

Mechanics, Physics, and Chemistry.

ON THE CHANGE OF COLOR PRODUCED IN CERTAIN CHEMICAL COMPOUNDS BY HEAT.

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At a meeting of the Optical Section of the Franklin Institute, held April 26th, 1871, Dr. Wm. H. Wahl exhibited specimens of the double iodides of mercury with copper and silver, discovered by Meusel.* The color of each of these salts is changed in a remarkable manner by the action of obscure heat rays. The author, in connection with Mr. Elihu Thomson, of the Central High School, was led to undertake an extended series of experiments, with a view of ascertaining the law by which these peculiar changes are governed. The author desires to state that Mr. Thomson's share of the investigations was equal to his own.

Familiar changes of a similar though less striking nature, at once suggested themselves, among the most prominent of which, might be mentioned the darkening of the red protoxide of mercury in the preparation of oxygen.

The experiments were conducted as follows: the substances were placed in the state of dry powders on strips of sheet copper, and heated by means of an ordinary Bunsen burner.

It soon became evident that quite a number of compounds underwent a change of color when so exposed. The colors observed, however, together with those already known, appeared at first to present facts of the most discordant nature.

In some cases the colors were changed so as to approach the violet end of the spectrum, while in others they approached the red end. To avoid all sources of error, the conditions of the original experiment were carefully considered. Briefly they are as follows:—

1. A certain color presented by the compound at ordinary temperatures.

2. A decided change of color, on the application of obscure heat rays.

* Ber. d. deutsch. Chem. Gesell. III. 123. Jr. für Prak. Chem. ii. II. 136.

3. A complete return of the original color on the removal of the heat, and the cooling of the body to its former temperature.

Bodies not presenting all these phenomena were rejected.

The largest class of bodies that was excluded by this method, was that in which a permanent change of color was produced by heat. In this case the change is caused either by the heat being raised to a temperature sufficient to cause a decomposition of the body, by a change from the amorphous to the crystalline state, by a partial sublimation and subsequent deposition of the sublimate, by a change in the crystalline form, or by some other permanent change in the arrangement of the molecules.

Changes in color produced by dehydration were also rejected, as for instance, in the case of the chloride of cobalt, which, when hydrated, is a pale pink, but when anhydrous, a deep blue. Hydrated and anhydrous salts are distinct chemical compounds, and have therefore a different molecular arrangement. A class of cases of a somewhat similar nature was also rejected. Here the change of color was produced by a loss of the water of crystallization, as for instance, the sulphate of copper, which changes from a deep blue to a white.

After these sources of error were removed and quite a number of bodies discovered presenting phenomena fulfilling all the requirements of the original experiment, the law became evident. *In every case the color in its change approached the red or heat end of the spectrum.* Not a single exception to this law was observed.

Before stating the explanation of the way in which these changes are produced, a few words in reference to the relation existing between light and heat may be necessary. That light and heat are produced by a vibratory motion of the molecules of bodies, and that they differ from each other, merely in the rapidity of the vibrations of these molecules, the facts presented by the science of the present day, leaves scarcely room for doubt. A hot body differs from another cooler than itself, not in virtue of any peculiar substance or fluid, which it possesses, but simply in the fact that its molecules are in more rapid motion. Increasing the temperature of a body is equivalent to increasing the rapidity of the vibration of its molecules. As the body is made hotter, its molecules vibrate more and more rapidly, until finally a red heat is obtained, and light is emitted along with the heat. Now we know that a ray of white light, popularly speaking, is a mixture of seven different kinds of

rays, viz., the colors of the solar spectrum. Moreover, we know by actual measurement, that these colors, in the order of the number of vibrations required to produce them, commencing with the least, are as follows: red, orange, yellow, green, blue, indigo and violet; those of the violet being about twice as rapid as those of the red.

If then light differs from heat, merely in the fact that the molecules of a body emitting light, are in more rapid motion than those of a body emitting heat, when that rapidity in the vibrations of the molecules of a hot body is reached, that it commences to give out light along with the heat, the color first emitted should be red, since that color is produced by the least number of vibrations per second, and the colors which successively appear should be orange, yellow, green, blue, indigo and violet, until finally, these by their intermixture produce white light, and the body becomes *white hot*. These considerations are fully sustained by the beautiful experiment of Draper, who viewed through a prism, the light emitted by a platinum wire, heated by a current of dynamical electricity. The color which first appeared was red, and then successively, orange, yellow, green, blue, indigo and violet, or more accurately when the platinum wire became white hot, it gave a continuous spectrum from the red to the violet.

