

XV. *On the Change of Colour in the Biniodide of Mercury.*
By ROBERT WARINGTON, Esq.

Read February 1, 1842.

IT is well known that when a solution of the iodide of potassium is added to a solution of the bichloride or pernitrate of mercury, a yellow precipitate, passing rapidly to a scarlet, is formed; this is the biniodide of mercury. It is soluble in an excess of either of the agents employed for its production, and if this act of solution be assisted by heat, the biniodide may be obtained, as the solution cools in fine scarlet crystals, having the form of the octohedron with the square base, or its modifications.

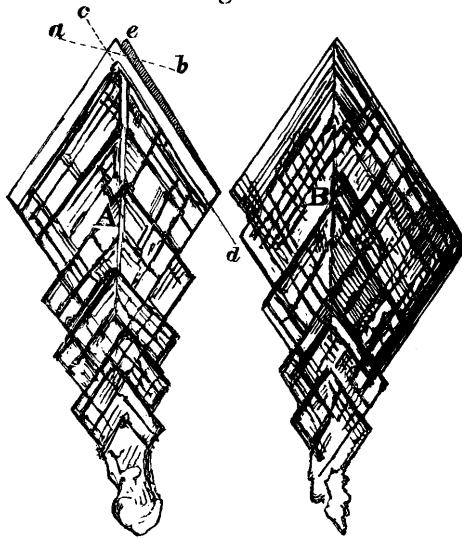
If this precipitated biniodide, in the dry state, be subjected to the action of heat, it becomes of a bright pale yellow colour, fuses into a deep amber-coloured fluid, and gives off a vapour which condenses in the form of rhombic plates of the same bright yellow; these crystals, by any mechanical disturbance, arising from the unequal contraction of their molecules in cooling, from varying thickness in different parts of the same crystal, or from partial disintegration, return again to the original scarlet colour of the precipitate, the change commencing, in the latter case, from the point ruptured, and spreading over the whole of the crystalline mass; they may however be frequently preserved in the yellow state for a great length of time, if sublimed slowly and not exposed to the contact of other substances, which is readily effected by conducting the sublimation in closed vessels, and allowing the crystals to remain in them undisturbed.

The resumption of the scarlet colour has been attributed to an alteration in the molecular arrangement of the crystals, and it was with the view of clearly ascertaining this point that the following microscopic investigations were undertaken.

When a quantity of the precipitated biniodide is sublimed, the resulting crystals are very complicated in their structure, consisting of a number of rhombic plates, of varying size, superposed, sometimes overlapping each other and causing considerable variability in their thickness, but generally leaving the extreme angle and the two lateral edges clear and well-defined; the annexed sketch, taken by the camera lucida from the field of view of the microscope, will give a better idea of their character. The length of these crystals were about $\cdot 015$ of an inch in length. On cooling, the first change that is observed is usually a scarlet marking, commencing at the extreme angle and extending gradually inwards, always retaining a perfectly well-defined line in its progress; when this

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change has reached as far as the line *ab*, fig. 1, the scarlet
Fig. 1.

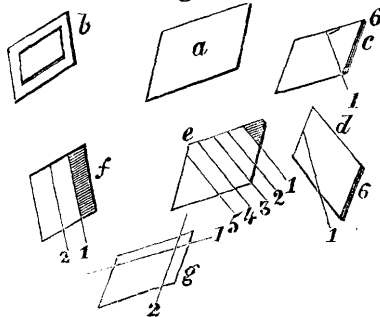


line will suddenly shoot along one of the lateral edges, as shown at *cd*, and instantly the whole mass is converted, in a most rapid and confused manner, which the eye in vain endeavours to follow, to the scarlet colour, the crystal being frequently, if detached, twisted and contorted during the transition.

In order to obtain these crystals in a more defined and clearly developed form, a small glass cell was constructed of two slips of window-glass, leaving a space of about the thickness of cartridge paper between the upper and under plates, in which the sublimations could be readily conducted, and the whole of the subsequent changes at once submitted to the microscope; by this means beautifully well-defined and perfect crystals were obtained, having the form of right rhombic prisms, as in the accompanying outlines,

fig. 2, *a* and *b*. The following interesting phænomena were then observed: a defined scarlet line of varying breadth would shoot across the crystal, as at 1. *c*, *d*, *e*, *f*, fig. 2, and then gradually spread throughout the whole of its structure, keeping a straight and well-defined line in its onward progress,

Fig. 2.



until the whole had undergone the change of colour. Nos. 2, 3, 4, 5 in *e*, and No. 2 in *f*, are the stages which the transition had reached at intervals of observation; in many cases, after the crystal has undergone this metamorphosis, two angles can be distinctly seen, as at *e*, fig. 1, and at times two edges are visible, as at *c* 6 and *d* 6, fig. 2. This observation must of course depend entirely on the position of the crystal to the eye of the observer.

