Philosophical Magazine Series 5

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tphm16

IV. Disruption of the silver haloid molecule by mechanical force

M. Carey Lea [a]

[a] Philadelphia

Version of record first published: 08 May 2009

the observed values, were practically identical with Persoh's supposed constant of $-160°$, whereas in the case of the third solvent, sulphuric acid, for which I got a very different value for the temperature of no crystallization, this substance happened to be the very one in which my calculated freezing-points could not be regarded as satisfactory.

IV. *Disruption of the Silver Haloid Molecule by Mechanical Force. By* M. Carey Lea*.

In a paper published about a year ago on the subject of Allotropic Silver, there was included an investigation into the action of the different forms of energy upon silver chloride and bromide†. It was there shown that these substances possessed an equilibrium so singularly balanced as to be affected by the slightest action of any form of energy. Such action produced a change which, though it might be wholly invisible, yet caused the breaking up of the haloid when subsequently placed in contact with a reducing agent. The forms of energy with which this effect was observed are—

1st. Heat.
2nd. Light.
3rd. Mechanical force.
4th. Electricity (high tension spark).
5th. Chemism.

It follows, therefore, that it is not light only that is capable of producing an invisible image, *but that this power belongs alike to all forms of energy.* So that a slight impulse from any one of the forces just mentioned brings about a change in the equilibrium of such a nature that the molecule is more easily broken up by a reducing agent.

As respects four out of these five forms of energy, it was further shown that when made to act more strongly, they were able of themselves to disrupt the molecule without external aid. One form alone of energy, mechanical force, made an apparent exception to this general rule. The other four, when applied to a moderate extent, produced a latent image; applied more strongly, they broke up the molecule.

The object of the present paper is to prove that this excep-

* From an advance proof, communicated by the Author, having been read before the National Academy, April 1892, by Dr. George F. Barker.

† Phil. Mag. April 1891, p. 320.

tion does not exist, and that as all forms of energy have been shown in the previous papers of this series to be capable of impressing an invisible image, so also with stronger manifestations, *any form of energy is capable of disrupting the molecule.*

I was able to show many years ago that mechanical force could produce a latent image. Lines drawn with a glass rod on a sensitive surface could be rendered visible by development in the same way as impressions of light. An embossed card pressed on a sensitive film left an invisible image, which could be brought out by a reducing agent. The raised portions of the embossed work exerted a stronger pressure on the sensitive film than the rest of the card, and these portions darkened when acted upon by a reducing agent. In the same way, the lines traced with a glass rod blackened under a developer. In each case, it was the portions which had been subjected to pressure which yielded first to the reducer. It was therefore clear that in the molecules which had received this slight pressure the affinities of the atoms had been loosened.

To bring these phenomena fully into line with the others, it is now necessary to prove that an increased pressure can take the place of a reducing agent, and disrupt the melecule. And this is actually the case.

It was found that the breaking up could be produced in two ways—by simple pressure and by shearing stress. Silver chloride and bromide formed and washed in absence of active light were subjected to these agencies.

1. *Simple Pressure.*—In the first trial made with silver chloride it was enclosed in asbestos paper, which had been first ignited with a blast lamp to remove all traces of organic matter present. This method was tried in order that the chloride should be in contact with perfectly inactive material only, but it was not found to answer. The great pressure employed forced the dry chloride into the pores of the paper, cementing it together, so that the opposite sides could not be separated. Platinum foil was then substituted with satisfactory results. With a pressure of about one hundred thousand pounds to the square inch, maintained for twenty-four hours, the chloride was completely blackened, except at the edges, where, owing to greater thinness, the pressure was less. Very bright foil was used in order to detect the slightest discoloration that might occur, but none resulted: it was impossible to distinguish the portions which had been in contact with the darkened chloride from those that had not. The chloride did

not assume the usual chocolate colour, but changed to a deep greenish black.

Silver bromide gave exactly the same results. It should be mentioned that the silver chloride and bromide were each precipitated with an excess of the corresponding acid.

As silver iodide precipitated with excess of potassium iodide is not darkened by light it seemed improbable that it should be by pressure. The experiment was, however, tried, and it was found that the iodide darkened fully to the same extent as the others. This result surprised me so much that the experiment was repeated with every possible precaution. The result left no doubt that silver iodide, as well as the chloride and bromide, is blackened by great pressure. All three silver haloids take on the same coloration—an intense greenish black. It was found best to use the material air-dried. If at all moist the platinum foil bursts under the pressure and the experiment is invalidated. The air-dried salt retains a sufficient quantity of moisture.