The boundary between heat and light then, is found at the extreme end of the red of the spectrum. It is evident that though the range of the spectrum must vary with the sensibility of the eye of the observer, that is that the heat vibrations will become light vibrations sooner to some eyes than to others, yet in all cases the color first observed will not be a pure red, but a dark brown; a color produced by the mixture of black, or the absence of color, with the few red rays first emitted.

It should be borne in mind that the arrangement of the spectrum into seven colors is merely a matter of convenience. In point of fact there is an almost infinite variety of tints. The red, for instance, is merely taken at the mean of the dark red and the orange-reds, and so for the other colors.

Remembering these preliminary considerations a fuller statement of the law of the changes may now be given.

In all cases in which the color of a body is changed by the application of heat, and the original color regained on cooling, the nature of the body being in no wise altered, the character of the change is as follows: the addition of heat causes the color to pass from one of a

greater to one of a less number of vibrations ; the abstraction of heat from one of less to one of a greater number.

In accordance with this law, violets are changed by heat into indigo-violets or indigoes, indigoes into blues, blues into bluish-greens or greens, greens into yellowish-greens or yellows, yellows into orange-yellows or oranges, oranges into orange-reds or reds, and finally reds into brownish-reds or blacks ; by cold the inverse order is observed. In many instances substances were noticed that ran down the scale two or more colors ; for example, the green iodide of mercury, which passes from yellowish-green through the yellow, and orange to the red.

Among the most sensitive substances noticed, are the following, arranged by their colors in the order of the spectrum.

REDS.—*Ferro-Cyanide of Copper.*—Color at ordinary temperature, mahogany-brown ; darkens by heat to brownish-black, original color returning slowly on cooling.

Brown-Red Sulphide of Antimony.—*Kermes Mineral.*—Color brownish-red ; changes to darker brownish-red.

Anhydrous Sesqui-Oxide of Iron.—Color, brownish-red ; changes to dark red, brown, brownish-black and black at a temperature greatly below a red heat.

Sub-Iodide of Copper.—Color, dark red. The changes presented by this substance are very remarkable. On the application of quite a low heat it changes to darker-red, and afterwards to a brownish-red, brown, brownish-black and finally almost a black. The return to its original color on cooling is rapid.

Proto-Sulphide of Mercury.—*Vermilion.*—Color, bright red, or vermilion ; darkens to brownish-red.

Sub-Chromate of Lead.—Color, red ; changes quite readily to dark red and brownish-red.

Red Oxide of Lead.—*Red Lead.*—Color, red ; changes readily to dark red.

Bi-Chromate of Potassa.—Color, red ; changes to dark red. The change in this case is best observed by heating a small crystal of the salt.

ORANGES.—*Bi-Sulphide of Arsenic.*—*Realgar.*—Color, when pulverized, orange-red ; changes to red, dark-red and brown ; returns readily.

Protoxide of Mercury.—*Red Precipitate.*—Color, orange-red ; changes to red, dark red and brownish-red.

Iodide of Lead.—Color, orange; changes to darker orange, orange-red and red.

Oxalate of the Protoxide of Iron.—Color, light orange; darkens. In this case the heat must be quite low, as the substance is readily decomposed.

YELLOWS.—*Chromate of Lead.*—Color, yellowish-orange; changes to orange, orange-red and deep orange-red.

Sub-Sulphate of Mercury.—*Turpith Mineral.*—Color, yellow; changes to orange-yellow, orange and orange-red.

Chromate of Baryta.—Color, yellow; changes to orange-yellow.

Bi-Sulphide of Tin.—*Mosaic Gold.*—Color, brownish orange-yellow; changes to a dark red very nearly approaching a black; quite sensitive.

Ter-Sulphide of Arsenic.—*Yellow Orpiment.*—Color, orange-yellow; changes to deep orange-yellow, yellow, orange-red and red.

