be as low as 90 or 92.

The zirconia and yttria earths mixed in the proportions given above, namely, about 85 and 15, or 90 and 10, and about 5 per cent. of starch or gum tragacanth, are thoroughly mixed and kneaded into a hard dough and squirted by pressure through a die of proper size. This string, as it may be called, is dried and then broken into suitable lengths which are roasted to an intense white heat in a platinum box. The pieces are then ready to have terminals placed upon them.

A Nernst terminal is made by winding stranded platinum wire about the end of the stick of material and then pasting over with a paste composed of ground glowers and zirconium chloride, thus forming a hard cement.

The Hanks terminal has the platinum embedded in the glower material, the operation being carried on by the aid of an electric arc in which the glower material is fused.

It appears certain that the mode of conducting the current is partly electrolytic in character. The specific resistance varies with the relative proportions of the constituents. In order to obtain glowers of the same specific resistance when using yttria earths of high atomic weights as when low atomic weight earths are used, it is necessary to have the presence of the higher atomic weight materials in proportion to the atomic weights.

Upon direct current circuits the positive end of the glower generally runs much hotter than the negative end, and a black discoloration appears at the negative end, especially if impurities are present. In fact, this is one of the most certain indications of the presence of an impurity.

A glower operated in vacuum soon destroys the vacuum, probably due to oxygen gas liberated by electrolytic action. That all the current is carried by electrolytic means seems incredible, for the current carried per square unit of cross-section is far greater than can easily be accounted for by our usual conceptions of electrolytic laws. For example, upon direct current and calculated by electrochemical equivalents the entire glower would be decomposed into the constituent elements in a very few minutes. Doubtless electrolytic decomposition and recombination do take place, but is it possible to account for the entire transport of current in this way? The assumption that the current is all so carried seems unnecessary in view of what is known of the power of highly incandescent bodies to ionize air to render it conducting. The air in the neighborhood of a glower is conducting, and to such an extent that the leakage currents from glower to heater had to be reckoned with early in the experimental work, and the difficulty was obviated by the use of a double pole cut-out which disconnected the heaters completely from electrical connection with the remainder of the lamp after the glower started.

In connection with these speculations as to the real nature of the process by which the current traverses the glower, it is a fact that glowers which have operated for even a short time upon direct current will, when the current strength is diminished sufficiently to maintain the glower at only a good red heat, explode with considerable violence. This may be accounted for by considering that the conductivity at low temperatures is insufficient to ionize the surrounding and contained gases. The means of conducting the current then being largely electrolytic in character, the combination of the products of electrolytic decomposition cannot so readily take place, since the ions cannot so readily traverse the length of the glower to combine at the lower temperature, and consequently disruption occurs.

The suggestion that has so often been made, namely, that the current be reversed in direction at intervals, as, for instance, every time the lamp is started, is altogether impracticable for the reason that a glower once operated upon direct current must never have its poles reversed, for a reversal means almost instant disruption. The potential difference across the terminals of the glower immediately after such a reversal is lower, indicating something analogous to polarization effects as we know them in aqueous electrolytes.

In general, with the Nernst terminal the potential difference across the glower at the normal current value is the same with alternating or direct current. With the Hanks terminal, or embedded type, the potential difference with direct current may be as much as 20 volts lower. The Hanks terminal will operate on direct current, but not satisfactorily as a commercial proposition. The life of the alternating current glowers is greater upon high frequencies than upon low frequencies, again suggesting electrolytic conductivity, at least in part.

The small glowers, up to 0.5 ampere, are made solid in cross-section, the larger ones are generally made tubular, and, in fact, one-ampere glowers must be made so. The reason for this is not that greater efficiency is sought by increasing the ratio of surface to volume, which is, of course, a fallacy, but inasmuch as the glower possesses a decided negative temperature coefficient as regards electrical conductivity, the center of a large solid glower would become molten before the outside surface reached an efficient temperature, the center being the better conductor. Glowers which have been greatly overrun often exhibit this truth by the appearance of a nodule of molten material which has spurted out to the surface.

Glowers in Vacuum.—A glower will operate in vacuum but the vacuum rapidly deteriorates, as before stated. A blue aurora or luminous haze surrounds the glower thus operated, either with direct or alternating current, and has been thought to be due in some way to vaporized metal (zirconium or yttrium) recombining with the slight amount of oxygen liberated. This idea seems plausible from the fact that objects, such as wire or glass, near the glower become coated with a white deposit of the glower oxides in a comparatively short time.

It would seem that oxygen necessarily plays a part in conducting the current, for a glower in an atmosphere of hydrogen or nitrogen behaves similarly to the one operated in a vacuum. In carbon monoxide or dioxide the glower exhibits the same characteristics as in air. The glower operated in vacuum exhibits a peculiar sluggishness in responding to changes in voltage at its terminals.