2. *Shearing-Stress.*—As a means of applying this form of force, the silver chloride, precipitated with excess of hydrochloric acid and well washed, was put into a porcelain mortar and well triturated. The improbability that the small quantity of force that can be applied in this way would break up a stable molecule like that of silver chloride seemed so great, that at first a substance tending to aid the reaction was added. Tannin was selected, and when forcibly ground up with silver chloride the latter was soon darkened. Next a substance capable of taking up acid, but having no reducing action, was tried. Sodium carbonate was used. This also caused the chloride to darken. Finally, it was determined to ascertain if the molecule of silver chloride could not be disrupted by stress alone. The chloride was placed in a chemically clean porcelain mortar and well triturated. For some time no effect was visible. After about ten minutes' action dark streaks began to appear, and after five minutes' more work a considerable portion of the chloride was darkened. The end of the pestle was covered with a shining purple varnish. It had not become perceptibly warmer to the touch. On the violet-purple substance nitric acid had no action, but aqua regia slowly whitened it. It was therefore what I have proposed to call silver photochloride, that is, a molecular combination of chloride and hemichloride. This experiment was carefully repeated with the same result. Silver bromide similarly treated gave a similar result. It was noticed that both chloride and bromide, in darkening, took on the familiar colour between chocolate and purple, so generally seen in the darkening of

these silver salts, and differing strikingly from the greenish-black colour assumed by all three silver haloids under simple pressure.

The fact that the platinum foil remained absolutely unattacked when the silver haloid was reduced by simple pressure in actual contact with it is interesting, and would seem to show that in the reduction of the silver haloid the halogen is not at any time set free; but that water, if present, is decomposed at the same moment, with formation of halogen acid.

The observations recorded in this paper prove the existence of a perfect uniformity in the action of all kinds of energy on the silver haloids. The balance of the molecule is at once affected by the action of any form of energy. A slight application produces an effect which, though invisible to the eye, is instantly made evident by the application of a reducing agent. The bonds which unite the atoms have evidently been in some way loosened, so that these molecules break up more easily than those to which energy has not been applied. Consequently, if the substance is submitted to the action of light, heat, or electricity, or if lines are drawn by a glass rod (shearing-stress), or with sulphuric acid (chemism), a reducing agent blackens the parts so treated before it affects the parts not so treated. This justifies the statement made earlier in this paper, that the phenomena of the latent image and of its development are not exclusively, or even especially, connected with light, as hitherto supposed, but belong to all other forms of energy as well.

It is therefore true that every form of energy is not only capable of producing an invisible image (that is, of loosening the bonds which unite the atoms), but is also capable, if applied more strongly, of totally disrupting the molecule. This law, in a general form, was proved in previous papers with but a single exception, and that one exception is removed by the observations recorded in this paper.

As far as observation has gone, silver compounds are the only ones that exhibit this universal sensitiveness. Of other substances some are decomposed by heat, some by electricity or by chemical action, and a few by light.

It has now been shown, as I believe for the first time, that mechanical force is competent, without the aid of heat, to break up a molecule that owes its existence to an exothermic reaction.

It is important to distinguish between the two treatments here described. In the case of shearing-stress, force is expended in overcoming friction, and in so doing produces heat. It may be questioned, however, whether the very small amount of heat thus generated has anything to do with the reaction. The heat is not perceptible, it is momentary; and it has been elsewhere shown that though moist silver chloride can be broken up by heat, the action is slow even at a temperature of 100° C.

In the case of simple pressure, heat certainly plays no part. The material is small in quantity, is folded up in metal, is placed between large and heavy pieces of metal, and the pressure is applied gradually by means of a screw. Even supposing a slight increase of temperature, it could not exceed one or two degrees and would be momentary. As just remarked, heat does not produce an effect except at about 100° C. and after many hours.

The powerful affinity which exists between silver and the halogens is well known. That this affinity can be counteracted and annulled by simple pressure—that the halogen can in part be forced out of the molecule by mechanical means unaided by heat—is remarkable.

It need scarcely be said that this phenomenon has nothing in common with decompositions produced by mechanical force in substances such as silver or mercury fulminate, nitrogen chloride, and similar explosives. Such substances are all formed by endothermic reactions, and their decompositions are exothermic. Heat does not need to be supplied, but only what Berthelot has named a "*travail préliminaire*," an impulse to start the reaction. But silver haloids are formed by exothermic reactions; consequently their decompositions are endothermic, and require that the energy which was disengaged in their formation should be returned to effect their decomposition. The experiments described in this paper show that mechanical force may be made to supply this energy, and so play the part of light, electricity, or heat, without previous conversion into any other form of energy.

The thermochemical reactions of the silver haloids have been studied by Berthelot, and their reductions were found to be endothermic*. There can be no doubt, therefore, that an endothermic reaction can be brought about by simple pressure.

Philadelphia, April 1892.

* *Mécanique Chimique*, vol. ii. p. 411. The reduction of silver chloride to metal involves an absorption of cal. 29·4. That to hemichloride has not been measured, but is, according to Berthelot, also endothermic. See also Ditte, *Les Métaux*, i. pp. 232, 233.