GREENS.—*Sub-Iodide of Silver.*—Color, greenish-yellow; very sensitive; changes first to an orange-yellow, and then to a deep orange.

Sub-Iodide of Mercury.—*Green Iodide.*—Color, yellowish-green; more sensitive than the preceding; changes to a yellowish-green, and then successively, to an orange-green, reddish-orange, red, and brownish-red. These changes succeed each other very rapidly. They may be best observed by heating at once up to the brownish-red, and noting the changes of color that occur as the body cools.

In all the above cases the original color is fully regained on cooling.

The substances named are by no means all that have been observed to come under the law. Quite a number of other compounds have been noticed; but none of them are as sensitive as those already mentioned. In no case, however, has any compound been found of the color of blue, indigo, or violet, that, in the solid state, undergoes any decided change whatever, on the application of a temperature short of that producing, either a decomposition, or a permanent change in the arrangement of its molecules. Nor is this fact contrary to what might be expected. Near the heat end of the spectrum, where the difference between the light and heat vibrations is not so great, we might reasonably expect the particles of a solid to be influenced by each, and to accept a motion which should be a mean of the two, but when we get as far in the spectrum as the blue or indigo, the greatest heat that we can intermingle with the

blue or indigo, even if pushed to the point of incandescence, would be but dull red. Now long before this temperature is reached, most bodies would undergo decomposition, and were this not the case, even then, we could hardly expect the particles of a solid, trammelled as they are in their freedom of motion by the force of cohesion, to accept a mean of two kinds of vibrations, which differ so greatly in their wave lengths. Still it must be borne in mind that solids differ very greatly from each other in the freedom of motion of their molecules, and it is not improbable that a number of solids as high in the scale of color as the blues, indigos or violets, may eventually be found conforming to the law.

A few very significant facts were noticed in this connection in the case of two pure white substances, viz., the oxides of zinc and of tin; their behavior is as follows:

Oxide of Zinc. Nihil Album; color, white; changes on the application of heat to a scarcely perceptible bluish-white, green and yellowish-green. Does not entirely return on cooling though it resumes nearly its original color.

Oxide of Tin; color, white; here the range is more remarkable. It changes first to a pale-green, then to a decided yellowish-green, and even runs as far down the scale as orange and reddish-orange: returns on cooling to a greenish-white.

These two substances have not been included in the regular list of solids, as they fall somewhat short of the conditions of the original experiment. They conform sufficiently to it, however, to call attention to their behavior.

Experiments were also made on solutions of various solids. As a general rule, it has been found that a substance in solution is more sensitive to the action of heat, than when in the solid state. This, indeed, should be so, as the action of the solvent is simply, by its adhesion for the solid, to separate it into very small particles and to give them much greater freedom of motion. Solids in solution have been found, as high in the scale as the violet, which conform perfectly to the law.

These experiments were conducted as follows; the solution was made of the required strength and then divided between two thin glass test-tubes, of the same size and thickness. They were then held, side by side, between the eye and the light, and carefully compared by transmitted light. If any difference in tint was observed, the solutions were poured together and again thoroughly mixed.

If any difference still existed on again dividing them between the two test tubes, one of the tubes was rejected as differing in thickness or color from the other, and replaced by another until exactly the same tint was obtained. It will readily be seen that these precautions were necessary, in order that the results obtained should not be equivocal. One of the solutions was heated in a Bunsen burner, and the change carefully noted by comparison from time to time. Of course the highest temperature was limited to the boiling point of the solution under the pressure of the atmosphere. In many cases, however, decided changes were observed long before even this point was reached. No experiments were tried on temperatures obtained by boiling under high pressures in confined glass vessels, though there is every reason to believe that by these means splendid results would be obtained. It is purposed, if time allows, to pursue the investigation in this direction, at some future day.

Of course, in all cases where the color did not entirely re-appear on cooling, the experiment was rejected.

The solvent used was water. As the color of a solid in solution varies with the strength of the solution, it will be understood that in all cases the amount of solid dissolved was that requisite to produce the tint described.

The following are among the most sensitive substances noticed.

REDS.—*Rose Aniline*; solution of a strength sufficient to produce a decided red; darkens perceptibly on the application of a boiling heat.