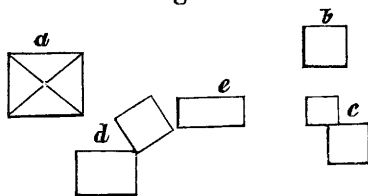
These phænomena prove, I consider, in the most perfect manner, that the change in the colour of this compound arises from the plates of the crystal having been separated from each other, by the means alluded to, in the direction of their cleavages; and in further confirmation of this view, the laminæ so separated may, by the sudden application of heat, be again fused together, and the yellow colour reproduced without materially altering the dimensions of the crystal, a slight rounding of the edges from partial sublimation being the only other concomitant.

When the temperature is raised slowly and the sublimation conducted with great care, a very large proportion of red crystals, having a totally different form, are obtained, the octahedron with the square base, as shown fig. 3, *a*, *b*, *c*, *d*, *e*.

If, however, the heat is quickly raised, the whole mass of the sublimed crystals are yellow and of the rhombic form. It is evident from these facts, that the biniodide of mercury has two vapours which are given off at different temperatures, and also that it is dimorphous, which facts have been substantiated by some experiments of M. Frankenheim, who has carefully examined this part of the subject.

From the circumstance that the first effect which occurs in the process for preparing this iodide by precipitation is the production of a yellow powder which passes rapidly through the orange colour to a scarlet, I was induced to submit this phænomenon also to the test of microscopic examination, and with this valuable instrument of research, results were exhibited which could not have been anticipated. As I expected, the precipitate was in small crystalline grains, and the first step of the investigation was to effect its formation in the field of view of the microscope, so as to observe, directly as they occurred, the transitions of colour which have been alluded to, and this was effected by the following means:—A slip of common win-

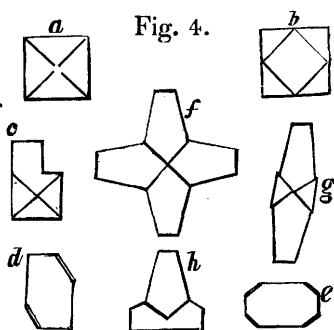
Fig. 3.



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dow-glass, about three inches long by one and a half wide, and having a very narrow slip attached on one of its edges, so as to act as a ledge, was taken, and a drop of the salt of mercury employed placed on it; this was then covered with a small piece of extremely thin glass, about one inch long by half an inch wide, and the whole carefully adjusted to focus in the field of the instrument; the iodide of potassium was then introduced by capillary attraction between the glasses. The instant the solutions came in contact, a myriad of pale-yellow crystals, having the same rhombic form as those obtained by sublimation, formed in a curved line across the field of view and extended slowly downwards; by the strong transmitted light these minute crystals appeared colourless; but when viewed by reflected light, the pale yellow colour was readily apparent. After a short interval a very extraordinary change commenced; the crystals, which had been perfectly sharp and well-defined, became ragged at their edges, as though some dissolving action were going on, gradually decreased in size, and at last disappeared altogether; but as this act of solution progressed, numbers of red crystals made their appearance, forming across the field and following at a regular distance the yellow crystals as they disappeared, and occupying their place. These red crystals, which appear to be formed by the disintegration through the medium of solution, if I may be allowed the expression, from those first produced, had the form of the octohedron with the square base, exactly similar to those procured by careful sublimation at a low heat, only modified in the most beautiful manner. Some few of these

are sketched in the forms, *a, b, c, d, e, f, g, h*, fig. 4. When either the salt of mercury or the iodide of potassium, employed in the production of the biniodide of mercury, was in excess, another curious act of disintegration took place; the red crystals in fig. 4 were slowly dissolved, a property mentioned in the first part of this paper, the first act of solution commencing apparently by the disjunction of the crystals *a, b,*



c, f, g, h, at the lines of marking, these lines being at first bright red, and gradually deepening in colour when the act of solution commenced, and at last perfect separation taking place, so that the light could be seen between the compartments. At times the field would become dry from

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evaporation, and some of the yellow rhombic crystals which had not been dissolved, prior to the formation of the octohedra with the square base, were observed with scarlet lines on them similar to the first act of transition in the sublimed crystals, as shown at *g* 1 and 2 in fig. 2.

By polarized light the appearances now described were beautiful beyond all description, the yellow crystals presenting the most superb and brilliant colours, varying in hue with the varied thickness of the crystalline plate, and in the dark field having the appearance of the most splendid gems the imagination can conceive: the red crystals do not appear to be affected by polarized light, so far as the display of colour is concerned.

The magnifying powers used in these investigations were, for the experiments on the sublimed crystals, 200 times linear measurement or diameters; in the precipitated compound, 620 diameters.