A commercial glower must operate at a high temperature to be efficient. Nernst glowers operate at about 2,300° C., it is supposed from determinations made by photometric means and at about twice the efficiency of a carbon incandescent lamp. The spectrum of a glower is a continuous one and no evidences of selective emission in any particular region are noted. During the life of a glower, which averages about 800 hours under normal conditions of manufacture and voltage regulation, a depreciation of candle-power takes place, due to a number of causes. In the first place, all oxides of the rare earths do depreciate rather rapidly in light intensity per unit of surface at any given temperature. This is true even when heated by gas or electricity, and a platinum plate coated on one side with rare earths and heated from the rear by an oxyhydrogen flame behaves similarly. It is an inherent property of these oxides and a depreciation of 10 or 20 per cent. may occur during the first hour. There is then a slow diminution of intensity of light, also inherent, and seemingly accompanying the tendency of the glower to change from an amorphous to a crystalline structure. A rise of potential difference across the glower terminals is usual, though it is possible to counteract this tendency, at least in part. The effect of a rise in potential difference, obviously, is to diminish the intensity of light by permitting less current to traverse the glower running on a constant potential circuit.

With carbon incandescent lamps the useful life or smashing-point is considered to be that number of lamp-hours during which the candle-power decreases 20 per cent. from the initial candle-power. Nernst lamps are similarly rated, counting as initial candle-power that measured after the initial decrease above mentioned.

Another cause of depreciation in candle-power is blackening of the enclosing glassware and reflecting surfaces. In this connection the blackening is due largely to platinum which has been vaporized and deposited upon these surfaces. It has been found that the purest platinum is far better than that containing iridium or other of the platinum group, since pure platinum vaporizes much more slowly than alloys with these other metals.

It is to produce uniform chemicals and glowers in which the tendency to depreciate in light intensity and increase in potential difference shall be a minimum that makes the problem so intricate and so fascinating, and still capable of much improvement.

Curiously enough not the least of the problems to be solved in the development of the Nernst lamp was to overcome the tendency of porcelains to conduct electricity, the very property which in the case of the rare earths made such a lamp as the Nernst possible. A heater is necessary to start the glower. The heater is made by winding fine platinum wire upon a porcelain tube. It was necessary to produce a suitable porcelain which would withstand the high temperatures required and at the same time not conduct electricity. A porcelain composed of kaolin, alumina and silica is sufficiently refractory and porous to withstand the heat and is an almost perfect non-conductor at high temperatures. The porcelain piece upon which the glowers and heaters are mounted is also of the same composition.

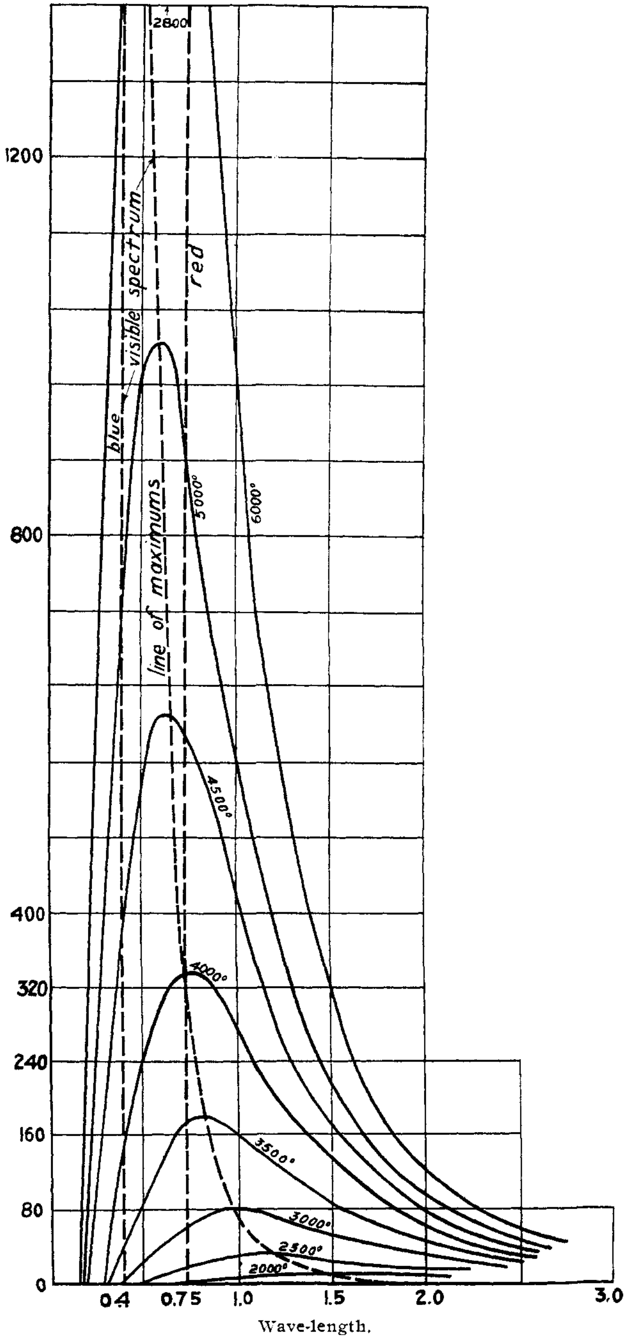
Another form of heater, used more abroad than in this country, is helical in shape, and the glower is mounted in its axis. This is made of pure kaolin and after squirting into tubes about a millimeter in diameter, winding with fine platinum wire and covering over the wire with a paste, the small tube is bent into a helix upon a mandrel, a pointed blowpipe flame playing upon the kaolin tube at the point where it bends on to the mandrel.