Decoction of Logwood; solution of a deep red; darkens on the application of heat.

Chloride of Cobalt; color of solution, pinkish red; changes to a darker pinkish red.

Sesqui-Sulphate of Iron; color of solution, light-red; changes to brownish-red.

ORANGES.—*Chromic Acid*; color of solution, reddish-orange; changes to an orange mixed with a greater amount of red.

Bichromate of Ammonia; color of solution, orange-red; changes to a pure red.

Sesqui-Chloride of Iron; color of a weak solution, orange-red; very sensitive; changes to red and brownish-red.

Bi-Chromate of Potassa; solution of an orange-red; changes to a red.

YELLOWS.—*Sesqui-Nitrate of Iron* ; color of solution, brownish yellow ; changes to brownish red.

GREENS.—*Ferro-Cyanide of Potassium* ; solution of a yellowish green ; changes to a yellow.

Chromate of Potassa ; solution of a yellowish-green ; changes to a yellow.

Nitrate of Nickel ; solution, pale-green ; changes to pale yellowish-green.

Sulphate of Nickel ; solution, green ; changes to yellowish-green.

BLUES.—*Chloride of Copper* ; color of weak solution, bluish-green ; changes to a very decided yellowish-green. This substance is quite sensitive, the color returning rapidly on cooling.

Sulphate of Copper ; solution of a decided blue ; changes to a very decided green at the boiling point of the solution. Returns to its original color rapidly on removal from the heat.

VIOLETS.—*Ammonio-Oxide of Nickel* ; solution of a violet-blue ; changes to a light blue ; returns fully on cooling, and cannot therefore be attributed to any loss of ammonia.

Solution of Litmus ; color, violet ; changes to an indigo-blue.

It may be objected that the substances noticed do not present as great a range of changes as those observed in solids. It must be remembered, however, that the temperature in no case differed much from the ordinary temperature, being never much greater than 220° F., while in the experiments with solids the temperature was often more than three times as great. We feel sure that experiments with liquids at higher boiling points, will show substances running down the scale much further than the observed solids.

The Action of Cold.—It would appear from the law already stated, that the color of a body is affected by its temperature, and that in proportion as this temperature is raised, the color is lowered ; moreover, considering the color emitted by the body at its higher temperature, the color is always raised in the spectrum as the body cools. For example, take the case of the green iodide of mercury, which, as before mentioned, is yellowish-green at ordinary temperatures. By the action of heat, its color is successively lowered through the yellow, orange and red, which latter is reached at the maximum temperature of exposure. Cool the body from this point, and its color will become orange, yellow, and yellowish-green, respectively.

Now, the same reasoning that applies to the cooling of the body

from this higher temperature, should also apply, though not with equal force, to its cooling from any temperature, such, for instance, as that of the place in which the body is situated. The color emitted by a body at any temperature, is always lower than it would be were it not for the intermingling of the heat vibrations. Remove it as much as possible from the influence of these vibrations, or in other words, cool it, and the emitted light must be of a higher pitch or color. It would appear then, that as the effect of raising the temperature of a body above its ordinary temperature is, to lower the pitch of the emitted light, so cooling it below that temperature, must be to raise the pitch. The raising, however, would hardly be as great, proportionally, as the lowering. As we recede from the boundary of the heat and light vibrations, we lessen the chance of their producing by intermingling a resulting mean vibration.

With a view of testing the truth of these theoretical considerations, experiments on the action of cold on substances in both the solid and liquid condition were made.

Solids.—The reduction of temperature was obtained by the evaporation of Ether, Bi-Sulphide of Carbon, or liquid Sulphurous Acid. The liquid was placed in a metallic box, furnished with eight vertical sides. Strips of paper, on which the substances were painted, were pasted on the sides of the vessel. Corresponding strips of paper, similarly prepared, were kept for comparison. Cold was produced by blowing a blast of air from a small bellows upon the surface of the liquid. The results obtained were somewhat vitiated by the deposition of the moisture of the air on the sides of the metallic vessel. This difficulty was obviated to some extent by having the paper slip, kept for comparison, equally moist. The results, which are open to this objection, were as follows:

Sulphide of Mercury; changes from a bright red to a brighter red.

