

XX. "Note upon the Behaviour of Oxalic Acid and the Oxalates of the Alkalies, and of Potassium Iodide, in Sunlight." By ARTHUR DOWNES, M.D., and THOMAS P. BLUNT, M.A. Oxon. Communicated by Professor HUXLEY, Sec. R.S. Received June 16, 1879.

In a previous communication\* we stated that a decinormal solution of oxalic acid may be entirely destroyed by sunlight, the decomposition being due to oxidation. By a comparison, under like conditions, of oxalic acid and neutral potassium oxalate respectively we further concluded, since the last-named salt appeared to remain unchanged while the former was wholly decomposed, that this destruction of oxalic acid by light was due to the oxidation of its hydrogen.

During the present year, however, we have made a closer and fuller investigation, which shows that the immunity of neutral potassium oxalate is not absolute, and that we must further extend our views as regards the power of light to promote the oxidation of certain of the elements.

A measured quantity of normal solution of oxalic acid was carefully neutralised with—

1. Potassium hydrate.
2. Sodium „
3. Ammonium „
4. Lithium carbonate.

The solution was then diluted up to ten times the volume of the normal oxalic acid originally taken, so that in each case the resultant neutral solutions contained the same weight of the oxalic radical, that, namely, which would be found in an equal bulk of decinormal oxalic acid. Selecting sixteen test-tubes of similar size and bore, we divided them into four sets of two pairs each. In each set respectively we placed one of the above-named solutions (each tube receiving 50 grain measures carefully measured by means of a pipette), a corresponding batch being charged in precisely the same way with a freshly prepared decinormal solution of oxalic acid. All were next raised to boiling point, to prevent development of organisms, and plugged with cotton wool. They were then placed on an outside window-sill, one pair of each batch being incased in laminated lead, the other left freely exposed to the sun's rays. This was on March 28. On each of the dates given in the subjoined table an insulated and an incased tube of each set were compared by titration in the following manner. By appropriate dilution and measurement exactly a fifth part of the con-

\* "Proc. Roy. Soc.," vol. xxviii, p. 204.

tents of each tube was taken, treated with an excess of sulphuric acid, and a standardised solution of potassium permanganate run in until a faint permanent pink tinge remained in the solution when warmed. A direct measure, inversely as the quantity of permanganate required, was thus obtained of previous oxidation.

Experiment started March 28.

| Potassium permanganate solution required for oxidation.* |             |            |           |            |
|--|-------------|------------|-----------|------------|
|  | April 25th. |            | June 9th. |            |
|  | Incased.    | Insolated. | Incased.  | Insolated. |
| Oxalic acid.....   | 7.5 c.c.    | 2.0 c.c.   | 7.25 c.c. | 0.0 c.c.   |
| Ammonium oxalate.....                                    | 7.5 "       | 5.1 "      | 7.3 "     | 2.2 "      |
| Sodium oxalate.....                                      | 7.4 "       | 6.05 "     | 7.2 "     | 5.2 "      |
| Potassium oxalate.....                                   | 7.5 "       | 6.1 "      | 7.1 "     | 5.4 "      |
| Lithium oxalate.....                                     | 7.3 "       | 6.2 "      | 7.25 "    | 6.0 "      |
| Freshly prepared decinormal solution of oxalic acid..... | } 7.3 c.c.  |            | 7.2 c.c.  |            |

Our previous statement as to the total oxidation of oxalic acid in sunlight is thus confirmed, but we learn for the first time that in no case does an oxalate of an alkali entirely escape the oxidising action of sunlight, although whether the various alkali salts always obey the relative proportions of the table above given is a question on which at present we express no opinion whatever. It is, however, an interesting question which constituent of their molecules is the subject of oxidation. Hydrogen, except in the case of the ammonium salt,† is out of question. The uniformity of the initial action indicated the possibility of an oxidation of carbon, but a collateral study of the

\* Disregarding the trifling differences in the decimals as due to unavoidable error the incased liquids remain practically unchanged. From other experiments, not here given, however, it would appear that to obtain this stability the solutions must be boiled, probably on account of the tendency to development of low organisms in the dark.

† Speculation as to the cause of the greater oxidation of this compound, as compared with the other alkali-oxalates in the above experiment, would be premature; and, although the suggestion that a portion of the hydrogen of the  $\text{NH}_4$  is seized upon, offers itself, it is only right to say that the possibility of other explanation has presented itself to us. This we leave for the present.

We may remark incidentally, that a mixture of gaseous ammonia ( $\text{NH}_3$ ) and oxygen in a glass tube over mercury, underwent no change in volume after months of insolation last year.

well-known decomposition of potassium iodide in sunlight has led us to believe that in this case (KI) the phenomenon is of similar character. The nature of this decomposition of potassium iodide has been much discussed, and observers, misled as it seems to us by a supposed analogy with ordinary photographic reactions, have singularly failed to recognise the possibility of the oxidation of metallic elements by light. Hence they have ascribed this behaviour of potassium iodide to acids, carbonic and other, of the atmosphere. On this point, however, we have satisfied ourselves; first, that in a Sprengel vacuum a 10 per cent. solution remains perfectly colourless in sunlight; and, secondly, that decomposition invariably occurs in an isolated solution when no other gases than nitrogen and oxygen are present.\* Here the oxidation can only be that of the alkali metal, and analogy would suggest a similar inference in the case of the oxalates. We are, however, still engaged on the investigation, and our present object is rather to qualify the statement in our previous paper as to the supposed indestructibility of an alkali-oxalate by sunlight, than to advance to a conclusion for which the evidence is not yet sufficient.

XXI. "Preliminary Experiments on the Effects of Long-continued Stress on the Elasticity of Metals." By J. T. BOTTOMLEY, M.A., F.R.S.E. Communicated by Sir W. THOMSON, F.R.S. Received June 14, 1879.

The following paper is intended to describe the results of experiments on elasticity of wires which have been carried on during the past two years, in the Natural Philosophy Laboratory in the University of Glasgow.

In 1875, at the Glasgow meeting of the British Association, a Committee was appointed, at the suggestion of Sir William Thomson, for the purpose of commencing secular experiments on the elasticity of wires, and a grant of money was placed at the disposal of the Committee.

These experiments have accordingly been commenced. An iron tube about 70 feet long has been erected in the tower of the University. Two wires of gold, two of platinum, and two of palladium,

\* The mode in which we insured, as we believe, the absolute freedom of the air employed from acid impurity was the following:—Exhausting tubes to a good Sprengel vacuum, we admitted—by means of the apparatus we described in "Proc. Roy. Soc.," vol. xxviii, p. 210—air which had been standing, with frequent agitation, for six days over a solution of potassium hydrate. To make doubly sure, the exhaustion was again repeated and the purified air a second time admitted. The tubes thus treated acquired a brown tinge in light as quickly as did similar ones simply plugged with cotton wool.