Possibilities of Self-starting Filaments.—Many oxides will conduct at room temperature. A mixture of iron and tin oxides, about 70 iron to 30 tin, will start without preliminary heating and withstand rather a high temperature. There are many other similar combinations, likewise other possibilities exist, such as carbides, silicides and borides, operated either in vacuum or gases.

A Nernst glower may be made to conduct the current at low temperatures by running it for a short time in a rarefied atmosphere containing a carbon gas. If to a globe in which a glower is operating in a good vacuum an amount of hydrocarbon gas is admitted sufficient to lower the vacuum even less than a millimeter, the potential difference across the terminals of the glower will decrease rather rapidly and in the space of a few minutes, or even seconds, the glower will have become a conductor when cold or, in other words, self-starting.

The following experiment was tried:

A glower was mounted in a glass bulb and in the axis of a carbon filament of helical shape. The bulb was well exhausted and sealed off. The carbon filament was used four or five times to start the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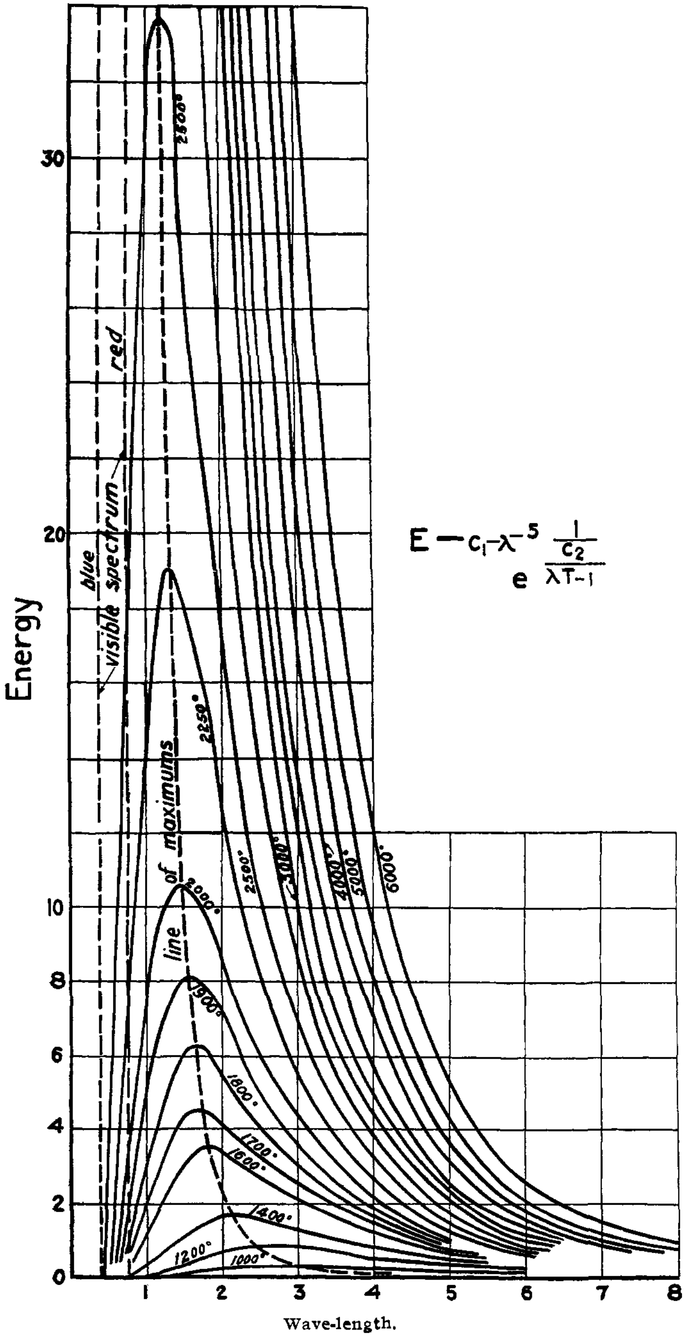
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glower, alternating current being employed. After the glower had run a few hours it was noted that it was changing color at its terminals. The discoloration gradually crept toward the center and after about twenty-four hours the glower could then be started without preliminary heating. Apparently enough of the carbon filament was oxidized during the short time it was in use to give a slight quantity of free carbon monoxide in the bulb, the source of oxygen being the glower itself.