Bi-Sulphide of Tin; changes from a brownish orange-yellow to a lighter brownish-yellow.

Sub-Sulphate of Mercury; changes from a yellow to a greenish-yellow.

Iodide of Lead; changes from an orange to a lighter orange.

Chromate of Lead; changes from a yellowish-orange to a yellowish-green.

The substances occupying the remaining sides of the vessel did not present any appreciable change.

Liquids.—The experiments with liquids were, with a few exceptions, of an unsatisfactory character. The solvent in most cases was water, and the cold could not safely be pushed lower than the point of maximum density of the solutions. The solutions were prepared in test tubes, in a manner similar to the experiments with heat. The limitation in the application of cold was, in all probability, the cause of the changes not being of a more decided character.

The following are among some of the substances experimented with:

Sulphate of Copper; solution of a pure blue; deepens on the application of cold.

Ferro-Cyanide of Potassium; saturated solution of a nearly pure yellow; becomes tinted slightly with green.

Chloride of Copper; solution of a bluish-green; becomes a more decided bluish-green.

Sesqui-Chloride of Iron; solution, orange-yellow; becomes an orange yellow in which the yellow is more predominant than in the preceding.

Sesqui-Nitrate of Iron; solution, orange-yellow, like the chloride.

Wishing to obtain a solution that could be exposed to a much lower temperature without freezing, a solution of the chloride of copper in ether was prepared. The color was yellowish-green. When exposed to a low temperature by the evaporation of the bisulphide of carbon, the color changed very decidedly to a pure green. It is purposed, at our earliest convenience, to pursue these investigations at lower temperatures obtained by means of solid carbonic acid and ether. Meanwhile, we would be much pleased if any investigators throughout the country, who may be using a solution of the solid carbonic acid in ether, would observe the action of intense cold on the ethereal solution of chloride of copper, or on any solution of a similar nature.

The law already stated seems now to have been clearly established, both by the number of cases that come under it, and by the fact that, so far, no exceptions have been noticed. It can hardly be urged, with fairness, that all colored compounds should be equally influenced by the action of the less rapid heat vibrations, for the differences presented by bodies, as regards their transparency or opacity to light, or their diathermancy or adiathermancy to heat, clearly indicate a very great difference in their molecular structure, which difference offers reasons amply sufficient to explain why the

colors of some compounds should be more influenced by heat than others. Again, there can be little doubt that more extended observations will increase the great number of compounds already noticed. For, instance, the well known change from red to yellow, presented by the red iodide of mercury, dissuaded us at first from submitting it to an experiment. On a careful trial, however, it was found to illustrate the law, changing to a decidedly darker red up to the temperature requisite to alter its crystalline form.

The theory also receives further support and confirmation from the following considerations.

It is well known that when a yellow and a red substance, which have no chemical action on each other, are mixed together, the resulting color is orange. The explanation is undoubtedly to be found in the raising of the less rapid red vibrations by the yellow, and the consequent lowering of the yellow by the red, the mean, resulting vibration being that capable of producing orange light.

This case, though analogous to the change produced in color by the action of the heat, is not strictly identical with it. In an orange substance, which emits red light when heated, the change is produced as follows; its molecules, while vibrating in periods requisite to produce orange light, are, at the same time, forced to accept the less rapid vibrations of heat. They are unable to do this without lowering the rapidity of the light vibrations, and the emitted light is red. Here, however, the molecules themselves transmit red light to the ether surrounding the intermolecular spaces, which ether in its turn transmits it to the eye for the purposes of vision. Now, in the case of the orange light emitted after the commingling of a yellow and a red substance, as no change other than that of mixture is produced, we must still conceive of the particles of the red and of the yellow substance vibrating in periods requisite to produce red and yellow, and the interference taking place in the intermolecular spaces. Briefly the difference is as follows: In the substance whose color is changed by heat, the *molecules* transmit the changed light directly to the surrounding ether, while in the commingled bodies, the change occurs in the ether surrounding the molecules. The two cases become strictly analogous when we mingle red and yellow light.

In accordance with this view, pure orange and green when mingled should produce yellow; yellow and blue, green; green and indigo, blue; and blue and violet, indigo.

When we come to the boundary of the spectrum on the light side, in other words when we come to the violet, an apparent objection meets us. We know that violet can be produced by the mingling of indigo or blue light with red. That is *two lower vibrations*, and one of them at the lowest extremity of the visible spectrum, produce by their mingling a resultant *higher vibration*, a fact certainly improbable, and seemingly at variance with theory. It must, however, not be forgotten that the violet of the spectrum marks not the limit of the etherial vibrations, but merely our power of appreciating them. The existence of higher vibrations is shown by the actinism of the spectrum, or the effect in producing chemical decomposition, existing some considerable distance beyond the violet. In fact, Herschel, by concentrating this invisible light beyond the violet, succeeded in rendering it visible, and gave its color the name of lavender. This light is of a pale red, inclining to a tinge of violet.

The explanation is now simple. The violet of the spectrum is not produced by the mingling of the indigo or blue with the remoter or lower red, but with that of the higher red or lavender. Indeed, we are strongly led to the belief in the existence of a spectrum beyond the visible spectrum, whose colors, could the eye be trained to appreciate them, would be lighter tints of the lower color. This spectrum would then begin with a paler, shriller, higher red, which we actually have in the lavender. The next, which will probably some day be rendered visible, would be a paler, shriller, higher orange; and so on through the yellow, green, and the other colors.

The analogy of the less rapid vibrations requisite to produce sound is in strict accordance with these considerations. Take, for instance, the note C of the natural gamut; it requires for its production, say 128 vibrations per second; if we increase the rapidity of the vibrations to 144, we get the next higher note, or D; at 160 vibrations, E; at $170\frac{2}{3}$, F; at 192, G; at $213\frac{1}{3}$, A; at 240, B; and at 256, or just twice the number of vibrations requisite to produce c, we get a higher note, which we call c', which, though it differs from c in its pitch, and probably in its timbre, still bears to it in many respects a striking resemblance.

The visible range of colored notes also constitute one octave, viz: red, corresponding, say, to c; and then orange, yellow, green, blue, indigo and violet, corresponding respectively to D, E, F, G, A and B. The octave, or the lavender, corresponding to c', can only be appreciated by the eye under favorable circumstances.

It is most probably more than a mere coincidence that the interval between the lower and the higher red, which is $\frac{1}{2}$, is exactly the same as the interval between the higher and the lower c. Indeed, calculations we have made, show a remarkable similarity in the intervals between the different colors of the spectrum, and the notes of the natural gamut with which we have compared them.

The same reasoning applies to the colors of the spectrum beyond the red, on the heat side, the next color to which, could it be appreciated by the eye, would probably be a very dark reddish-violet, or a purple. In confirmation of this view, we have noticed that some reds, in turning into browns and blacks, possess a slight tinge of purple.

THE SUN.

A Course of Five Lectures, before the Peabody Institute of Baltimore.

By Dr. B. A. GOULD.

(Continued from page 66.)

IN 1852, nine years after Schwabe's discovery of a period in the spottiness upon the sun, Prof. Wolf, of Berne, was led, by careful study of the observations in connection with ancient records, to a modification* of the length of the period, which Schwabe had roughly fixed at about ten years. The large spot which Kepler saw before the discovery of telescopes and took for the planet Mercury, in 1607, indicates that the time of maximum could not then have been far off, and since Fabricius saw the sun at times without spots, his observations must have been during a period of minimum spottiness. Critically examining the various observations of Galileo, Scheiner and others in the early days, and thus following the records of different observers for about two and a half centuries, he found† that the total series was best represented by a period of $11\frac{1}{3}$ years. Only a year earlier than these researches of Wolf, Lamont in Munich had found out the remarkable fact‡ that the variations of the earth's magnetism are subject to a periodic recurrence

* *Astron. Nachrichten*, XXXV, 369.

† *Neue Untersuchungen über die Periode der Sonnenflecken, etc. Mittheilungen d. Berner naturf. Gesellschaft.* 1852.

‡ *Ueber die 10-jährige Periode, welche sich in der Grösse der täglichen Bewegung der Magnetnadel darstellt.*—Pogg. *Annalen*, LXXXIV, 572.