It is uncertain whether this gas was effective in reducing some of the glower material to its metallic form, or whether a conducting carbide was formed by the action of the carbon gas upon the glower materials. The former explanation seems preferable for the reason that it was noticed that the darkened portion at the negative end of direct current glowers is of higher conductivity than the glower proper, and it seems quite likely that this deposit is a metal separated out by electrolytic action. Metallic zirconium, for example, withstands very high temperatures in the open air without oxidizing, and its melting- and vaporizing-points where air is excluded must be very high.

Many possibilities exist, such as are suggested by the above experiments, and many of them have been tried. Boron carbide, for example, withstands very high temperatures and is a conductor while cold, though it seems to vaporize somewhat too rapidly; at least this was the case with samples tried, which probably were not very pure.

A Nernst glower, as well as those composed of thoria, magnesia, and almost any of the refractory oxides, may be made conducting by treatment with a hydrocarbon gas. Sodium and potassium vapor also affect a reduction to the self-starting condition, though not generally so readily as carbon.

There is a broad field still open and much that is not known of the properties of the rare metals. Oftener than not the supposedly pure metal is very impure, and the properties generally ascribed to it are in reality those of its carbide or other little known combination. Note the difference in properties of pure iron and iron containing even less than 1 per cent. of carbon. Is it not a fact, then, that almost nothing is known of the physical properties of the rare metals? A good example of this point, and one bearing directly on our subject, is the recently developed tantalum lamp, the filament of which is a fine thread of tantalum metal. Tantalum metal, until recently, was not known to possess properties which now make it a promising addition to electric illuminants.

More or less experimental work has been done, particularly in Europe, in using the rare earths in electric arcs with the idea of obtaining better efficiency and more pleasing light. Lamps have even been tried with electrodes composed entirely of the rare earth oxides, though at the present time the greatest advances in arc lighting are being made along the lines of introducing such elements as boron and titanium into the electrodes.

In conclusion, your attention is directed to a set of curves which has been plotted to show the relation between the temperature and the energy radiated in the various wave-lengths of light for incandescent black bodies. Various temperatures are assumed, and curves calculated, showing the energy radiated at each wave-length. The visible spectrum is defined by the vertical broken lines marked red and blue. The exceedingly small proportion of the total energy which is radiated within the limit of the visible spectrum even at a temperature as high as 3500° C., is startling enough. We are, apparently, at the present only on the border of possibilities.

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NEW BOOKS.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Third English edition, translated from the Russian (seventh edition) by George Ramensky. Edited by Thomas H. Pope. Longmans, Green & Co. 2 vols. 1190 pp. Price, $10.00.

The third edition of this standard work is a more important revision than its predecessor. The author assures us that "the additions and alterations have, in many instances, cost as much labor as the original compilation." Additions to fact are numerous, among the more noteworthy of which, the liquefaction of gases, the rare atmospheric elements, and the subject of radioactivity, are treated in some detail; but the theoretical portions of the book have acquired a preponderating interest, since they are evidently to be regarded as a final statement of the author's views. His own words are: "In carefully preparing this edition, I have not lost sight of the fact that I am hardly likely to publish another, and I have, therefore, in many instances spoken more definitely than formerly." Many of these views have already been published singly, but this is the first time they have appeared together as parts of one whole.

The periodic system is enlarged by the addition of a zero group (of zero valence) embracing helium and the rare gases of the air. Regarding former discrepancies in the periodic table, Mendeléeff reaffirms his belief that the order I–Te, Ni–Co, K–Ar will eventually be reversed. The position of the rare earths is still problematic. Brauner, who contributes a chapter on the subject, presents his view, previously published elsewhere, that these elements taken together form a division occupying a single space in the table, sustaining a relation similar to the elements of Group VIII.

Mendeléeff's views of solutions have not changed, but his